Chapter 6

Heuristics for Process Synthesis

6.0 OBJECTIVES

This chapter returns to the steps of preliminary process synthesis in Section 2.3 in which a strategy is recommended that involves assembling the process operations to create a *base-case* process flowsheet in a specific order, as follows:

1. Chemical reactions (to eliminate differences in molecular type).
2. Mixing and recycle (to distribute the chemicals).
3. Separation (to eliminate differences in composition).
4. Temperature, pressure, and phase change.
5. Task integration (to combine operations into unit processes).

In Section 2.3, as the operations are inserted into alternative flowsheets to manufacture vinyl chloride, *rules of thumb* or *heuristics* are utilized. For example, when positioning the direct chlorination operation, it is assumed that because the reaction is nearly complete at 90°C, ethylene and chlorine can be fed in stoichiometric proportions. Furthermore, when positioning the pyrolysis operation, the temperature and pressure are set at 500°C and 26 atm to give a 60% conversion. These assumptions and specifications are based upon many factors, not the least of which is experience in the manufacture of vinyl chloride and similar chemicals. In this case, a patent by the B. F. Goodrich Co. [British Patent 938,824 (October 9, 1963)] indicates the high conversion of ethylene and chlorine over a ferric chloride catalyst at 90°C and recommends the temperature and pressure levels of the pyrolysis section. The decision not to use ethylene in excess, to be sure of consuming all of the toxic chlorine, is based upon the favorable experimental conversions reported by chemists. In the distillation operations, the choice of the key components, the quality of the feed streams and the distillation products, and the pressure levels of the towers are also based upon rules of thumb. In fact, heuristics like these and many others can be organized into an *expert system*, which can be utilized to synthesize sections of this and similar chemical processes.

Normally, design teams use heuristics when generating the alternatives that make up the synthesis tree, such as that shown in Figure 2.7. For the most part, heuristics are easy to apply; that is, they involve the setting of temperatures, pressures, excess amounts of chemicals, and so on. Often they require little analysis in that simple material balances can be completed without iterations before proceeding to the next synthesis step. Consequently, several promising flowsheets, or *base-case designs*, are generated rapidly with relatively little effort. For these flowsheets, the assumptions are checked, a process flow diagram is assembled (e.g., Figure 2.17), and a complete material balance is carried out, often using the process simulators discussed in Chapter 7.

Clearly, the heuristics used by a design team to generate the synthesis tree are crucial in the design process. Section 2.3 provides just a brief introduction to these heuristics, and hence, it is the objective of this chapter to describe the principal heuristics used in a process design more thoroughly. A total of 53 heuristics are presented in Sections 6.2 through 6.9. In many cases, the heuristics are accompanied by examples. For quick reference, the heuristics are collected together in Table 6.2 at the end of this chapter. Additional guidance in the selection of equipment is given in Chapters 16 and 17 when determining equipment purchase and operating costs, Chapter 8 when designing chemical reactors, Chapter 12 when designing heat exchangers, Chapter 13 when sizing distillation towers, and Chapter 14 when sizing pumps, compressors, and gas expanders.

After studying this chapter and the heuristics in Table 6.2, the reader should:

1. Understand the importance of selecting reaction paths that do not involve toxic or hazardous chemicals and when unavoidable, to reduce their presence by shortening residence times in the process units and avoiding their storage in large quantities.
2. Be able to distribute the chemicals, when generating a process flowsheet, to account for the presence of inert species that would otherwise build up to unacceptable concentrations, to achieve a high selectivity to the desired products, and to accomplish, when feasible, reactions and separations in the same vessels (e.g., reactive distillations).
3. Be able to apply heuristics in selecting separation processes to separate liquids, vapors, vapor–liquid mixtures and other operations involving the processing of solid particles, including the presence of liquid and/or vapor phases.

4. Be able to distribute the chemicals, by using excess reactants, inert diluents, and cold (or hot) shots, to remove the exothermic (supply the endothermic) heats of reaction. These distributions can have a major impact on the resulting process integration.

5. Understand the advantages, when applicable, of pumping a liquid rather than compressing a vapor.

Through several examples, including the synthesis of a process to hydrodealkylate toluene to benzene, and the exercises at the end of the chapter, the reader should be able to apply the heuristics in Table 6.2 when generating a synthesis tree and creating *base-case* designs.

6.1 INTRODUCTION

As introduced in Chapter 2, the first step in process design involves process synthesis, that is, the creation of alternative process flowsheets to produce a specific chemical product. For this purpose, heuristics (rules of thumb) are commonly used, at least initially. In this chapter, many more heuristics are discussed, far beyond those used in the synthesis of the vinyl-chloride and tissue plasminogen activator (tPA) processes in Chapter 2. Through usage of these heuristics, it is normally possible to create a promising "base-case flowsheet(s)," which is subsequently analyzed more carefully using process simulators, as discussed in Chapter 7. When used properly, heuristics permit the *rapid* creation of a promising base-case flowsheet(s)—one that can be refined and optimized through careful material and energy balance analysis, equipment sizing, and cost estimation using process simulators.

For each of the five synthesis steps, this chapter systematically presents a more complete set of heuristics, beginning with the first step: Select Raw Materials and Chemical Reactions in Section 6.2. Then, after sets of heuristics are presented, with examples to illustrate their use, some of the heuristics are applied for the synthesis of a base-case design, one involving the hydrodealkylation of toluene to produce benzene, which begins in Example 6.1. This chapter is intended to show how such a base-case design can be created rapidly prior to the active usage of process simulators. Note, however, that even when using heuristics, process simulators are often used for supporting calculations (e.g., to estimate physical properties) as illustrated occasionally in the examples that follow. The formal usage of process simulators for design specifications, recycle calculations, equipment sizing, cost estimation, and the like, is introduced in Chapter 7.

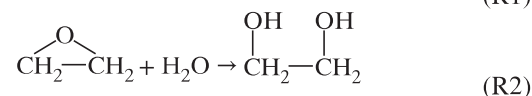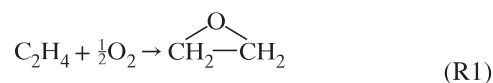## 6.2 RAW MATERIALS AND CHEMICAL REACTIONS

Heuristic 1: **Select raw materials and chemical reactions to avoid, or reduce, the handling and storage of hazardous and toxic chemicals.**

As discussed in Section 2.3, the selection of raw materials and chemical reactions is often suggested by chemists, biologists, biochemists, or other persons knowledgeable about the chemical conversions involved. In recent years, with the tremendous increase in awareness of the need to avoid handling hazardous and toxic chemicals, in connection with environmental and safety regulations (as discussed in Sections 3.4 and 3.6), raw materials and chemical reactions are often selected to protect the environment and avoid the safety problems that are evident in Material Safety Data Sheets (MSDS). For example, recall that when the vinyl-chloride process was synthesized in Section 2.3, the reaction of acetylene with HCl was rejected because of the high cost of acetylene. Today, in addition, the reaction path would be rejected on the basis of the high reactivity of acetylene and the difficulty of ensuring safe operation in the face of unanticipated disturbances.

In connection with the handling of hazardous chemicals, the 1984 accident in Bhopal, India, in which water was accidentally mixed with the active intermediate methyl isocyanate, focused worldwide attention on the need to reduce the handling of highly reactive intermediates. As discussed in Section 3.6, within an hour of the accident, a huge vapor cloud swept across Bhopal, leading to the death of over 3,800 victims in the vicinity of the Union Carbide plant. This accident, together with the discovery of polluted groundwaters adjacent to chemical plants, especially those that process nuclear fuels, have led safety and environment experts to call for a sharp reduction in the handling of hazardous chemicals.

For these reasons, societal needs are increasingly being formulated that call for new processes to avoid or sharply reduce the handling of hazardous chemicals. As an example, consider the manufacture of ethylene glycol, the principal ingredient of antifreeze. Ethylene glycol is produced commonly by two reactions in series:

$$C_2H_4 + \tfrac{1}{2}O_2 \rightarrow \overset{O}{\overset{\diagup\diagdown}{CH_2-CH_2}} \tag{R1}$$

$$\overset{O}{\overset{\diagup\diagdown}{CH_2-CH_2}} + H_2O \rightarrow \overset{OH \quad OH}{\underset{|\qquad\;|}{CH_2-CH_2}} \tag{R2}$$

The first reaction involves the partial oxidation of ethylene over an Ag-gauze catalyst. Because both reactions are highly exothermic, they need to be controlled carefully. More important from a safety point of view, a water spill into an ethylene oxide storage tank could lead to an accident similar to the Bhopal incident. Yet it is common in processes with two reaction steps to store the intermediates so as to permit the products to be generated continuously, even when maintenance problems shut down the first reaction operation.

Given the societal need to eliminate the storage of large quantities of reactive intermediates such as ethylene oxide, four alternative processing concepts are possible:

1. Eliminate the storage tank(s), causing intermittent interruptions in the production of ethylene glycol when the oxidation reaction shuts down.

2. Use costly chlorine and caustic (compared to oxygen from air) in a single reaction step:

$$CH_2{=}CH_2 + Cl_2 + 2NaOH(aq) \rightarrow \overset{OH}{\underset{|}{CH_2}}{-}\overset{OH}{\underset{|}{CH_2}} + 2\,NaCl$$

(R3)
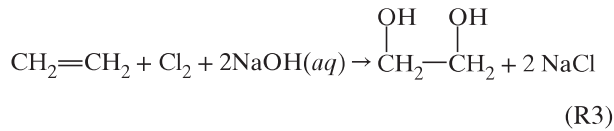
This alternative requires more expensive raw materials, but completely avoids the intermediate.

3. As ethylene oxide is formed, react it with carbon dioxide to form ethylene carbonate, a much less active intermediate. This reaction

$$\overset{O}{\underset{|}{CH_2}}{-}CH_2 + CO_2 \rightarrow O\overset{\overset{O}{\|}{C}}{\underset{\underset{CH_2-CH_2}{|}}{}}O$$

(R4)
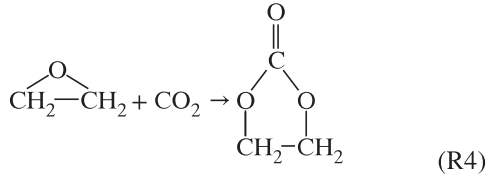
occurs smoothly over a tetraethylammonium bromide catalyst. Ethylene carbonate can be stored safely and hydrolyzed to form the ethylene glycol product as needed.

4. Carry out reactions (R1) and (R4) consecutively over an Ag-gauze catalyst by reacting ethylene in a stream containing oxygen and carbon monoxide. To consider this as an alternative processing concept, laboratory or pilot-plant data on the rates of reaction are necessary.

In summary, there is an increasing emphasis on retrofitting processes to eliminate active intermediates and in the design of new processes to avoid these chemicals entirely. Furthermore, the designers of new processes are being asked with increasing frequency to select raw materials and reactions accordingly. These have become important considerations in the early stages of process design.

EXAMPLE 6.1 *Synthesis of a Process to Hydrodealkylate Toluene*

This example involves the synthesis of a process to hydrodealkylate toluene, which was actively used following World War II, when it became favorable to convert large quantities of toluene, which was no longer needed to make the explosive TNT, to benzene for use in the manufacture of cyclohexane, a precursor of nylon. In this case, a product design alternative involves the conversion of toluene to benzene and, for this purpose, the principal reaction path is well defined. It involves

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4 \tag{R1}$$

which is accompanied by the side reaction

$$2C_6H_6 \rightarrow C_{12}H_{10} + H_2 \tag{R2}$$
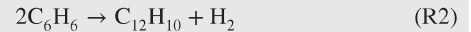
Laboratory data indicate that the reactions proceed irreversibly without a catalyst at temperatures in the range of 1,200–1,270°F with approximately 75 mol% of the toluene converted to benzene and approximately 2 mol% of the benzene produced in the hydrodealkylation reaction converted to biphenyl. Because the reactions occur in series in a single processing unit, just a single reaction operation is positioned in the flowsheet, as shown in Figure 6.1. The plant capacity is based on the conversion of 274.2 1bmol/hr of toluene, or approximately 200 MMlb/yr, assuming operation 330 days per year.

Here, the overall mass balance is carried out assuming that *all* of the unreacted toluene is recycled and consumed in the process to be synthesized. Furthermore, 2 mol% of the entire production of benzene is converted to biphenyl.

Before inserting the reaction operation into a flowsheet, it is important to check the feasibility of the economic potential, *EP* (i.e., the sales minus the cost of raw materials, not including the cost of utilities and operating costs). Using prices for C_6H_6 and C_7H_8 from *ICIS Chemical Business* in late 2013 and 2014 estimates for H_2 and CH_4

	Cost (cent/lb)
H_2	0.59
CH_4	0.21
C_6H_6	0.54
C_7H_8	0.47
$C_{12}H_{10}$	unavailable

the economic potential per pound of benzene (assuming negligible conversion to $C_{12}H_{10}$) is only 1.4 cent/lb C_6H_6. Note, however, that after World War II with a large excess of toluene available, its unit cost was much lower—and the economic potential was much higher. Even without the cost of equipment and its operation, the *EP* was sufficiently large to proceed with the next step in process synthesis, Distribution of Chemicals.
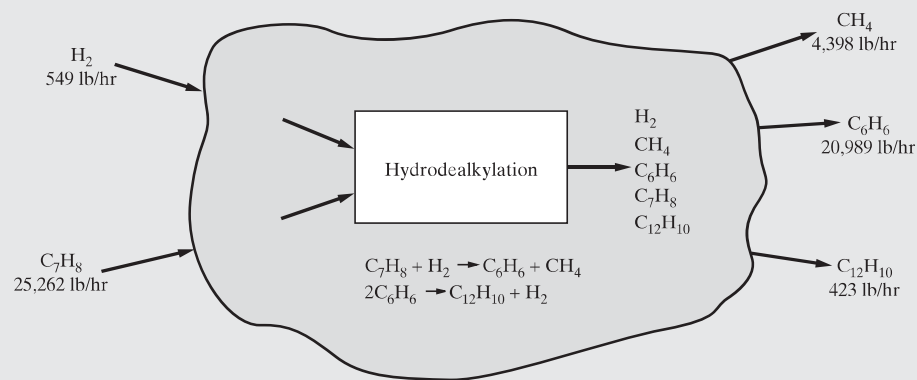

Figure 6.1 Reaction operation for the hydrodealkylation of toluene.

6.3   DISTRIBUTION OF CHEMICALS

In this subsection, several heuristics are presented beginning with the need for excess chemicals in carrying out reaction operations.

Excess Chemicals

Heuristic 2:   *Use an excess of one chemical reactant in a reaction operation to consume completely a valuable, toxic, or hazardous chemical reactant. The MSDSs will indicate which chemicals are toxic and hazardous.*

After the reaction operations are positioned in a process flowsheet, the sources of chemicals (i.e., the feed streams and reactor effluents) are distributed among the sinks for chemicals (i.e., the feed streams to the reaction operations and the products from the process). In this distribution, decisions are made concerning (1) the use of one chemical reactant in excess in a reaction operation, (2) the handling of inert species that enter in the feed streams, and (3) the handling of undesired byproducts generated in side reactions. For example, as we have seen in Figure 2.3, one distribution of chemicals for the vinyl-chloride process involves stoichiometric amounts of ethylene and chlorine fed to the direct-chlorination reactor. Alternatively, an excess of ethylene can be utilized as shown in Figure 6.2. In this distribution, the reactor is designed to consume completely the hazardous and toxic chlorine, but the recovery of unreacted ethylene from the dichloroethane product is required. Clearly, an important consideration is the degree of the excess, that is, the ethylene/chlorine ratio. It governs the costs of separation and recirculation, and often plays a key role in the process economics. In many design strategies, this ratio is set using heuristics, with larger ratios used to ensure consumption of the most hazardous chemicals. Eventually, as a *base-case design* evolves, the ratio is varied systematically, often using a process simulator. In mathematical programming strategies, it is treated as a *design variable* to be

varied during optimization with a lower bound. Note that for exothermic reactions, the excess chemical often serves the useful function of absorbing the heat of reaction and thereby maintaining more moderate temperatures. This is an important approach to handling large heats of reaction and is considered with several common alternatives in Section 6.5 in the subsection on heat removal from exothermic reactors. An excess of one chemical reactant is also used to increase conversion of the other (limiting) reactant when the extent of reaction is limited by equilibrium. Also, side reactions can be minimized by using an excess of one reactant.
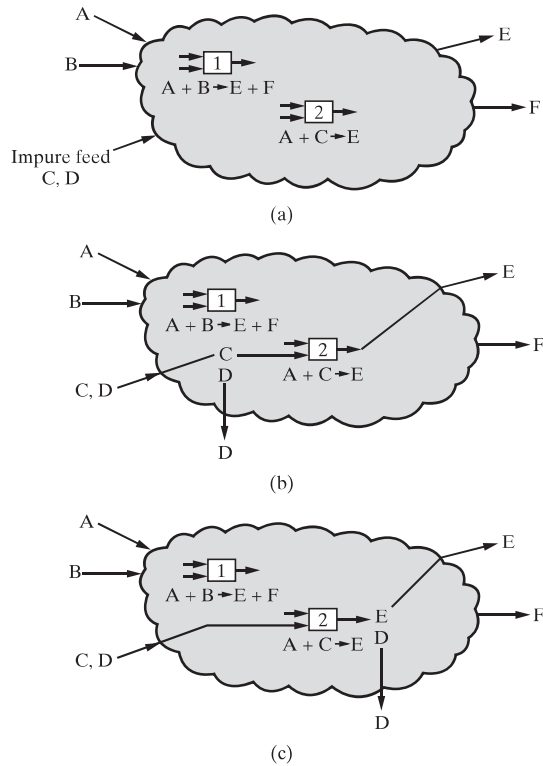
Inert Species

Heuristic 3:   *When nearly pure products are required, eliminate inert species before the reaction operations when the separations are easily accomplished and when the catalyst is adversely affected by the inert, but not when a large exothermic heat of reaction must be removed.*

Often impure feed streams contain significant concentrations of species that are inert in chemical reaction operations. When nearly pure products are required, an important decision concerns whether impurities should be removed before or after reaction operations. As an example, consider the flowsheet in Figure 6.3a in which two reaction operations have been positioned. An impure feed stream of reactant C contains the inert species D, and hence a decision is required concerning whether to remove D before or after reaction step 2, as shown in Figures 6.3b and 6.3c, respectively. Clearly, the ease and cost of the separations, that is, D from C, and D from E (plus unreacted A and C), must be assessed. This can be accomplished by examining the physical properties on which the separations are based. For example, when considering distillation, estimates of the relative volatilities are used. When the mixtures are ideal, the relative volatility, α_{ij},
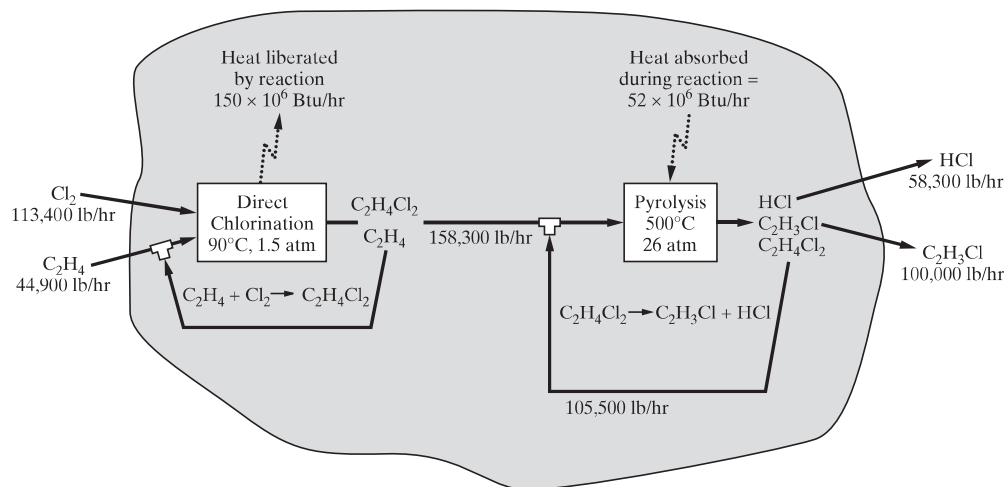
Figure 6.2 Distribution of chemicals for the production of vinyl chloride involving an excess of ethylene.

(a)

(b)

(c)

Figure 6.3 Partial distribution of chemicals showing the alternatives for removing inert species D: (a) reaction operations; (b) recovery before reaction; and (c) recovery after reaction.

is simply a ratio of the vapor pressures ($\alpha_{ij} = P_i^s/P_j^s$). Otherwise, activity coefficients are needed ($\alpha_{ij} = \gamma_i P_i^s/\gamma_j P_j^s$). When the relative volatilities differ significantly from unity, an easy and inexpensive separation is anticipated. Similarly, when considering crystallization, the differences in the freezing points are examined, and for dense membrane separations, the permeabilities of the pure species are estimated as the product of the solubility in the membrane and the molecular diffusivity. Other considerations are the sizes of the reactors and separators with larger reactors required when the separations are postponed. Also, for exothermic reactions, the inert species absorb some of the heat generated, thereby lowering the outlet temperatures of the reactors.

EXAMPLE 6.2 *Removing Inert Chemical Species*

To satisfy the Clean Air Act of 1990, gasoline must have a minimum oxygen alom content of 2.0 mol%. In the 1990s, the most common source of this oxygen was methyl *tertiary-butyl* ether (MTBE), which is manufactured by the reaction

$$\text{CH}_3\text{OH} + \textit{iso}\text{-butene} \rightleftharpoons \text{MTBE}$$
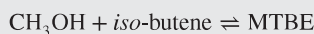
It is desired to construct an MTBE plant at your refinery, located on the Gulf Coast of Texas. Methanol will be purchased and *iso*-butene is available in a mixed-C_4 stream that contains

	Wt%
1-Butene	27
iso-Butene	26
1,3-Butadiene	47

During process synthesis, in the distribution of chemicals, a key question involves whether it is preferable to remove 1-butene and 1, 3-butadiene before or after the reaction operation. In this example, distillation is considered, although other separation methods normally are evaluated as well. It should be noted that recently MTBE was found to contaminate groundwater and, thus, in most locations is no longer the preferred source of oxygen.
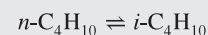
SOLUTION

These hydrocarbon mixtures are only mildly nonideal, and hence it is satisfactory to examine the boiling points of the pure species or, better yet, their vapor pressures. These can be tabulated and graphed as a function of temperature using a simulator; for example, the following curves are obtained from ASPEN PLUS (and can be reproduced using the EXAM6-2.bkp file in the Program and Simulation Files folder, which can be downloaded from the Wiley Web site associated with this textbook).
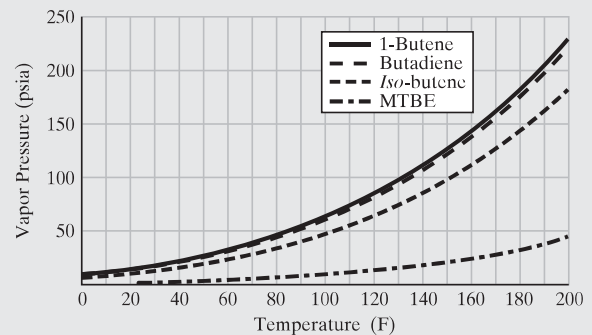

With respect to MTBE, the relative volatilities, $\alpha = P^s/P_{\text{MTBE}}^s$, at 200°F, are 5.13 (1-butene), 4.96 (1,3-butadiene), and 4.04 (*iso*-butene). Clearly, the relative volatilities of 1-butene and 1,3-butadiene are very close, but each differs significantly from the value for *iso*-butene. On this basis, the former two compounds can be separated by distillation before or after the reaction operation. Other considerations, such as their impact on the catalyst, the volumes of the reactors and distillation towers, and the temperature levels in the exothermic reactors, should be evaluated in making this decision.

EXAMPLE 6.3 *Positioning an Equilibrium Reaction Operation*

Consider the reaction and distillation operations for the isomerization of *n*-butane to *iso*-butane according to the reaction

$$n\text{-}C_4H_{10} \rightleftharpoons i\text{-}C_4H_{10}$$

The feed to the process is a refinery stream that contains 20 mol% *iso*-butane. Show the alternatives for positioning the reaction and distillation operations.

SOLUTION
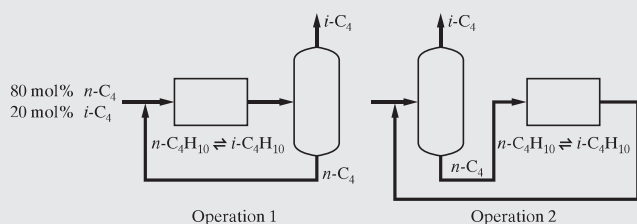
As shown in the diagram, either operation can be placed first. By positioning the distillation column first, a nearly pure feed is sent to the reaction operation, providing a higher conversion to *iso*-butane. The effectiveness of this configuration depends on the relative difficulty of achieving the distillation separation. To determine this, the two configurations should be simulated.

Purge Streams

Heuristic 4: *Introduce purge streams to provide exits for species that enter the process as impurities in the feed or are formed in irreversible side reactions, when these species are in trace quantities and/or are difficult to separate from the other chemicals. Lighter species leave in vapor purge streams, and heavier species exit in liquid purge streams.*

Trace species, often introduced as impurities in feed streams or formed in side reactions, present special problems when the chemicals are distributed in a flowsheet. In a continuous process, these accumulate continuously unless a means is provided for their removal either by reaction, separation, or through purge streams. Because the reaction or separation of species in low concentration is usually costly, purge streams are used when the species are nontoxic and have little impact on the environment. Purge streams are also used for removing species present in larger amounts when their separation from the other chemicals in the mixture is difficult. As an example, consider the distribution of chemicals in the ammonia process ($N_2 + 3H_2 \rightleftharpoons 2NH_3$) in Figure 6.4. Trace amounts of argon accompany nitrogen, which is recovered from air, and trace amounts of methane accompany hydrogen, which is produced by steam reforming ($CH_4 + H_2O \rightleftharpoons 3H_2 + CO$). After reforming, the carbon monoxide and unreacted methane and steam are recovered, leaving trace quantities of methane. Although nitrogen and hydrogen react at high pressures, in the range of 200–400 atm depending on the
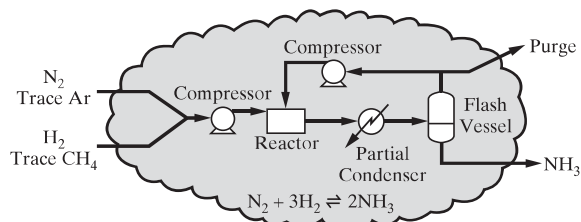
process throughput, the conversion is low (usually in the range of 15–20 mol%), and large quantities of unreacted nitrogen and hydrogen are recirculated. The purge stream provides a sink for the argon and methane, which otherwise would build to unacceptable concentrations in the reactor bed, which is packed with reduced iron oxide catalyst. The light gases from the flash vessel are split into purge and recycle streams with the purge/recycle ratio being a key decision variable. As the purge/recycle ratio increases, the losses of nitrogen and hydrogen increase with an accompanying reduction in the production of ammonia. This is counterbalanced by a decrease in the recirculation rate. In the early stages of process synthesis, the purge/recycle ratio is often set using heuristics. Eventually, it can be varied with a process simulator to determine its impact on the recirculation rates and equipment sizes. Then it can be adjusted, also using a process simulator, to optimize the return on investment for the process, as discussed in Chapters 17 and 21. Note that the alternative of separating trace species from the vapor stream, thereby avoiding the purge of valuable nitrogen and hydrogen, may also be considered. These separations—for example, adsorption, absorption, cryogenic distillation, and gas permeation with a membrane—may be more expensive. Finally, it should be recognized that argon and methane are gaseous species that are purged from the vapor recycle stream. Other processes involve heavy impurities that are purged from liquid streams.


EXAMPLE 6.4 *Ammonia Process Purge*

In this example, the ammonia reactor loop in Figure 6.4 is simulated using ASPEN PLUS to examine the effect of the purge-to-recycle ratio on the compositions and flow rates of the purge and recycle streams. For the ASPEN PLUS flowsheet below, the following specifications are made:

Simulation Unit	Subroutine	T (°F)	P (atm)
Rl	REQUIL	932	200
Fl	FLASH2	−28	136.3

and the Chao-Seader option set is selected to estimate the thermophysical properties. Note that REQUIL calculates chemical equilibria at the temperature and pressure specified, as shown on the multimedia module *ASPEN → Chemical Reactors → Equilibrium Reactors → REQUIL*, which can be downloaded from www.seas.upenn.edu/~dlewin/multimedia.html.

The combined feed stream, at 77°F and 200 atm, is composed of

	lbmol/hr	Mole Fraction
N_2	24	0.240
H_2	74.3	0.743
Ar	0.6	0.006
CH_4	1.1	0.011
	100.0	1.000

Figure 6.4 Ammonia reactor loop.
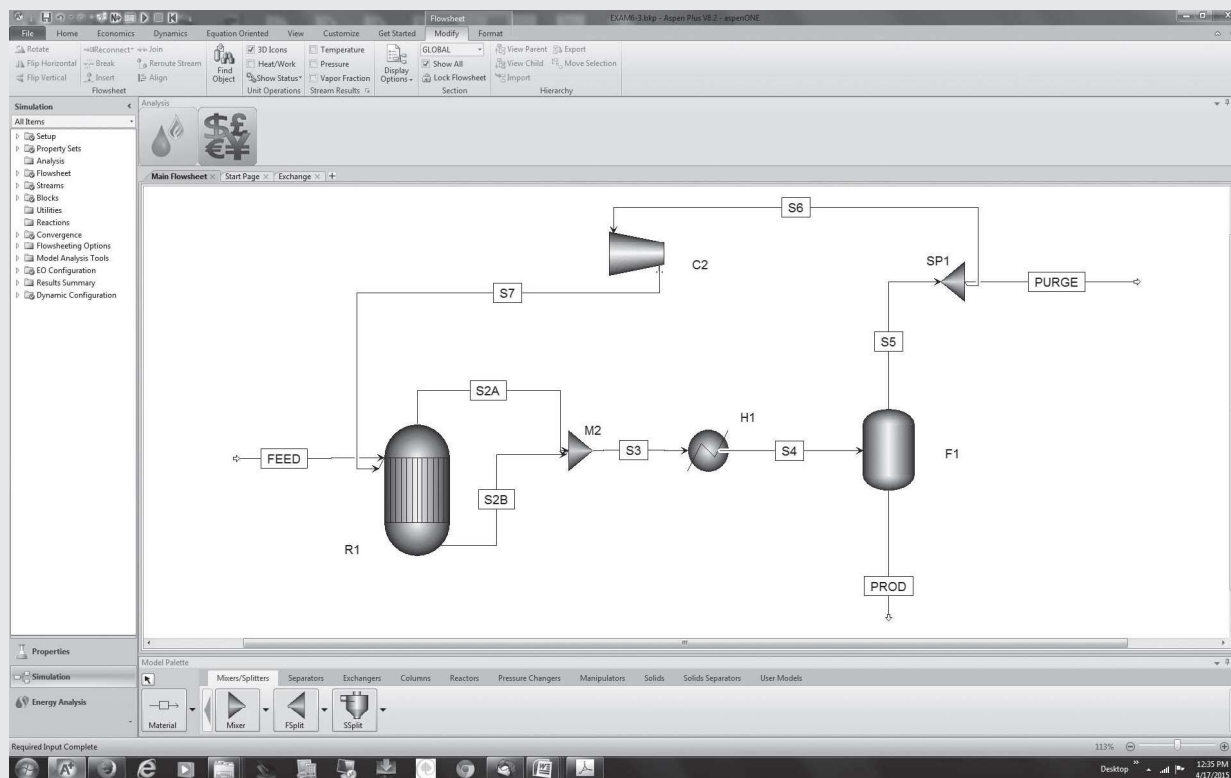
(*Source:* © AspenTech).

SOLUTION

Several variables are tabulated as a function of the purge/recycle ratio:

Purge/Recycle Ratio	PROD Flow Rate (lbmol/hr)	Recycle Flow Rate (lbmol/hr)	Purge Flow Rate (lbmol/hr)	Purge Mole Fraction Ar	Purge Mole Fraction CH_4
0.1	39.2	191.0	19.1	0.028	0.052
0.08	40.75	209.3	16.7	0.033	0.060
0.06	42.4	233.9	14.0	0.040	0.074
0.04	44.3	273.5	10.9	0.053	0.093
0.02	45.8	405.6	8.1	0.072	0.133

In all cases, the mole fractions of Ar and CH_4 in the purge are significantly greater than in the feed. As the purge/recycle ratio is decreased, the vapor effluent from the flash vessel becomes richer in the inert species and less H_2 and N_2 are lost in the purge stream. However, this is accompanied by a significant increase in the recycle rate and the cost of recirculation, as well as the reactor volume. Note that the EXAM6.4.bkp file (in the Program and Simulation Files folder, which can be downloaded from the Wiley Web site associated with this book) can be used to reproduce these results. Although not implemented in this file, the purge/recycle ratio can be adjusted parametrically by varying the fraction of stream S5 purged in a *sensitivity analysis,* which is one of the *model analysis tools* found in most simulators. The capital and operating costs can be estimated and a profitability measure optimized as a function of the purge/recycle ratio.

Heuristic 5: *Do not purge valuable species or species that are toxic and hazardous, even in small concentrations (see the MSDSs). Add separators to recover valuable species. Add reactors to eliminate, if possible, toxic and hazardous species.*

In some situations, the recovery of trace species from waste streams is an important alternative to purging. This, of course, is the case when an aqueous stream contains trace quantities of rare metals, as can occur when catalysts are impregnated on ceramic supports. In other situations—for example, in the handling of aqueous wastes—environmental regulations are such that trace quantities of organic and inorganic chemicals must be recovered or converted into an environmentally acceptable form. One process to treat aqueous streams in the vicinity of leaking tanks is *supercritical oxidation*, using acoustic waves
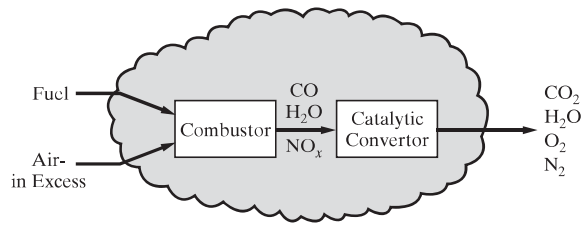
Figure 6.5 Catalytic conversion of combustion effluents.

or lasers to produce plasmas. In this process, the waste species [including chlorinated hydrocarbons, pesticides, phenols (e.g., *p*-nitrophenol), and esters] are oxidized at temperatures and pressures associated with supercritical water (Hua et al., 1995a, b). Yet another example involves the catalytic conversion of hydrocarbons and carbon monoxide in the exhaust gases from internal combustion engines. As illustrated in Figure 6.5, rather than purge the exhaust gases from a combustion engine, catalytic converters commonly convert carbon monoxide and nitrogen oxides to carbon dioxide and nitrogen, respectively. Again, the decision to insert a reaction step, rather than to separate or purge, in the early stages of process design is made often based on the availability of a catalyst and experience; that is, heuristics.

EXAMPLE 6.5 *Hydrodealkylation of Toluene—Example 6.1 Revisited*

Turning to Step 2, the Distribution of Chemicals, in the synthesis of a process to hydrodealkylate toluene, return to the flowsheet in Figure 6.1 and determine a distribution of chemicals.

SOLUTION

One distribution of chemicals involves a large excess of hydrogen gas to prevent carbon deposition and absorb much of the heat of the exothermic hydrodealkylation reaction. Furthermore, to avoid an expensive separation of the product methane from the hydrogen gas, a purge stream is utilized in which methane leaves the process, unavoidably with a comparable amount of hydrogen. Because the performance of the separation system, to be added in the next synthesis

step, is unknown, the amount of hydrogen that accompanies methane in the purge stream is uncertain at this point in the synthesis. Hence, the distribution of chemicals in Figure 6.6 is known incompletely. Note, however, that the sources and sinks of the chemicals can be connected and an estimate for the toluene recycle prepared based upon the assumption of 75 mol% conversion and complete recovery of toluene from the effluent stream. Also, at 1,268°F and 494 psia, a typical operating pressure, the heat of reaction is 5.84×10^6 Btu/hr, as computed by ASPEN PLUS using the RSTOIC subroutine and the Soave-Redlich-Kwong equation of state.

Recycle to Extinction

Heuristic 6: *Byproducts that are produced in small quantities in reversible reactions are usually not recovered in separators or purged. Instead, they are usually recycled to extinction.*

Often small quantities of chemicals are produced in side reactions, such as the reaction of benzene to form biphenyl in the toluene hydrodealkylation process. When the reaction proceeds *irreversibly*, small quantities of byproducts must be separated away. As shown in Figure 6.6, the biphenyl byproduct is collected in small quantities, or purged; otherwise, it will build up in the process until the process must be shut down.

When the reaction proceeds *reversibly*, in this case for the dimerization of benzene to form biphenyl, it becomes possible to achieve an equilibrium conversion at steady state by recycling product species without removing them from the process. In so doing, it is often said that undesirable byproducts are *recycled to extinction*. It is important to recognize this when distributing chemicals in a potential flowsheet so as to avoid the loss of chemicals through purge streams or the insertion of expensive separation operations. Recycle to extinction, which is considered in more detail in Section 8.8, is most effective when the equilibrium conversion of the side reaction is limited by a small chemical equilibrium constant at the temperature and pressure conditions in the reactor.
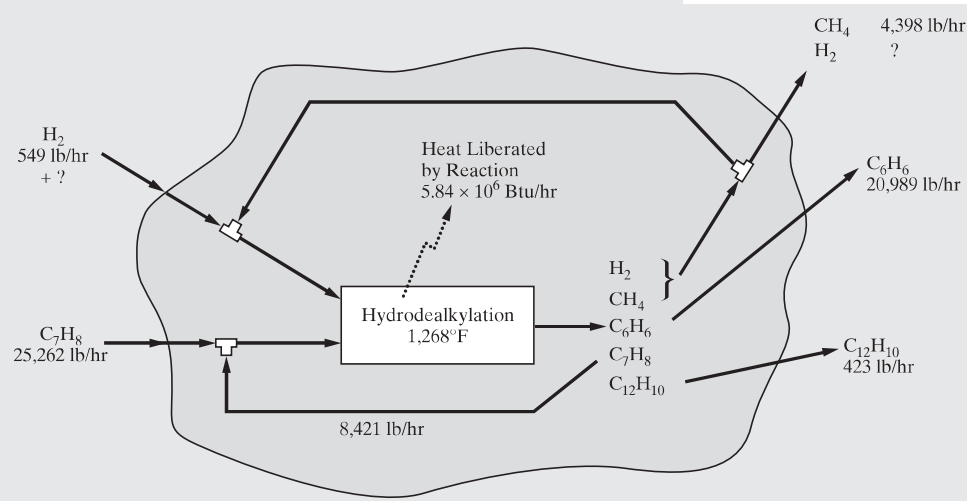

Figure 6.6 Distribution of chemicals for the hydrodealkylation of toluene.

Selectivity

Heuristic 7: *For competing reactions, both in series and parallel, adjust the temperature, pressure, and catalyst to obtain high yields of the desired products. In the initial distribution of chemicals, assume that these conditions can be satisfied. Before developing a base-case design, obtain kinetics data and check this assumption.*

When chemical reactions compete in the formation of a desired chemical, the reaction conditions must be set carefully to obtain a desirable distribution of chemicals. Consider, for example, the series, parallel, and series-parallel reactions in Figure 6.7, where species B is the desired product. For these and similar reaction systems, it is important to consider the temperature, pressure, ratio of the feed chemicals, and the residence time when distributing the chemicals. One example of series-parallel reactions occurs in the manufacture of allyl chloride. This reaction system, which involves three competing second-order exothermic reactions, is shown in Figure 6.7d with the heats of reaction, ΔH_R, activation energies, E, and pre-exponential factors, k_0, in Table 6.1. Note that because $E_1/E_2 > 1$ and $E_1/E_3 < 1$, the conversion to allyl chloride is highest at intermediate temperatures. In the early stages of process synthesis, when distributing the chemicals, these considerations are helpful in setting the temperature, pressure, and the ratio of propylene/chlorine in the feed.

(a)

(b)

(c)

(d)
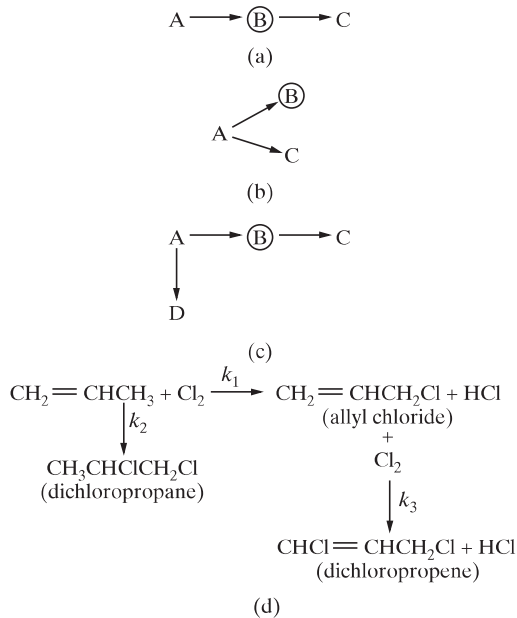
Figure 6.7 Competing reactions: (a) series reactions; (b) parallel reactions; (c) series-parallel reactions; (d) exothermic allyl-chloride reactions.

Table 6.1 Heats of Reaction and Kinetics Constants for the Allyl Chloride Process

| Reaction	ΔH_R (Btu/lbmol)	k_0 [lbmol/(hrft^{3}atm^2)]	E/R (°R)
1	−4,800	206,000	13,600
2	−79,200	11.7	3,430
3	−91,800	4.6 x 10^8	21,300

When selectivity is the key to the success of a process design, it is not uncommon to carry out an extensive analysis of the reactor alone, before distributing the chemicals, and proceeding with the synthesis of the flowsheet. In other cases using simulation models, the distribution of chemicals is carried out as the process is optimized to achieve an economic objective.

EXAMPLE 6.6   *Selectivity of the Allyl Chloride Reactions*

To demonstrate the advantages of running the reactions at intermediate temperatures, show the rate constants for the three competing reactions as a function of temperature.

SOLUTION

As shown in the following graph, the rate constant of the desirable Reaction 1 is the largest relative to the rate constants of the other two reactions at the intermediate temperatures.
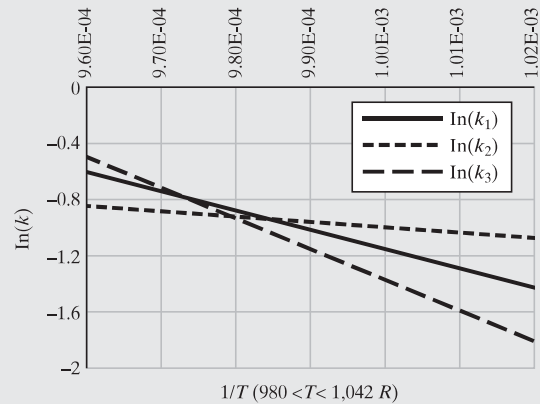
Often, adequate selectivities cannot be achieved by simply adjusting the temperature and pressure of the reactions. In these cases, the field of catalysis plays a crucial role. Chemists, biochemists, and chemical engineers work closely to design catalysts that permit the desired reactions to proceed more rapidly at lower temperatures while reducing the rates of side reactions. For this purpose, many successful reaction operations utilize crystalline zeolites, which are very effective *shape-selective catalysts.* In fact, it is possible to synthesize zeolite structures in which the cavities are just small enough to prevent the reactant molecules for the undesired side reactions from migrating to the reaction sites. Other commonly used catalysts involve the rare metals; for example, Platinum, palladium, and rhodium. Clearly, when distributing chemicals in process synthesis, it is crucial to understand the relative rates of the competing reactions. Company laboratories are a key source of this information, as are patents and articles in the scientific journals. Process designers spend considerable time searching the extensive literature to locate appropriate catalysts.

Of course, many fine books have been written on the subject of catalysis. To study how to design reactors to achieve the desired selectivity, several outstanding textbooks are available;

consider, for example, *Essentials of Chemical Reaction Engineering* (Fogler, 2011) and *The Engineering of Chemical Reactions* (Schmidt, 2004).

Reactive Separations

> ***Heuristic 8:*** *For reversible reactions especially, consider conducting them in a separation device capable of removing the products and hence driving the reactions to the right. Such reaction-separation operations lead to very different distributions of chemicals.*

The last step in process synthesis recommended in Section 2.3 is *task integration,* that is, the combination of operations into process units. In the synthesis steps recommended there, reaction operations are positioned first, chemicals are distributed (as discussed earlier in this section), and separation operations are positioned, followed by temperature-, pressure-, and phase-change operations, before task integration occurs. In some cases, however, this strategy does not lead to effective combinations of reaction and separation operations, for example, reactive distillation towers, reactive absorption towers, and reactive membranes. Alternatively, when the advantages of merging these two operations are examined by a design team, a combined reaction-separation operation is placed in the flowsheet before chemicals are distributed, with a significant improvement in the economics of the design. Although the subject of reactive separations is covered in Section 9.5, a brief introduction to reactive distillation is provided next.

   Reactive distillation is used commonly when the chemical reaction is reversible, for example,

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$
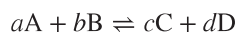
and there is a significant difference in the relative volatilities of the chemicals at the conditions of temperature and pressure suitable for the reaction. In conventional processing, when a reversible reaction operation is followed by a distillation column, it is common to use an excess of a feed chemical to drive the reaction forward. Alternatively, when the reaction takes place in the gas phase, the pressure is raised or lowered, depending on whether the summation of the stoichiometric coefficients is negative or positive. An advantage of reactive distillation, as shown for the production of methyl acetate,

$$\text{MeOH} + \text{HOAc} \rightleftharpoons \text{MeOAc} + \text{H}_2\text{O}$$
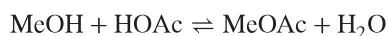
in Figure 6.8, is that the product chemicals are withdrawn from the reaction section in vapor and liquid streams, thereby driving the reaction forward without excess reactant or changes in pressure. Because methanol is more volatile than acetic acid, it is fed to the bottom of the reaction zone where it concentrates in the vapor phase and contacts acetic acid, which is fed at the top of the reaction zone and concentrates in the liquid phase. As methyl acetate is formed, it concentrates in the vapor phase and leaves the tower in the nearly pure distillate. The water product concentrates in the liquid phase and is removed from the tower in a nearly pure bottoms stream.
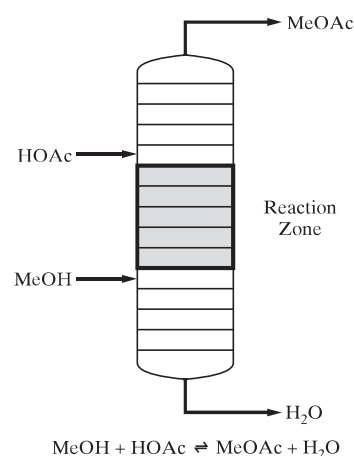

$$\text{MeOH} + \text{HOAc} \rightleftharpoons \text{MeOAc} + \text{H}_2\text{O}$$

Figure 6.8 Reactive distillation to produce methyl acetate.

   In summary, when the advantages of a combined operation (involving a reversible reaction and distillation, in this case) are clear to the design team, the operation can be inserted into the flowsheet *before* the chemicals are distributed in process synthesis. This is a heuristic design procedure that can simplify the synthesis steps and lead to a more profitable design.

Optimal Conversion

Consider the case of a single reaction with a large chemical equilibrium constant such that it is possible to obtain a complete conversion. However, the optimal conversion may not be complete conversion. Instead, an economic balance between a high reactor section cost at high conversion and a high separation section cost at low conversion determines the optimum. Unfortunately, a heuristic for the optimal conversion is not available because it depends on many factors. This subject is considered in more detail in Section 8.5 on reactor-separator-recycle networks.

6.4 SEPARATIONS

Separations Involving Liquid and Vapor Mixtures

> ***Heuristic 9:*** *Separate liquid mixtures using distillation, stripping, enhanced (extractive, azeotropic, reactive) distillation, liquid–liquid extraction, crystallization, and/or adsorption. The selection among these alternatives is considered in Chapter 9.*

> ***Heuristic 10:*** *Attempt to condense or partially condense vapor mixtures with cooling water or a refrigerant. Then, use Heuristic 9.*

> ***Heuristic 11:*** *Separate vapor mixtures using partial condensation, cryogenic distillation, absorption, adsorption, membrane separation, and/or desublimation. The selection among these alternatives is considered in Chapter 9.*

The selection of separation processes is dependent on the phase of the stream to be separated and the relative physical properties of its chemical species. Liquid and vapor streams are separated often using the strategy recommended by Douglas (1988) in
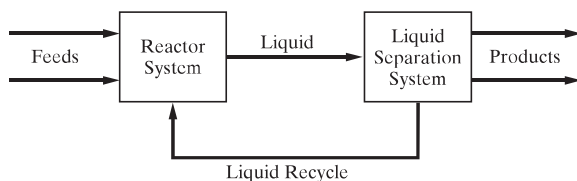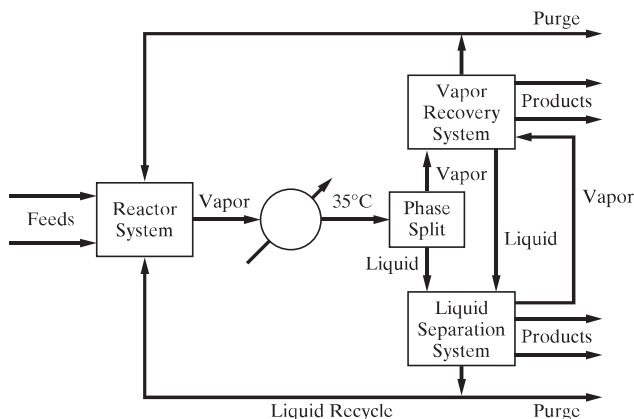
Figure 6.9 Flowsheet to separate liquid reactor effluents.
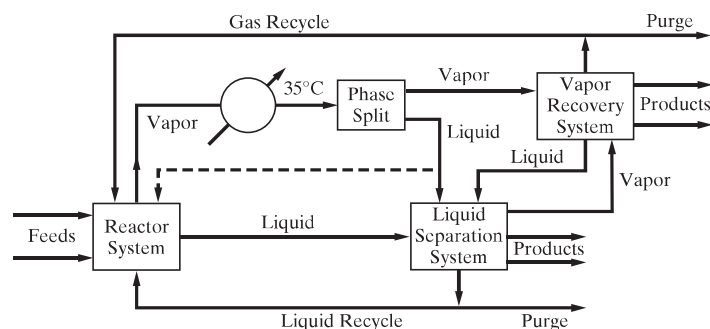(*Source:* Modified and reprinted with permission from Douglas, 1988).

Conceptual Design of Chemical Processes. This strategy is reproduced here using the original figures, slightly modified, with the publisher's permission. It is expanded upon in Chapter 9. Note that the choice of type of separator is often influenced by the scale of the process, with distillation often favored by economies-of-scale at large throughputs, and adsorption and membrane separation gaining favor as throughputs decrease.

When the reaction products are in the liquid phase, Douglas recommends that a liquid-separation system be inserted in the flowsheet, as shown in Figure 6.9. The liquid-separation system involves one or more of the following separators: distillation and enhanced distillation, stripping. liquid–liquid extraction, and so on, with the unreacted chemicals recovered in a liquid phase and recycled to the reaction operation.

For reaction products in the vapor phase, Douglas recommends that an attempt be made to partially condense them by cooling with cooling water or a refrigerant. Cooling water can cool the reaction products typically to 35°C, as shown in Figure 6.10. However, in warm climates, a higher temperature (e.g., 45°C) is required. The usual objective is to obtain a liquid phase, which is easier to separate without using refrigeration, which involves an expensive compression step. When partial condensation occurs, a liquid-separation system is inserted with a liquid purge added when necessary to remove trace inerts that concentrate in the liquid and are not readily separated. The vapor phase is sent to a vapor recovery system, which involves one or more of the following separations: partial condensation (at elevated pressures and cryogenic temperatures), cryogenic distillation, absorption, adsorption, membrane separation, and

Figure 6.11 Flowsheet to separate vapor/liquid reactor effluents.
(*Source:* Modified and reprinted with permission from Douglas, 1988).

desublimation. Unreacted chemicals are recycled to the reactor section and vapor products are removed. A vapor purge is added when necessary to remove inerts that concentrate in the vapor and are not readily separated. Any liquid produced in the vapor recovery system is sent to the liquid recovery system for product recovery and the recycle of unreacted chemicals.

When the reactor effluent is already distributed between vapor and liquid phases, Douglas combines the two flowsheets, as shown in Figure 6.11. It should be recognized that the development of the separation systems for all three flowsheets involves several heuristics. First, certain separation devices, such as membrane separators, are not considered for the separation of liquids. Second, to achieve a partial condensation, cooling water is utilized initially rather than compression and refrigeration. In this regard, it is presumed that liquid separations are preferred. An attempt is made to partially condense the vapor products, but no attempt is made to partially vaporize the liquid products. Although these and other heuristics are based on considerable experience and usually lead to profitable designs, the designer needs to recognize their limitations and be watchful for situations in which they lead to suboptimal designs. Furthermore, for the separation of multicomponent streams, formal methods have been developed to synthesize separation trains involving vapors or liquids. These are covered in Chapter 9.

Figure 6.10 Flowsheet to separate vapor reactor effluents.
(*Source:* Modified and reprinted with permission from Douglas, 1988).

EXAMPLE 6.7   *Hydrodealkylation of Toluene—Examples 6.1 and 6.5 Revisited*

Returning to the synthesis of a process to hydrodealkylate toluene, having completed the distribution of chemicals in Figure 6.6, the need to separate H_2 and CH_4 from C_6H_6, C_7H_8, and $C_{12}H_{10}$ is established. Clearly, the two vaporlike species can be easily removed in a simple vapor–liquid separator (i.e., a flash separation operation). Then, the heaviest three species can be separated in the liquid phase, as recommended by Douglas.

In the resulting flowsheet in Figure 6.12, the flash operation is adjusted to 100°F and 484 psia, slightly reduced from 494 psia in the reaction operation. The temperature is reduced using cooling water to recover the three heaviest species in the liquid phase. Then, following Douglas Heuristic 9, three distillation operations are selected to recover three products [Fuel (H_2 and CH_4), C_6H_6, and $C_{12}H_{10}$], and unreacted toluene to be recycled.
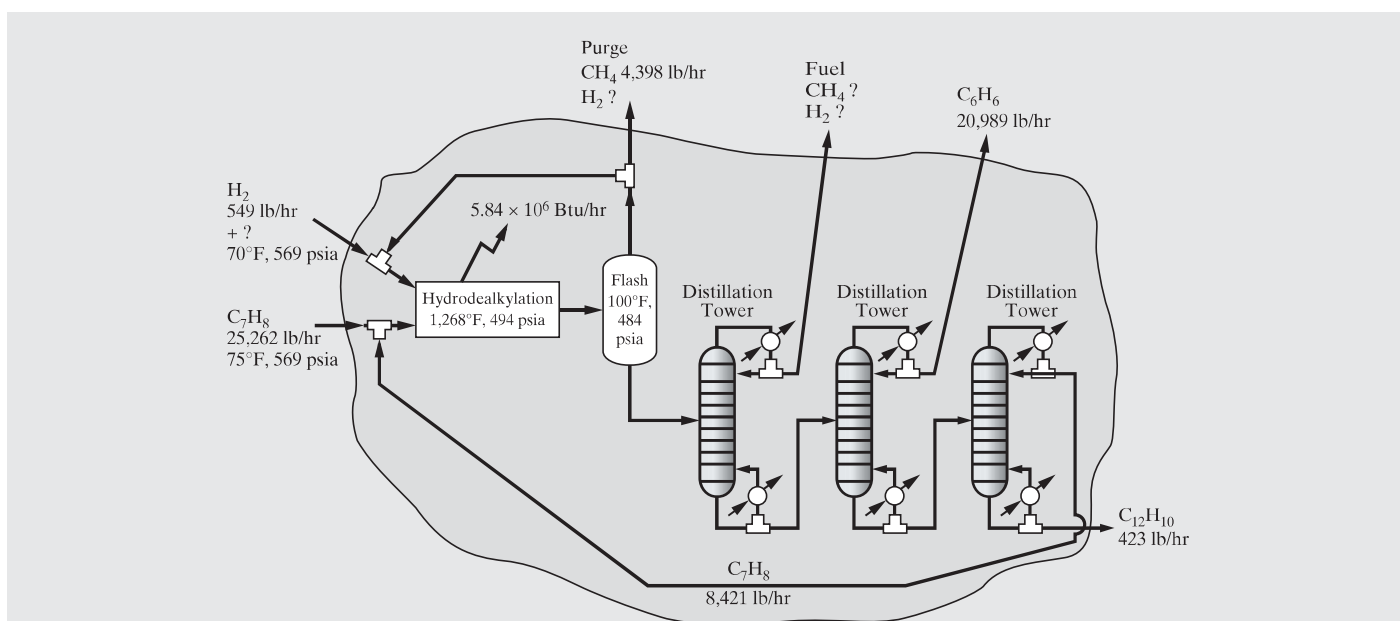
Figure 6.12 Flowsheet including the separation operations for the toluene hydrodealkylation process.
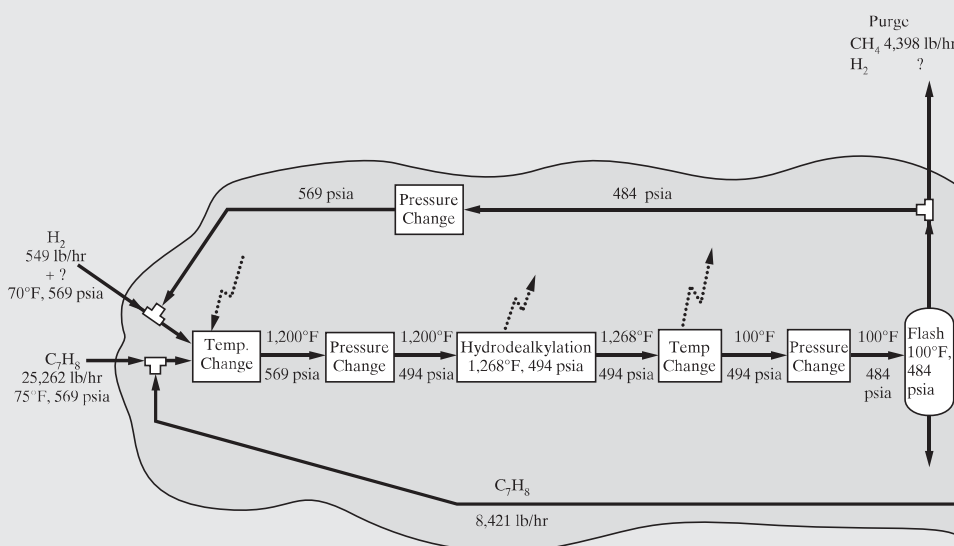
Figure 6.13 Reaction section for the toluene hydrodealkylation process with the temperature-, pressure-, and phase-change operations.

The next synthesis step involves positioning operations to change the temperatures, pressures, and phases where differences exist between the reaction and separation operations, as well as the sources of the raw materials and sinks for the product chemicals. For this process, the toluene and hydrogen feed streams are assumed to be available at elevated pressure, above that required in the hydroalkylation reactions. When this is not the case, the appropriate operations to increase the pressure must be inserted. One arrangement of the temperature-, pressure-, and phase-change operations is shown in Figure 6.13 for the reaction section only. Clearly, large quantities of heat are needed to raise the temperature of the feed chemicals to 1,200°F, and similarly large quantities of heat must be removed to partially condense the reactor effluent. These heat loads are calculated by ASPEN PLUS as discussed shortly.

The next synthesis step involves task integration, that is, the combination of operations into process units. In one task integration, shown in Figure 6.14, reactor effluent is quenched rapidly to 1,150°F, primarily to avoid the need for a costly high-temperature heat exchanger, and is sent to a feed/product heat exchanger. There, it is cooled as it heats the mixture of feed and recycle chemicals to 1,000°F. The stream is cooled further to 100°F, the temperature of the flash separator. The liquid from the quench is the product of the reactor section, yet a portion of it is recycled to quench the reactor effluent. The vapor product is recycled after a portion is purged to keep methane from building up in the process. This recycle is compressed to the pressure of the feed chemicals, 569 psia. Returning to the feed/product heat exchanger, the hot feed mixture leaves at 1,000°F and is sent to a gas-fired furnace for further heating to 1,200°F, the temperature of the feed to the reactor. Note that the gases are heated in a tube bank that resides in the furnace, and hence a high pressure drop is estimated (70 psia). On the other hand, the hydrodealkylation reactions take place in a large-diameter vessel that has negligible pressure drop. Clearly, at a later stage in the process design, these pressure drops, along with pressure drops in the connecting pipes, can be estimated. Normally, however, small errors in the pressure drops have only a small impact on the equipment sizes and costs as well as the operating costs.
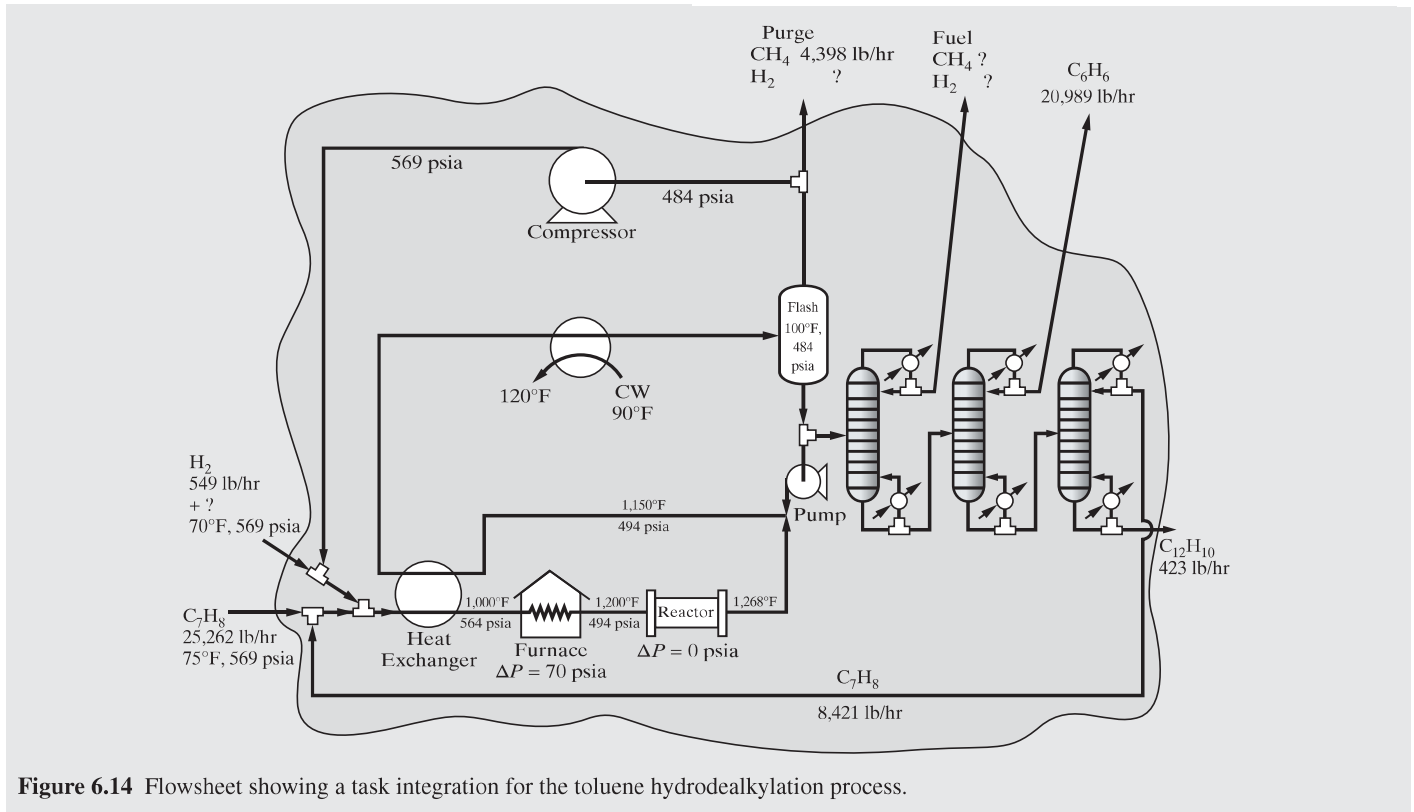
Figure 6.14 Flowsheet showing a task integration for the toluene hydrodealkylation process.

Separations Involving Solid Particles

For streams that involve solid phases or species that crystallize or precipitate, additional considerations are necessary when selecting a separation system because several steps may be necessary due to the impossibility of removing dry solids directly from a liquid. When separating inorganic chemicals, in an aqueous solution especially, the stream is often cooled or partially evaporated to recover solids by crystallization followed by filtration or centrifugation, and then drying. Often slurries are concentrated by settling, centrifugation, or filtration, before drying, as discussed in Section 9.7. Other devices for the removal of solid particles from gases and liquids are cyclones and hydroclones, respectively, as discussed in Section 6.9.

Crystallization occurs in three different modes. *Solution crystallization* applies mainly to inorganic chemicals, which are crystallized from a solvent, often water, with an operating temperature far below the melting point of the crystals. *Precipitation* is fast solution crystallization that produces large numbers of very small crystals. It usually refers to the case where one product of two reacting solutions is a solid of low solubility, for example, the precipitation of insoluble silver chloride when aqueous solutions of silver nitrate and sodium chloride are mixed together. In *melt crystallization,* two or more chemicals of comparable melting points are separated at an operating temperature in the range of the melting points. Crystallization is capable of producing very pure chemicals when conducted according to the following heuristics, noting that recovery by any mode of crystallization may be limited by a eutectic composition.

Heuristic 12: **Crystallize inorganic chemicals from a concentrated aqueous solution by chilling when solubility decreases significantly with decreasing temperature. Keep the solution at most 1–2°F below the saturation temperature at the prevailing concentration. Use crystallization by evaporation, rather than chilling, when solubility does not change significantly with temperature.**

Heuristic 13: **Crystal growth rates are approximately the same in all directions, but crystals are never spheres. Crystal growth rates and sizes are controlled by limiting the extent of supersaturation, $S = C/C_{saturation}$, where C is concentration, usually in the range $1.02 < S < 1.05$. Growth rates are influenced greatly by the presence of impurities and of certain specific additives that vary from case to case.**

Heuristic 14: **Separate organic chemicals by melt crystallization with cooling, using suspension crystallization followed by removal of crystals by settling, filtration, or centrifugation. Alternatively, use layer crystallization on a cooled surface with scraping or melting to remove the crystals. If the melt forms a solid solution, instead of a eutectic, use repeated melting and freezing steps, called fractional melt crystallization, or zone melting to obtain nearly pure crystalline products.**

Prior to crystallization, it is common to employ evaporation to concentrate a solution, particularly an aqueous solution of inorganic chemicals. Because of the relatively high cost of evaporating water with its very large heat of vaporization, the following heuristics are useful for minimizing the cost.

Heuristic 15: *Using multiple evaporators (called effects) in series, the latent heat of evaporation of water is recovered and reused. With a single evaporator, the ratio of the amount of water evaporated to the amount of external steam supplied to cause the evaporation is typically 0.8. For two effects, the ratio becomes 1.6; for three effects 2.4, and so forth. The magnitude of the boiling-point elevation caused by the dissolved inorganic compounds is a controlling factor in selecting the optimal number of effects. The elevation is often in the range of 3–10°F between solution and pure water boiling points. When the boiling-point rise is small, minimum evaporation cost is obtained with 8 to 10 effects. When the boiling point rise is appreciable, the optimal number of effects is small, 6 or less. If necessary, boost interstage steam pressures with steam-jet or mechanical compressors.*

Heuristic 16: *When employing multiple effects, the liquid and vapor flows may be in the same or different directions. Use forward feed, where both liquid and vapor flow in the same direction, for a small number of effects, particularly when the liquid feed is hot. Use backward feed, where liquid flows in a direction opposite to vapor flows, for cold feeds and/or a large number of effects. With forward feed, intermediate liquid pumps are not necessary, whereas they are necessary for backward feed.*

Solution crystallization produces a slurry of crystals and mother liquor, which is partially separated by filtration or centrifugation into a wet cake and a mother liquor. Filtration through a filter medium of porous cloth or metal may be carried out under gravity, vacuum, or pressure. Centrifugation may utilize a solid bowl or a porous bowl with a filter medium. Important factors in the selection of equipment include (1) moisture content of the cake, (2) solids content of the mother liquor, (3) fragility of the crystals, (4) crystal particle size, (5) need for washing the crystals to replace mother liquor with pure water, and (6) filtration rate. Filtration rate is best determined by measuring the rate of cake thickness buildup using a small-scale laboratory vacuum leaf filter test with the following criteria: Rapid, 0.1–10 cm/s; Medium, 0.1–10 cm/min; Slow, 0.1–10 cm/hr.

Heuristic 17: *When crystals are fragile, effective washing is required and clear mother liquor is desired, use gravity, top-feed horizontal pan filtration for slurries that filter at a rapid rate; vacuum rotary-drum filtration for slurries that filter at a moderate rate; and pressure filtration for slurries that filter at a slow rate.*

Heuristic 18: *When cakes of low moisture content are required, use solid-bowl centrifugation if solids are permitted in the mother liquor; centrifugal filtration if effective washing is required.*

Wet cakes from filtration or centrifugation operations are sent to dryers for removal of remaining moisture. A large number of different types of commercial dryers have been developed to handle the many different types of feeds, which include not only wet cakes, but also pastes, slabs, films, slurries, and liquids. The heat for drying may be supplied from a hot gas in direct contact with the wet feed or it may be supplied indirectly through a wall. Depending on the thickness of the feed and the degree of agitation, drying times can range from seconds to hours. The following heuristics are useful in making a preliminary selection of drying equipment:

Heuristic 19: *For granular material, free flowing or not, of particle sizes from 3 to 15 mm, use continuous tray and belt dryers with direct heat. For free-flowing granular solids that are not heat sensitive, use an inclined rotary cylindrical dryer, where the heat may be supplied directly from a hot gas or indirectly from tubes carrying steam that run the length of the dryer and are located in one or two rings concentric to and located just inside the dryer rotating shell. For small, free-flowing particles of 1–3 mm in diameter when rapid drying is possible, use a pneumatic conveying dryer with direct heat. For very small free-flowing particles of less than 1 mm in diameter, use a fluidized-bed dryer with direct heat.*

Heuristic 20: *For pastes and slurries of fine solids, use a drum dryer with indirect heat. For a liquid or pumpable slurry, use a spray dryer with direct heat.*

6.5 HEAT REMOVAL FROM AND ADDITION TO REACTORS

After positioning the separation operations, the next step in process synthesis, as recommended in Section 2.3, is to insert the operations for temperature, pressure, and phase changes. To accomplish this, many excellent algorithms for heat and power integration have been developed. These are presented in Chapter 11. The objective of this section, which considers several approaches to remove the heat generated in exothermic reaction operations and to add the heat required by endothermic reaction operations, is more limited. The subject is discussed at this point because several of the approaches for heat transfer affect the distribution of chemicals in the flowsheet and are best considered after the reaction operations are positioned. These approaches are discussed next, together with other common approaches to remove or add the heat of reaction. First, the methods for removing the heat generated by exothermic reaction operations are presented. Then, some distinctions are drawn for the addition of heat to endothermic reaction operations. For the details of heat removal from or addition to complex reactor configurations, the reader is referred to Section 8.4.

Heat Removal from Exothermic Reactors

Given an exothermic reaction operation, an important first step is to compute the *adiabatic reaction temperature,* that is, the maximum temperature attainable, in the absence of heat transfer. Note that this can be accomplished readily with any of the process simulators. Furthermore, algorithms have been presented for these iterative calculations by Henley and Rosen (1969) and Myers and Seider (1976), among many sources.

EXAMPLE 6.8   Adiabatic Reaction Temperature

Consider the reaction of carbon monoxide and hydrogen to form methanol:

$$CO + 2H_2 \rightarrow CH_3OH$$
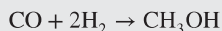
With the reactants fed in stoichiometric amounts at 25°C and 1 atm, calculate the standard heat of reaction and the adiabatic reaction temperature.

SOLUTION

In ASPEN PLUS, the RSTOIC subroutine is used with a feed stream containing 1 1bmol/hr CO and 2 1bmol/hr H_2 and the PSRK method (Soave-Redlich-Kwong equation of state with Holderbaum-Gmehling mixing rules). To obtain the heat of reaction, the fractional conversion of CO is set at unity with the product stream temperature at 25°C and the vapor fraction at 1.0. The latter keeps the methanol product in the vapor phase at 2.44 psia, and hence both the reactants and product species are vapor. The heat duty computed by RSTOIC is −38,881 Btu/hr, and hence the heat of reaction is $\Delta H_r = -38,881$ Btu/1bmol CO.

To obtain the adiabatic reaction temperature for complete conversion, the heat duty is set at zero and the pressure of the methanol product stream is returned to 1 atm. This produces an effluent temperature of 1,158°C (2,116°F), which is far too high for the Cu-based catalyst and the materials of construction in most reactor vessels. Hence, a key question in the synthesis of the methanol process, and similar processes involving highly exothermic reactions, is how to lower the product temperature. In most cases, the designer is given or sets the maximum temperature in the reactor and evaluates one of the heat-removal strategies described in this section.

Note that these results can be reproduced using the EXAM6-6.bkp file in the Program and Simulation Files folder, which can be downloaded from the Wiley Web site associated with this book. Also, RSTOIC-type subroutines are described in Section 8.1.

Heuristic 21: *To remove a highly exothermic heat of reaction, consider the use of excess reactant, an inert diluent, or cold shots. These affect the distribution of chemicals and should be inserted early in process synthesis.*

Heuristic 22: *For less exothermic heats of reaction, circulate reactor fluid to an external cooler or use a jacketed vessel or cooling coils. Also, consider the use of intercoolers between adiabatic reaction stages.*

To achieve lower temperatures, several alternatives are possible, beginning with those that affect the distribution of chemicals.

1. Use an excess of one reactant to absorb the heat. This alternative was discussed earlier in Section 6.3 and is illustrated in Figure 6.15a, where excess B is recovered from the separator and recirculated to the reaction operation. Heat is removed in the separator or by exchange with a cold process stream or a cold utility (e.g., cooling water).

EXAMPLE 6.9   Excess Reactant

Returning to Example 6.8, an excess of H_2 is specified such that the mole ratio of H_2/CO is arbitrarily 10 and the temperature of the reactor effluent stream is computed.

SOLUTION

Again, using the RSTOIC subroutine in ASPEN PLUS with a complete conversion of CO, the effluent temperature is reduced to 337°C (639°F), a result that can be reproduced using EXAM6-9.bkp file in the Program and Simulation Files folder, which can be downloaded from the Wiley Web site associated with this book. The Sensitivity command can be used to compute the effluent temperature as a function of the H_2/CO ratio, as in Exercise 6.8.

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2. Use of an inert diluent, S. Figure 6.15b illustrates this alternative. One example occurs in the manufacture of methanol, where carbon monoxide and hydrogen are reacted in a fluidized bed containing catalyst. In the Marathon Oil process, a large stream of inert oil is circulated through the reactor, cooled, and recirculated to the reactor. Note that diluents like oil, with large heat capacities, are favored to maintain lower temperatures with smaller recirculation rates. The disadvantage of this approach, of course, is that a new species, S, is introduced, which, when separated from the reaction mix, cannot be removed entirely from the desired product. As in Alternative 1, heat is removed in the separator or by exchange with a cold process stream or a cold utility.

EXAMPLE 6.10   n-Dodecane Diluent

Returning to Example 6.8, 5 1bmol/hr of *n*-dodecane is added to the reactor feed (1 1bmol/hr CO and 2 1bmol/hr H_2) and the temperature of the reactor effluent stream is computed.

SOLUTION

In this case, the effluent temperature is reduced sharply to 77.6°C (171.7°F), a result that can be reproduced using the EXAM6-10.bkp file in the Program and Simulation Files folder, which can be downloaded from the Wiley Web site associated with this book. The *n*-dodecane flow rate is adjusted to give an adequate temperature reduction. This is accomplished in Exercise 6.9.
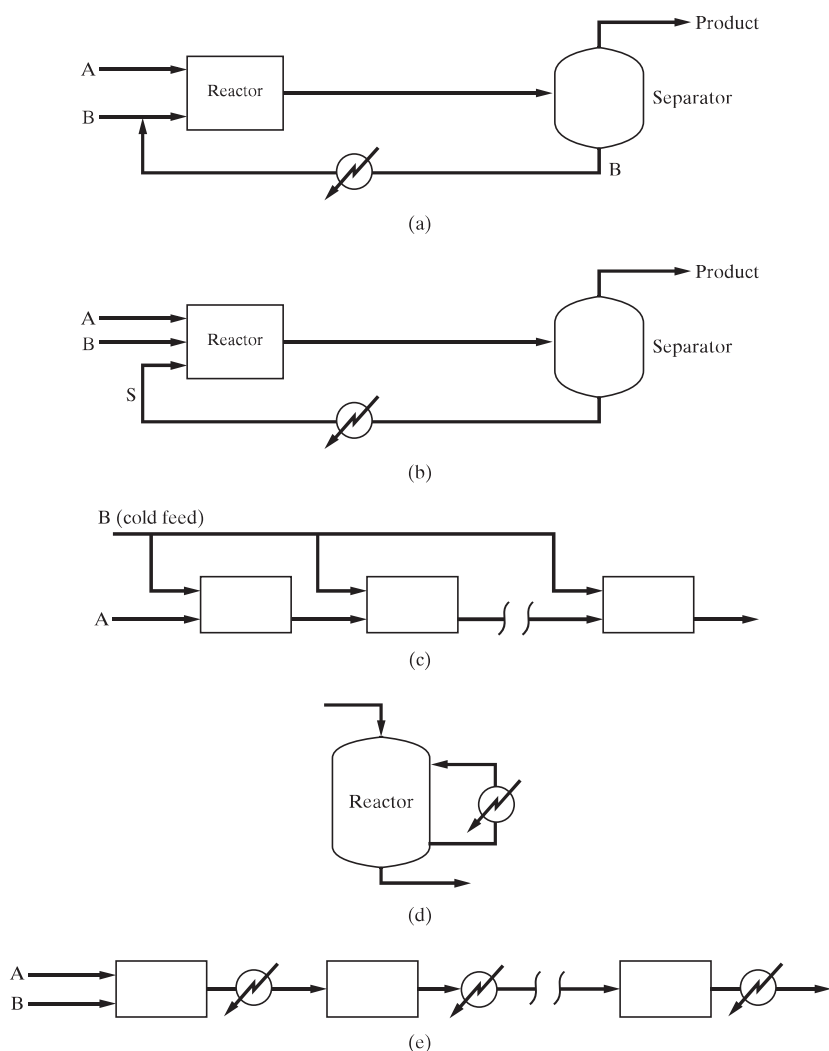
Figure 6.15 Flowsheets to remove the heat of reaction: (a) use of excess reactant; (b) use of inert diluent, S; (c) use of cold shots; (d) diabatic operation; (e) use of intercoolers.

3. Use of cold shots. In this alternative, as illustrated in Figure 6.15c, one of the reactants is cooled and distributed among several adiabatic reaction operations in series. The effluent from each stage, at an elevated temperature, is cooled with a cold shot of reactant B. In each state, additional A is reacted until it is completely consumed in the last stage. The reader is referred to Example 8.5, which shows how to adjust the cold-shot distribution in an ammonia synthesis reactor to maximize the conversion of synthesis gas to ammonia.

The next two alternatives do not affect the distribution of chemicals and are usually considered for moderately exothermic reactions, later in process synthesis—that is, during heat and power integration when opportunities are considered for heat exchange between high- and low-temperature streams.

4. Diabatic operation. In this case, heat is removed from the reaction operation in one of several ways. Either a cooling jacket is utilized or coils are installed through which a cold process stream or cold utility is circulated. In some cases, the reaction occurs in catalyst-filled tubes, surrounded by coolant, or in catalyst-packed beds interspersed with

tubes that convey a coolant stream, which is often the reactor feed stream, as illustrated for the ammonia reactor (TVA design) in Figure 6.16. Here, heat transfer from the reacting species in the catalyst bed preheats the reactants, N_2 and H_2, flowing in the cooling tubes, with the tube bundle designed to give adequate heat transfer as well as reaction. The design procedure is similar to that for the design of heat exchangers in Chapter 12. It is noted that for the large-capacity, ammonia-synthesis reactors, the optimal design usually calls for a series of adiabatic beds packed with catalyst, with cooling achieved using cold shots, as shown in Figure 6.15c. Most of the commercial ammonia reactors use a combination of these two cooling arrangements. Another alternative is to circulate a portion of the reacting mixture through an external heat exchanger in which the heat of reaction is removed, as shown in Figure 6.15d.

5. Use of intercoolers. As shown in Figure 6.15e, the reaction operation is divided into several adiabatic stages with heat removed by heat exchangers placed between each stage. Here, also, heat is transferred either to cold process streams that require heating or to cold utilities.
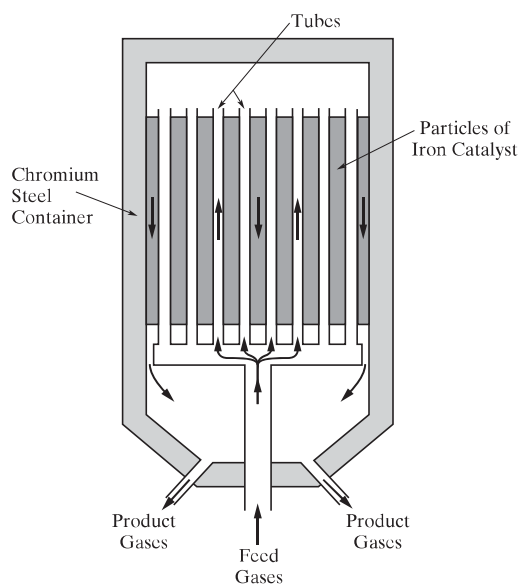
Figure 6.16 Tubular ammonia reactor. (*Source:* Based on TVA Design, from Baddour et al., 1965).

In all of these alternatives, the design team selects acceptable temperature levels and flow rates of the recirculating fluids. These are usually limited by the rates of reaction, and especially the need to avoid thermal runaway or catalyst deterioration, as well as the materials of construction and the temperature levels of the available cold process streams and utilities, such as cooling water. It is common to assign temperatures on the basis of these factors early in process synthesis. However, as optimization strategies are perfected, temperature levels are varied within bounds. See Chapters 11 and 21 for discussions of the use of optimization in process synthesis and optimization of process flowsheets, as well as Example 8.5 to see how constrained optimization is applied to design an ammonia cold-shot converter.

Heat Addition to Endothermic Reactors

Heuristic 23: **To control temperature for a highly endothermic heat of reaction, consider the use of excess reactant, an inert diluent, or hot shots. These affect the distribution of chemicals and should be inserted early in process synthesis.**

Heuristic 24: **For less endothermic heats of reaction, circulate reactor fluid to an external heater or use a jacketed vessel or heating coils. Also, consider the use of interheaters between adiabatic reaction stages.**

For endothermic reaction operations, sources of the heat of reaction are needed. As in the case of exothermic reaction operations, the heat of reaction and the adiabatic reaction temperature can be computed using a simulator. The latter provides a lower bound on the temperature of the reactor effluent.

When adding heat to endothermic reaction operations, three approaches for heat addition affect the distribution of chemicals in the flowsheet and are best considered immediately after the reaction operations are positioned. Given that the feed stream is preheated, these approaches closely parallel the first three approaches for heat removal from exothermic reaction operations in Figures 6.15a–6.15c. When an excess of a reactant is utilized, the decrease in effluent temperature varies inversely with the degree of excess. Similarly, when an inert diluent is added, the effluent temperature is decreased inversely with the amount of diluent. For example, when ethylbenzene is pyrolyzed to produce styrene,

$$\text{Ethylbenzene} \rightarrow \text{Styrene} + H_2$$
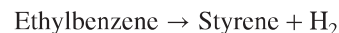
superheated steam is added to provide the heat of reaction and keep the reaction temperature elevated. Of course, the addition of steam significantly increases the reactor volume and both the operating and installation costs. Finally, it is possible to add hot shots of reactants to a series of reactors in a way similar to the cold shots added in Figure 6.15c.

The same two alternatives that do not affect the distribution of chemicals apply for the addition of heat to endothermic reaction operations. In this case, the diabatic operation in Figure 6.15d involves the addition of heat in ways similar to the removal of heat. Jackets, coils, and heat exchanger designs are very common. Also, interheaters between stages, as in Figure 6.15e, are used in many situations in place of intercoolers.

6.6 HEAT EXCHANGERS AND FURNACES

As discussed in the previous two sections, heat exchange is commonly used in conjunction with separation and reaction steps to change the temperature and/or phase condition of a process stream. When using a process simulator to perform heat-exchange calculations, it is necessary to select a method of heat exchange from the following six possibilities, where all but the last two involve the separation, by a solid wall, of the two streams exchanging heat.

1. Heat exchange between two process fluids using a double-pipe, shell-and-tube, or compact heat exchanger.

2. Heat exchange between a process fluid and a utility, such as cooling water or steam, using a double-pipe, shell-and-tube, air-cooled, or compact heat exchanger.

3. High-temperature heating of a process fluid using heat from the products of combustion in a furnace (also called a fired heater).

4. Heat exchange within a reactor or separator, rather than in an external heat-exchange device such as a shell-and-tube heat exchanger or furnace, as described in Section 6.5.

5. Direct heat exchange by mixing the two streams that are exchanging heat.

6. Heat exchange involving solid particles.

The following heuristics are useful in selecting an initial basis for the heat-exchange method and the operating conditions. Details of heat exchanger selection and design are presented in Chapter 12.

Heuristic 25: *Unless required as part of the design of the separator or reactor, provide necessary heat exchange for heating or cooling process fluid streams, with or without utilities, in an external shell-and-tube heat exchanger using countercurrent flow. However, if a process stream requires heating above 750°F, use a furnace unless the process fluid is subject to chemical decomposition.*

Preliminary estimates of exit temperatures of streams flowing through a heat exchanger can be made with the following heuristics.

Heuristic 26: *Near-optimal minimum temperature approaches in heat exchangers depend on the temperature level as follows:*

10°F or less for temperatures below ambient.

20°F for temperatures at or above ambient up to 300°F.

50°F for high temperatures.

250 to 350°F in a furnace for flue gas temperature above inlet process fluid temperature.

As an example, suppose it is desired to heat 25,000 1b/hr of toluene at 100°F and 90 psia with 25,000 1b/hr of styrene at 300°F and 50 psia. Under these conditions, assume that both streams will be liquid, but this must be verified by flash calculations after the exit temperatures and pressures have been determined. From the previous two heuristics, use a shell-and-tube heat exchanger with countercurrent flow and a minimum approach temperature of 20°F. Let the average specific heats of the two streams be 0.43 Btu/1b-°F for toluene and 0.44 Btu/1b-°F for styrene. Initially it is not known to which end of the heat exchanger the 20°F minimum approach applies. Assume it applies at the toluene inlet end. If so, the styrene exit temperature is $100 + 20 = 120$°F. This gives a heat-exchanger duty, based on styrene, of:

$$Q = 25,000(0.44)(300 - 120) = 1,980,000 \text{ Btu/hr}$$

Using this duty, the exit temperature of toluene, $T_{\text{toluene out}}$, can be computed from:

$$Q = 1,980,000 = 25,000(0.43)(T_{\text{toluene out}} - 100)$$

Solving, $T_{\text{toluene out}} = 284.2$°F. But this gives a temperature approach of $300 - 284.2 = 15.8$°F at the styrene inlet end, which is less than the minimum approach of 20°F. Therefore, the minimum approach must be applied to the styrene inlet end. Similar calculations give $T_{\text{toluene out}} = 280$°F and $T_{\text{styrene out}} = 124.1$°F. This corresponds to an approach temperature at the toluene inlet end of 24.1°F, which is greater than the minimum approach temperature and, therefore, is acceptable.

Heuristic 27: *When using cooling water to cool or condense a process stream, assume a water inlet temperature of 90°F (from a cooling tower) and a maximum water outlet temperature of 120°F.*

When cooling and condensing a gas, both sensible and latent heat can be removed in a single heat exchanger. However, because of the many two-phase flow regimes that can occur when boiling a fluid, it is best to provide three separate heat exchangers when changing a subcooled liquid to a superheated gas, especially when the difference between the bubble point and dew point is small. The first exchanger preheats the liquid to the bubble point; the second boils the liquid; and the third superheats the vapor.

Heuristic 28: *Boil a pure liquid or close-boiling liquid mixture in a separate heat exchanger, using a maximum overall temperature driving force of 45° F to ensure nucleate boiling and avoid undesirable film boiling as discussed in Section 12.1.*

As discussed in detail in Section 12.1, the minimum approach temperature in a countercurrent-flow heat exchanger may occur at an intermediate location rather than at one of the two ends when one of the two streams is both cooled and condensed. If the minimum temperature approach is assumed to occur at one of the two ends of the heat exchanger, a smaller approach or a temperature crossover that violates the second law of thermodynamics may occur at an intermediate location. To avoid this situation, the following heuristic should be applied.

Heuristic 29: *When cooling and condensing a stream in a heat exchanger, a zone analysis, described in Section 12.1, should be made to make sure that the temperature difference between the hot stream and the cold stream is equal to or greater than the minimum approach temperature at all locations in the heat exchanger. The zone analysis is performed by dividing the heat exchanger into a number of segments and applying an energy balance to each segment to determine corresponding stream inlet and outlet temperatures for the segment, taking into account any phase change. A process simulation program conveniently accomplishes the zone analysis.*

When using a furnace to heat and/or vaporize a process fluid, the following heuristic is useful for establishing inlet and outlet heating medium temperature conditions so that fuel and air requirements can be estimated.

Heuristic 30: *Typically, a hydrocarbon gives an adiabatic flame temperature of approximately 3,500°F when using the stoichiometric amount of air. However, use excess air to achieve complete combustion and give a maximum flue gas temperature of 2,000°F. Set the stack gas temperature in the range of 650–950°F to prevent condensation of corrosive components of the flue gas.*

Pressure drops of fluids flowing through heat exchangers and furnaces may be estimated with the following heuristics.

Heuristic 31: *Estimate   heat-exchanger   pressure   drops   as follows:*

1.5 psi for boiling and condensing.

> *3 psi for a gas.*
>
> *5 psi for a low-viscosity liquid.*
>
> *7–9 psi for a high-viscosity liquid.*
>
> *20 psi for a process fluid passing through a furnace.*

Unless exotic materials are used, heat exchangers should not be used for cooling and/or condensing process streams with temperatures above 1,150°F. Instead, use the following heuristic for direct heat exchange.

Heuristic 32: *Quench a very hot process stream to at least 1,150°F before sending it to a heat exchanger for additional cooling and/or condensation. The quench fluid is best obtained from a downstream separator as in Figure 7.31 for the toluene hydrodealkylation process. Alternatively, if the process stream contains water vapor, liquid water may be an effective quench fluid.*

Streams of solid particles are commonly heated or cooled directly or indirectly. Heat transfer is much more rapid and controllable when using direct heat exchange.

Heuristic 33: *If possible, heat or cool a stream of solid particles by direct contact with a hot gas or cold gas, respectively, using a rotary kiln, a fluidized bed, a multiple hearth, or a flash/pneumatic conveyor. Otherwise, use a jacketed spiral conveyor.*

6.7   PUMPING, COMPRESSION, PRESSURE REDUCTION, VACUUM, AND CONVEYING OF SOLIDS

As mentioned in the previous section, it is common to consider the integration of all temperature- and pressure-change operations. This is referred to as *heat and power integration* and is covered in Chapter 11 after important thermodynamic considerations are presented first in Chapter 10. At this point, however, there are several important heuristics that are useful in determining what type of operations to insert into the flowsheet to increase or decrease pressure. Details of the equipment used to perform pressure-change operations are presented in Chapter 14.

Increasing the Pressure

Gases.   To increase the pressure, the most important consideration is the phase state (vapor, liquid, or solid) of the stream. If the stream is a gas, the following heuristic applies for determining whether a *fan*, *blower*, or *compressor* should be used.

Heuristic 34: *Use a fan to raise the gas pressure from atmospheric pressure to as high as 40 inches water gauge (10.1 kPa gauge or 1.47 psig). Use a blower or compressor to raise the gas pressure to as high as 206 kPa gauge or 30 psig. Use a compressor or a staged compressor system to attain pressures greater than 206 kPa gauge or 30 psig.*

In Figure 6.14 for the toluene hydrodealkylation process, the pressure of the recycle gas leaving the flash drum at 100°F and 484 psia is increased with a compressor to 569 psia so that, after pressure drops 5 psia through the heat exchanger and 70 psia through the furnace, the recycle gas enters the reactor at a required pressure of 494 psia.

The following heuristic is useful for estimating the exit temperature, which can be significantly higher than the entering temperature, and the power requirement when increasing the gas pressure by a single stage of reversible, adiabatic compression.

Heuristic 35: *Estimate the theoretical adiabatic horsepower (THp) for compressing a gas:*

$$THp = SCFM \left(\frac{T_1}{8,130a} \right) \left[\left(\frac{P_2}{P_1} \right)^a - 1 \right] \qquad (6.1)$$

where SCFM = standard cubic feet of gas per minute at 60°F and 1 atm (379 SCF/1bmol); T_1 = gas inlet temperature in °R: inlet and outlet pressures, P_1 and P_2, are absolute pressures: and $a = (k-1)/k$ with k = the gas-specific heat ratio, C_p/C_v
    Estimate the theoretical exit temperature, T_2, for a gas compressor:

$$T_2 = T_1 (P_2/P_1)^a \qquad (6.2)$$

For example, if air at 100°F is compressed from 1 to 3 atm (compression ratio = 3) using $k = 1.4$, the *THp* is computed to be 128 Hp/standard million ft^3/day with an outlet temperature of 306°F.

When using a compressor, the gas theoretical exit temperature should not exceed approximately 375°F, the limit imposed by most compressor manufacturers. This corresponds to a compression ratio of 4 for $k = 1.4$ and $T_2 = 375$°F. When the exit gas temperature exceeds the limit, a single gas compression step cannot be used. Instead, a multistage compression system, with intercoolers between each stage, must be employed. Each intercooler cools the gas back down to approximately 100°F. The following heuristic is useful for estimating the number of stages, *N*, required and the interstage pressures.

Heuristic 36: *Estimate the number of gas compression stages, N, from the following table, which assumes a specific heat ratio of 1.4 and a maximum compression ratio of 4 for each stage.*

Final Pressure/Inlet Pressure	Number of Stages
< 4	1
4–16	2
16–64	3
64–256	4

Optimal interstage pressures correspond to equal Hp for each compressor. Therefore, based on the above equation for theoretical compressor Hp, estimate

interstage pressures by using approximately the same compression ratio for each stage with an intercooler pressure drop of 2 psi or 15 kPa.

For example, in Exercise 7.8. a feed gas at 100°F and 30 psia is to be compressed to 569 psia. From the above table with an overall compression ratio of $569/30 = 19$, a three-stage system is indicated. For equal compression ratios, the compression ratio for each stage of a three-stage system $= 19^{1/3} = 2.7$. The estimated stage pressures are as follows, taking into account a 2 psi drop for each intercooler and its associated piping:

Stage	Compressor Inlet Pressure, psia	Compressor Outlet Pressure, psia
1	30	81
2	79	213
3	211	569

When compressing a gas, the entering stream must not contain liquid, and the exiting stream must be above its dew point so as not to damage the compressor. To remove any entrained liquid droplets from the entering gas, a vertical knock-out drum equipped with a demister pad is placed just upstream of the compressor. To prevent condensation in the compressor, especially when the entering gas is near its dew point, a heat exchanger should also be added at the compressor inlet to provide sufficient preheat to ensure that the exiting gas is well above its dew point.

Liquids.   If the pressure of a liquid is to be increased, a pump is used. The following heuristic is useful for determining the types of pumps best suited for a given task where the head in feet is the pressure increase across the pump in psf (pounds force/ft^2) divided by the liquid density in 1b/ft^3.

> *Heuristic 37:*   *For heads up to 3,200 ft and flow rates in the range of 10–5,000 gpm, use a centrifugal pump. For high heads up to 20,000 ft and flow rates up to 500 gpm, use a reciprocating pump. Less common are axial pumps for heads up to 40 ft for flow rates in the range of 20–100,000 gpm and rotary pumps for heads up to 3,000 ft for flow rates in the range of 1–1,500 gpm.*

For liquid water with a density of 62.4 1b/ft^3, heads of 3,000 and 20,000 ft correspond to pressure increases across the pump of 1,300 and 8,680 psi, respectively.

When pumping a liquid from an operation at one pressure, P_1, to a subsequent operation at a higher pressure, P_2, the pressure increase across the pump must be higher than $P_2 - P_1$ to overcome pipeline pressure drop, control valve pressure drop, and possible increases in elevation (potential energy). This additional pressure increase may be estimated by the following heuristic.

> *Heuristic 38:*   *For liquid flow, assume a pipeline pressure drop of 2 psi/100 ft of pipe and a control valve pressure drop of at least 10 psi. For each 10-ft rise in elevation, assume a pressure drop of 4 psi.*

For example, in Figure 2.6 the combined chlorination reactor effluent and dichloroethane recycle at 1.5 atm is sent to a pyrolysis reactor operating at 26 atm. Although no pressure drops are shown for the two temperature-change and one phase-change operations, they may be estimated at 10 psi total. The line pressure drop and control valve pressure drop may be estimated at 15 psi. Take the elevation change as 20 ft, giving 8 psi. Therefore, the total additional pressure increase is $10 + 15 + 8 = 33$ psi, or 2.3 atm. The required corresponding pressure increase across the pump (pressure-change operation) is, therefore $(26 - 1.5) + 2.3 = 26.8$ atm. For a liquid density of 78 1b/ft^3 or 10.4 1b/gal, the required pumping head is $26.8(14.7)(144)/78 = 730$ ft, The flow rate through the pump is $(158,300 + 105,500)/10.4/60 = 422$ gpm. Using Heuristic 37, select a centrifugal pump.

The following heuristic provides an estimate of the theoretical pump *Hp*. Unlike the case of gas compression, the temperature change across the pump is small and can be neglected.

> *Heuristic 39:*   *Estimate the theoretical horsepower (THp) for pumping a liquid:*

$$THp = (gpm)(\text{Pressure increase, psi})/1{,}714 \quad (6.3)$$

For example, the theoretical *Hp* for pumping the liquid in Figure 2.6, using the above data, is $(422)(26.8)(14.7)/1{,}714 = 97$ Hp.

Decreasing the Pressure

The pressure of a gas or liquid stream can be reduced to ambient pressure or higher with a single throttle valve or two or more such valves in series. The adiabatic expansion of a gas across a valve is accompanied by a decrease in the temperature of the gas. The exiting temperature is estimated from Eq. (6.2) for gas compression. For a liquid, the exit temperature is almost the same as the temperature entering the valve. In neither case is shaft work recovered from the fluid. Alternatively, it is possible to recover energy in the form of shaft work that can be used elsewhere by employing a turbinelike device. For a gas, the device is referred to as an expander, expansion turbine, or turboexpander. For a liquid, the corresponding device is a power-recovery turbine. The following heuristics are useful in determining whether a turbine should be used in place of a valve.

> *Heuristic 40:*   *Consider the use of an expander for reducing the pressure of a gas or a pressure-recovery turbine for reducing the pressure of a liquid when more than 20 Hp and 150 Hp, respectively, can be recovered.*

> *Heuristic 41:*   *Estimate the theoretical adiabatic horsepower (THp) for expanding a gas:*

$$THp = SCFM \left(\frac{T_1}{8{,}130a} \right) \left[1 - \left(\frac{P_2}{P_1} \right)^{a} \right] \quad (6.4)$$

> *Heuristic 42:*   *Estimate the theoretical horsepower (THp) for reducing the pressure of a liquid:*

$$THp = (gpm)(\text{Pressure decrease, psi})/1{,}714 \quad (6.5)$$

In Figure 2.5, the pyrolysis effluent gas, following cooling to 170°C and condensation to 6°C at 26 atm, is reduced in pressure to 12 atm before entering the first distillation column. The flowsheet in Figure 2.5 shows the use of a valve following the condenser to accomplish the pressure reduction. Should a pressure-recovery turbine be used? Assume a flow rate of 422 gpm. The pressure decrease is $(26 - 12) \ (14.7) = 206$ psi. Using Eq. (6.5), $THp = (422)(206)/1,714 = 51$, which is much less than 150 Hp. Therefore, according to the above heuristic, a valve is preferred. Alternatively, the pressure reduction step could be inserted just prior to the condenser, using an expander on the gas at its dew point of 170°C. The total flow rate is $(58,300 + 100,000 + 105,500)/60 = 4,397$ lb/min. The average molecular weight is computed to be 61.9, giving a molar flow rate of 71 lbmol/min. The corresponding SCFM (standard cubic feet per minute at standard conditions of 60°F and 1 atm) is $(71)(379) = 26,000$. Assume $k = 1.2$, giving $a = (1.2 - 1)/1.2 = 0.167$. With a decompression ratio of $12/26 = 0.462$ and $T_1 = 797°R$, Eq. (6.4) gives 1,910 THp, which is much more than 120 Hp. Therefore, according to the above heuristic, an expander should be used. The theoretical temperature of the gas exiting the expander, using Eq. (6.2) is $797(0.462)^{0.167} = 701°R = 241°F = 116°C$.

Pumping a Liquid or Compressing a Gas

When it is necessary to increase the pressure between process operations, it is almost always far less expensive to pump a liquid rather than compress a vapor. This is because the power required to increase the pressure of a flowing stream is

$$W = \int_{P_1}^{P_2} V \, dP \tag{6.6}$$

where V is the volumetric flow rate, which is normally far less for liquid streams—typically two orders of magnitude less. Hence, it is common to install pumps having approximately 10 Hp, whereas comparable compressors require approximately 1,000 Hp and are far more expensive to purchase and install. For these reasons, if the low-pressure stream is a vapor and the phase state is also vapor at the higher pressure, it is almost always preferable to condense the vapor, pump it and revaporize it rather than compress it, as illustrated in Figure 6.17. If the low-pressure stream is a liquid
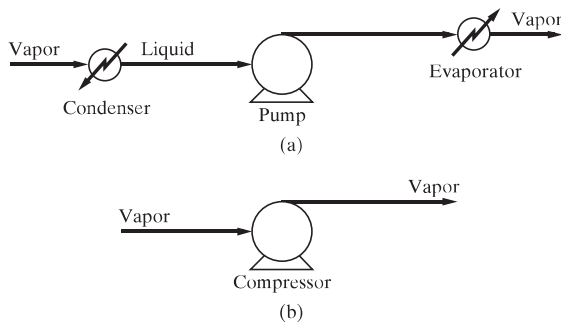
Figure 6.17 Alternatives for raising the pressure of a vapor stream: (a) pump a liquid and (b) compress the vapor.

and the high-pressure stream is a vapor, it is preferable to increase the pressure first with a pump and then vaporize the liquid rather than vaporize the liquid and then compress it. This is the subject of Exercise 6.12 and the following example.

Heuristic 43: ***To increase the pressure of a stream, pump a liquid rather than compress a gas unless refrigeration is needed.***

EXAMPLE 6.11 *Feed Preparation of Ethylbenzene*

Ethylbenzene is to be taken from storage as a liquid at 25°C and 1 atm and fed to a styrene reactor as a vapor at 400°C and 5 atm at 100,000 lb/hr. In this example, two alternatives are considered for positioning the temperature- and pressure-increase operations.

SOLUTION

1. Pump first. Using the PUMP and HEATER subroutines in ASPEN PLUS discussed on the multimedia modules, which can be downloaded from www.seas.upenn.edu/~dlewin/multimedia.html, 12.5 brake *Hp* are required to pump the liquid followed by 4.67×10^7 Btu/hr to vaporize the liquid and heat the vapor to 400°C.

2. Vaporize the liquid first. Using the HEATER and COMPR subroutines discussed on the multimedia CD-ROM, 4.21×10^7 Btu/hr, are required to vaporize the liquid and heat it to 349.6°C, followed by 1,897 brake *Hp* to compress the vapor to 5 atm at 400°C.

Clearly, the power requirement is substantially less when pumping a liquid. Note that these results can be reproduced using the EXAM6-11.bkp file in the Program and Simulation Files folder, which can be downloaded from the Wiley Web site associated with this book.

Vacuum

When process pressures less than the ambient pressure are required, special devices and considerations are necessary. Vacuum operation is most common in crystallization, distillation, drying, evaporation, and pervaporation operations. A vacuum inside the equipment causes inleakage of ambient-pressure air. A vacuum system is used to remove this air together with any associated vapor in the process stream that passes through the equipment. For continuous processes, vacuums are predominantly in the range of 1–760 torr (0.13–101.3 kPa). In this range, it is common to use a vacuum pump, which compresses the gas from vacuum (suction pressure) to ambient pressure, or a jet-ejector system, which uses a flow of pressurized water or steam to mix with and remove the gas to create the vacuum. To design the vacuum system, it is necessary to estimate the inleakage of air, determine the total amount of gas (inleakage

plus associated vapor) to be removed, and select an appropriate system for the vacuum level required. The following heuristics are useful. Details of vacuum equipment are presented in Section 16.6.

Heuristic 44:   Estimate inleakage of air by:

$$w = kV^{0.667} \qquad (6.7)$$

where w = lb/hr of air inleakage, V = ft³ of volume of the equipment under vacuum, and k = 0.2 for pressures greater than 90 torr, 0.15 for pressures between 21 and 89 torr, 0.10 for pressures between 3.1 and 20 torr, and 0.051 for pressures between 1 and 3 torr.

Heuristic 45:   To reduce the amount of gas sent to the vacuum system if its temperature is greater than 100°F, add a condenser using cooling water before the vacuum system. The gas leaving the condenser will be at a dew-point temperature of 100°F at the vacuum pressure.

Heuristic 46:   For pressures down to 10 torr and gas flow rates up to 10,000 ft³/min at the inlet to the vacuum system, use a liquid-ring vacuum pump. For pressures down to 2 torr and gas flow rates up to 1,000,000 ft³/min at the inlet to the vacuum system, use a steam-jet ejector system (one-stage for 100–760 torr, two-stage for 15–100 torr, and three-stage for 2–15 torr). Include a direct-contact condenser between stages.

Heuristic 47:   For a three-stage steam-jet ejector system used to achieve a vacuum of 2 torr, 100 pounds of 100 psig steam per pound of gas are required.

Conveying Granular Solids

The movement of streams of granular solids horizontally and/or vertically is achieved with conveyors and elevators. When selecting the type of equipment, important considerations are stickiness, abrasiveness, particle size, and density of the solid particles.

Heuristic 48:   If the solid particles are small in size, low in particle density, and not sticky or abrasive, use pneumatic conveying with air at 1–7 ft³/ft³ of solids and 35–120 ft/s air velocity for distances up to 400 ft. Otherwise, for sticky and/or abrasive solids of any size and density, use a screw conveyer and/or bucket elevator for distances up to 150 ft. For solid particles of any size and shape, and not sticky, use a belt conveyor with inclination up to 30° if necessary for long distances up to a mile or more.

Changing the Pressure of Granular Solids

Continuous processes frequently involve granular solids either alone, slurried in a liquid, or fluidized in a gas. In many cases, the streams containing the solids are at ambient pressure and are moved with ease by conveyors and elevators. However, in some cases, elevated pressure or vacuum may be required. If solid particles alone are being processed, they are placed in a closed hopper where the pressure is then adjusted to the required value. The solids are then conveyed under pressure or vacuum. For a slurry, the solids are placed in a hopper from which they are discharged into a liquid at ambient pressure. The resulting slurry is then pumped to the desired pressure. A gas–solid particles mixture is formed by discharging solid particles from a hopper, through a rotary valve (also referred to as a rotary air-lock valve), into a gas stream at elevated pressure. For discharge pressures up to 15 psig, a standard rotary valve is used. For discharge pressures in the range of 15 psig to almost 100 psig, high-performance rotary valves are available. Rotary valves must be carefully designed to minimize or avoid gas leakage, prevent bridging of solids in the valve, and avoid wear of the vanes in the valve.

6.8   CHANGING THE PARTICLE SIZE OF SOLIDS AND SIZE SEPARATION OF PARTICLES

It is frequently necessary to change the particle size of solids to meet product specifications or change reaction or drying rate. Methods to accomplish changes in particle size, discussed in detail in *Chemical Process Equipment—Selection and Design* by S.M. Walas (1988) and in *Perry's Chemical Engineers' Handbook*, 7th edition (Green and Perry, 2008), include crushing, grinding, and disintegration to reduce particle size; compression, extrusion, and agglomeration to increase particle size; and size separation devices to obtain a narrow range of particle size. Crushers and grinders are used with screens in closed circuits wherein oversize material is recycled. Grindability is determined mainly by hardness as measured by the following Mohs scale, which ranges from 1 for the softest material to 10 for the hardest:

Material	Mohs Scale
Talc, $Mg_3SiO_{10}(OH)_2$	1
Gypsum, $CaSO_4 \cdot 2H_2O$	2
Calcite, $CaCO_3$	3
Fluorite, CaF_2	4
Apatite, $Ca_5(PO_4)_3(OH, F, Cl)$	5
Feldspar, Na, Ca, K, Al silicates	6
Quartz, SiO_2	7
Topaz, $Al_2SiO_4(F, OH)_3$	8
Corundum, Al_2O_3	9
Diamond, C	10

Materials with a Mohs scale from 1 to 3 are considered soft and include graphite, many plastics, asphalt, sulfur, many inorganic salts, marble, and anthracite coal. Intermediate hardness extends from a Mohs scale of 4 to 6 and includes limestone, asbestos, and glass. Hard materials are characterized by a Mohs scale of 7 to 10 and include sand, granite, and emery. The following

heuristics apply to particle-size reduction. Size of small particles is commonly stated in terms of screen mesh size according to the following U.S. standard (ASTM EII), where not all mesh sizes are given:

Mesh (openings/inch)	Sieve Opening, mm
4	4.75
6	3.35
8	2.36
12	1.70
16	1.18
20	0.841
30	0.600
40	0.420
50	0.300
70	0.212
100	0.149
140	0.106
200	0.074
270	0.053
400	0.037

Heuristic 49: *Crushing of coarse solids. Use a jaw crusher to reduce lumps of hard, abrasive, and/or sticky materials of 4 inches to 3 feet in diameter to slabby particles of 1–4 inches in size. Use a gyratory crusher to reduce slabby materials of 8 inches to 6 feet in size to rounded particles of 1–10 inches in diameter. Use a cone crusher to reduce less hard and less sticky materials of 2 inches to 1 foot in diameter to particles of 0.2 inch (4 mesh) to 2 inches in diameter.*

Heuristic 50: *Grinding to fine solids. Use a rod mill to take particles of intermediate hardness as large as 20 mm and reduce them to particles in the range of 10–35 mesh. Use a ball mill to reduce particles of low to intermediate hardness of 1–10 mm in size to very small particles of less than 140 mesh.*

Heuristic 51: *Particle-size enlargement. Use compression with rotary compression machines to convert powders and granules into tablets of up to 1.5 inches in diameter. Use extruders with cutters to make pellets and wafers from pastes and melts. Use roll compactors to produce sheets from finely divided materials; the sheets are then cut into any desired shape. Use rotating drum granulators and rotary disk granulators with binders to produce particles in the size range of 2–25 mm.*

Heuristic 52: *Size separation of particles. Use a grizzly of spaced, inclined, vibrated parallel bars to remove large particles greater than 2 inches in diameter. Use a revolving cylindrical perforated screen to remove intermediate-size particles in the size range of 0.25 inch to 1.5 inches in diameter. Use flat, inclined woven screens (U.S. standard) that are vibrated, shaken, or impacted with bouncing balls to separate small particles in the size range of 3–80 mesh. Use an air classifier to separate fine particles smaller than 80 mesh.*

6.9   REMOVAL OF PARTICLES FROM GASES AND LIQUIDS

Fine particles are most efficiently removed from dilute suspensions in gases and liquids by using centrifugal force in cyclones and hydroclones, respectively.

Heuristic 53: *Use a cyclone separator to remove, from a gas, droplets or solid particles of diameter down to 10 microns (0.01 mm). Use a hydroclone separator to remove, from a liquid, insoluble liquid droplets or solid particles of diameter down to 5 microns (0.005 mm). However, small amounts of entrained liquid droplets are commonly removed from gases by vertical knock-out drums equipped with mesh pads to help coalesce the smallest droplets.*

6.10   CONSIDERATIONS THAT APPLY TO THE ENTIRE FLOWSHEET

The preceding discussion was directed primarily to the initial development of the process flowsheet, by considering particular sections of it and specific types of equipment within it. However, the flowsheet(s) resulting from the application of the 53 heuristics presented above need(s) additional development by applying some general considerations that may be able to improve the process, particularly with respect to efficiency, simplicity, and economics. The following general considerations, suggested by A. Brostow of Air Products and Chemicals, Inc., are typical of those used in process design by industrial chemical engineers:

(a) To increase second-law efficiency and reduce energy consumption, avoid, if possible, the mixing of streams of different temperatures, pressures, or compositions. This is considered in detail in Chapter 10 on second-law analysis.

(b) For a new process, determine how it differs from a similar conventional process and pinpoint the advantages and disadvantages of the new process, making changes where disadvantages are uncovered.

(c) For a new process, determine the maximum production rate and yield, and look for opportunities to increase the production rate and yield. Then, calculate theoretical efficiencies by applying lost-work analysis as presented in Chapter 10. Look for ways to increase the efficiency.

(d) Carefully examine the process flowsheet, looking for ways to eliminate equipment by combining, rearranging, or replacing process steps.

(e) Perform preliminary economic evaluations at different production rates and corresponding plant sizes using simple scaling methods, noting that what is not economical at a small size may be economical at a large size and vice versa.

6.11   SUMMARY

Having studied this chapter, the reader should:

1. Understand how to apply heuristics to obtain a base-case process flowsheet(s) rapidly.

2. Be able to implement the steps in Section 2.1 for process synthesis more effectively, using the many heuristics presented herein and summarized in Table 6.2. The examples and exercises should enable him or her to gain experience in their application.

3. Recognize the limitations of the heuristics in Table 6.2 and the role of the process simulator in permitting the systematic variation of parameters and the examination of alternative designs. The reader should also recognize that the heuristics listed are a subset of the many rules of thumb that have been applied by design teams in carrying out process synthesis.

Table 6.2   Heuristics in Chapter 6

	Heuristic
Reaction operations	
1	Select raw materials and chemical reactions to avoid, or reduce, the handling and storage of hazardous and toxic chemicals.
Distribution of chemicals	
2	Use an excess of one chemical reactant in a reaction operation to consume completely a valuable, toxic, or hazardous chemical reactant. The MSDSs will indicate which chemicals are toxic and hazardous.
3	When nearly pure products are required, eliminate inert species before the reaction operations when the separations are easily accomplished and when the catalyst is adversely affected by the inert but not when a large exothermic heat of reaction must be removed.
4	Introduce purge streams to provide exits for species that enter the process as impurities in the feed or are formed in irreversible side reactions when these species are in trace quantities and/or are difficult to separate from the other chemicals. Lighter species leave in vapor purge streams, and heavier species exit in liquid purge streams.
5	Do not purge valuable species or species that are toxic and hazardous, even in small concentrations (see the MSDSs). Add separators to recover valuable species. Add reactors to eliminate, if possible, toxic and hazardous species.
6	Byproducts that are produced in small quantities in *reversible* reactions are usually not recovered in separators or purged. Instead, they are usually recycled to extinction.
7	For competing reactions, both in series and parallel, adjust the temperature, pressure, and catalyst to obtain high yields of the desired products. In the initial distribution of chemicals, assume that these conditions can be satisfied. Before developing a base-case design, obtain kinetics data and check this assumption.
8	For reversible reactions especially, consider conducting them in a separation device capable of removing the products and hence driving the reactions to the right. Such reaction-separation operations lead to very different distributions of chemicals.
Separation operations—liquid and vapor mixtures	
9	Separate liquid mixtures using distillation, stripping, enhanced (extractive, azeotropic, reactive) distillation, liquid–liquid extraction, crystallization, and/or adsorption. The selection among these alternatives is considered in Chapter 9.
10	Attempt to condense or partially condense vapor mixtures with cooling water or a refrigerant. Then, use Heuristic 9.
11	Separate vapor mixtures using partial condensation, cryogenic distillation, absorption, adsorption, membrane separation, and/or desublimation. The selection among these alternatives is considered in Chapter 9.
Separation operations—involving solid particles	
12	Crystallize inorganic chemicals from a concentrated aqueous solution by chilling when solubility decreases significantly with decreasing temperature. Keep the solution at most 1 to 2°F below the saturation temperature at the prevailing concentration. Use crystallization by evaporation, rather than chilling, when solubility does not change significantly with temperature.

(Continued)

Table 6.2   (*continued*)

	Heuristic
13	Crystal growth rates are approximately the same in all directions, but crystals are never spheres. Crystal growth rates and sizes are controlled by limiting the extent of supersaturation, $S = C/C_{\text{saturation}}$, where C is concentration, usually in the range $1.02 < S < 1.05$. Growth rates are influenced greatly by the presence of impurities and of certain specific additives that vary from case to case.
14	Separate organic chemicals by melt crystallization with cooling, using suspension crystallization, followed by removal of crystals by settling, filtration, or centrifugation. Alternatively, use layer crystallization on a cooled surface with scraping or melting to remove the crystals. If the melt forms a solid solution instead of a eutectic, use repeated melting and freezing steps, called fractional melt crystallization, or zone melting to obtain nearly pure crystalline products.
15	Using multiple evaporators (called effects) in series, the latent heat of evaporation of water is recovered and reused. With a single evaporator, the ratio of the amount of water evaporated to the amount of external steam supplied to cause the evaporation is typically 0.8. For two effects, the ratio becomes 1.6; for three effects 2.4, and so forth. The magnitude of the boiling-point elevation caused by the dissolved inorganic compounds is a controlling factor in selecting the optimal number of effects. The elevation is often in the range of 3–10°F between solution and pure water boiling points. When the boiling-point rise is small, minimum evaporation cost is obtained with 8 to 10 effects. When the boiling-point rise is appreciable, the optimal number of effects is small, 6 or less. If necessary, boost interstage steam pressures with steam-jet or mechanical compressors.
16	When employing multiple effects, the liquid and vapor flows may be in the same or different directions. Use forward feed, where both liquid and vapor flow in the same direction, for a small number of effects, particularly when the liquid feed is hot. Use backward feed, where liquid flows in a direction opposite to vapor flows, for cold feeds, and/or a large number of effects. With forward feed, intermediate liquid pumps are not necessary, whereas they are necessary for backward feed.
17	When crystals are fragile, effective washing is required, and clear mother liquor is desired, use: gravity, top-feed horizontal pan filtration for slurries that filter at a rapid rate; vacuum rotary-drum filtration for slurries that filter at a moderate rate; and pressure filtration for slurries that filter at a slow rate.
18	When cakes of low moisture content are required, use: solid-bowl centrifugation if solids are permitted in the mother liquor; centrifugal filtration if effective washing is required.
19	For granular material, free flowing or not, of particle sizes from 3 to 15 mm, use continuous tray and belt dryers with direct heat. For free-flowing granular solids that are not heat sensitive, use an inclined rotary cylindrical dryer where the heat may be supplied directly from a hot gas or indirectly from tubes, carrying steam that run the length of the dryer and are located in one or two rings concentric to and located just inside the dryer rotating shell. For small, free-flowing particles of 1–3 mm in diameter, when rapid drying is possible, use a pneumatic conveying dryer with direct heat. For very small free-flowing particles of less than 1 mm in diameter, use a fluidized-bed dryer with direct heat.
20	For pastes and slurries of fine solids, use a drum dryer with indirect heat. For a liquid or pumpable slurry, use a spray dryer with direct heat.
Heat removal and addition	
21	To remove a highly exothermic heat of reaction, consider the use of excess reactant, an inert diluent, or cold shots. These affect the distribution of chemicals and should be inserted early in process synthesis.
22	For less exothermic heats of reaction, circulate reactor fluid to an external cooler or use a jacketed vessel or cooling coils. Also, consider the use of intercoolers between adiabatic reaction stages.
23	To control temperature for a highly endothermic heat of reaction, consider the use of excess reactant, an inert diluent, or hot shots. These affect the distribution of chemicals and should be inserted early in process synthesis.
24	For less endothermic heats of reaction, circulate reactor fluid to an external heater or use a jacketed vessel or heating coils. Also, consider the use of interheaters between adiabatic reaction stages.
Heat exchangers and furnaces	
25	Unless required as part of the design of the separator or reactor, provide necessary heat exchange for heating or cooling process fluid streams, with or without utilities, in an external shell-and-tube heat exchanger using countercurrent flow. However, if a process stream requires heating above 750°F, use a furnace unless the process fluid is subject to chemical decomposition.

Table 6.2   (*continued*)

	Heuristic

26	Near-optimal minimum temperature approaches in heat exchangers depend on the temperature level as follows:
	  10°F or less for temperatures below ambient.
	  20°F for temperatures at or above ambient up to 300°F.
	  50°F for high temperatures.
	  250 to 350°F in a furnace for flue gas temperature above inlet process fluid temperature.

27	When using cooling water to cool or condense a process stream, assume a water inlet temperature of 90°F (from a cooling tower) and a maximum water outlet temperature of 120°F.
28	Boil a pure liquid or close-boiling liquid mixture in a separate heat exchanger, using a maximum overall temperature driving force of 45°F to ensure nucleate boiling and avoid undesirable film boiling as discussed in Section 12.1.
29	When cooling and condensing a stream in a heat exchanger, a zone analysis, described in Section 12.1, should be made to make sure that the temperature difference between the hot stream and the cold stream is equal to or greater than the minimum approach temperature at all locations in the heat exchanger. The zone analysis is performed by dividing the heat exchanger into a number of segments and applying an energy balance to each segment to determine corresponding stream inlet and outlet temperatures for the segment, taking into account any phase change. A process simulation program conveniently accomplishes the zone analysis.
30	Typically, a hydrocarbon gives an adiabatic flame temperature of approximately 3,500°F when using the stoichiometric amount of air. However, use excess air to achieve complete combustion and give a maximum flue gas temperature of 2,000°F. Set the stack gas temperature in the range of 650–950°F to prevent condensation of the corrosive components of the flue gas.

31	Estimate heat-exchanger pressure drops as follows:
	  1.5 psi for boiling and condensing.
	  3 psi for a gas.
	  5 psi for a low-viscosity liquid.
	  7–9 psi for a high-viscosity liquid.
	  20 psi for a process fluid passing through a furnace.

32	Quench a very hot process stream to at least 1,150°F before sending it to a heat exchanger for additional cooling and/or condensation. The quench fluid is best obtained from a downstream separator as in Figure 7.31 for the toluene hydrodealkylation process. Alternatively, if the process stream contains water vapor, liquid water may be an effective quench fluid.
33	If possible, heat or cool a stream of solid particles by direct contact with a hot gas or cold gas, respectively, using a rotary kiln, a fluidized bed, a multiple hearth, or a flash/pneumatic conveyor. Otherwise, use a jacketed spiral conveyor.
Pressure increase operations	
34	Use a fan to raise the gas pressure from atmospheric pressure to as high as 40 inches water gauge (10.1 kPa gauge or 1.47 psig). Use a blower or compressor to raise the gas pressure to as high as 206 kPa gauge or 30 psig. Use a compressor or a staged compressor system to attain pressures greater than 206 kPa gauge or 30 psig.
35	Estimate the theoretical adiabatic horsepower (*THp*) for compressing a gas:

$$THp = SCFM \left(\frac{T_1}{8{,}130a} \right) \left[\left(\frac{P_2}{P_1} \right)^a - 1 \right] \qquad (6.1)$$

where $SCFM$ = standard cubic feet of gas per minute at 60°F and 1 atm (379 SCF/1bmol);
T_1 = gas inlet temperature in °R; inlet and outlet pressures, P_1 and P_2, are absolute pressures: and
$a = (k - 1)/k$, with k = the gas specific heat ratio, C_p/C_v.
Estimate the theoretical exit temperature, T_2, for a gas compressor:

$$T_2 = T_1(P_2/P_1)^a \qquad (6.2)$$

Table 6.2 (*continued*)

Heuristic

36	Estimate the number of gas compression stages, *N*, from the following table, which assumes a specific heat ratio of 1.4 and a maximum compression ratio of 4 for each stage.

Final Pressure/Inlet Pressure	Number of Stages
< 4	1
4–16	2
16–64	3
64–256	4

	Optimal interstage pressures correspond to equal *Hp* for each compressor. Therefore, based on the equation for theoretical compressor *Hp*, estimate interstage pressures by using approximately the same compression ratio for each stage with an intercooler pressure drop of 2 psi or 15 kPa.
37	For heads up to 3,200 ft and flow rates in the range of 10–5,000 gpm, use a centrifugal pump. For high heads up to 20,000 ft and flow rates up to 500 gpm, use a reciprocating pump. Less common are axial pumps for heads up to 40 ft for flow rates in the range of 20–100,000 gpm and rotary pumps for heads up to 3,000 ft for flow rates in the range of 1–1,500 gpm.
38	For liquid flow, assume a pipeline pressure drop of 2 psi/100 ft of pipe and a control valve pressure drop of at least 10 psi. For each 10-ft rise in elevation, assume a pressure drop of 4 psi.
39	Estimate the theoretical horsepower (*THp*) for pumping a liquid:

$$THp = (gpm)(\text{Pressure increase, psi})/1,714 \qquad (6.3)$$

Pressure decrease operations

40	Consider the use of an expander for reducing the pressure of a gas or a pressure-recovery turbine for reducing the pressure of a liquid when more than 20 Hp and 150 Hp, respectively, can be recovered.
41	Estimate the theoretical adiabatic horsepower (*THp*) for expanding a gas:

$$THp = SCFM\left(\frac{T_1}{8,130a}\right)\left[1 - \left(\frac{P_2}{P_1}\right)^a\right] \qquad (6.4)$$

42	Estimate the theoretical horsepower (*THp*) for reducing the pressure of a liquid:

$$THp = (gpm)(\text{Pressure decrease, psi})/1,714 \qquad (6.5)$$

Pumping liquid or compressing gas

43	To increase the pressure of a stream, pump a liquid rather than compress a gas unless refrigeration is needed.

Vacuum

44	Estimate inleakage of air by:

$$w = kV^{0.667} \qquad (6.7)$$

where w = lb/hr of air inleakage, V = ft^3 of volume of the equipment under vacuum, and $k = 0.2$ for pressures greater than 90 torr, 0.15 for pressures between 21 and 89 torr, 0.10 for pressures between 3.1 and 20 torr, and 0.051 for pressures between 1 and 3 torr.

45	To reduce the amount of gas sent to the vacuum system if its temperature is greater than 100°F, add a condenser using cooling water before the vacuum system. The gas leaving the condenser will be at a dew-point temperature of 100°F at the vacuum pressure.

Table 6.2   (*continued*)

|	Heuristic
46	For pressures down to 10 torr and gas flow rates up to 10,000 ft³/min at the inlet to the vacuum system, use a liquid-ring vacuum pump. For pressures down to 2 torr and gas flow rates up to 1,000,000 ft³/min at the inlet to the vacuum system, use a steam-jet ejector system (one-stage for 100–760 torr, two-stage for 15–100 torr, and three-stage for 2–15 torr). Include a direct-contact condenser between stages.
47	For a three-stage steam-jet ejector system used to achieve a vacuum of 2 torr, 100 pounds of 100 psig steam per pound of gas are required.
Conveying granular solids	
48	If the solid particles are small in size, low in particle density, and not sticky or abrasive, use pneumatic conveying with air at 1 to 7 ft³/ft³ of solids and 35 to 120 ft/s air velocity for distances up to 400 ft. Otherwise, for sticky and/or abrasive solids of any size and density, use a screw conveyer and/or bucket elevator for distances up to 150 ft. For solid particles of any size and shape, and not sticky, use a belt conveyor, with inclination up to 30° if necessary, for long distances up to a mile or more.
Solid particle size change and separation	
49	Crushing of coarse solids. Use a jaw crusher to reduce lumps of hard, abrasive, and/or sticky materials of 4 inches to 3 feet in diameter to slabby particles of 1–4 inches in size. Use a gyratory crusher to reduce slabby materials of 8 inches to 6 feet in size to rounded particles of 1–10 inches in diameter. Use a cone crusher to reduce less hard and less sticky materials of 2 inches to 1 foot in diameter to particles of 0.2 inch (4 mesh) to 2 inches in diameter.
50	Grinding to fine solids. Use a rod mill to take particles of intermediate hardness as large as 20 mm and reduce them to particles in the range of 10–35 mesh. Use a ball mill to reduce particles of low to intermediate hardness of 1–10 mm in size to very small particles of less than 140 mesh.
51	Particle-size enlargement. Use compression with rotary compression machines to convert powders and granules into tablets of up to 1.5 inches in diameter. Use extruders with cutters to make pellets and wafers from pastes and melts. Use roll compactors to produce sheets from finely divided materials; the sheets are then cut into any desired shape. Use rotating drum granulators and rotary disk granulators with binders to produce particles in the size range of 2–25 mm.
52	Size separation of particles. Use a grizzly of spaced, inclined, vibrated parallel bars to remove large particles greater than 2 inches in diameter. Use a revolving cylindrical perforated screen to remove intermediate-size particles in the size range of 0.25 inch to 1.5 inches in diameter. Use flat, inclined woven screens (U.S. standard) that are vibrated, shaken, or impacted with bouncing balls to separate small particles in the size range of 3–80 mesh. Use an air classifier to separate fine particles smaller than 80 mesh.
53	Use a cyclone separator to remove, from a gas, droplets or solid particles of diameter down to 10 microns (0.01 mm). Use a hydroclone separator to remove, from a liquid, insoluble liquid droplets or solid particles of diameter down to 5 microns (0.005 mm). However, small amounts of entrained liquid droplets are commonly removed from gases by vertical knock-out drums equipped with mesh pads to help coalesce the smallest droplets.

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EXERCISES

6.1 For the production of ethylene glycol, how much is the economic potential per pound of ethylene glycol reduced when chlorine and caustic are used to avoid the production of ethylene oxide?

6.2 Consider ethyl-tertiary-butyl-ether (ETBE) as an alternative gasoline oxygenate to MTBE. Although the latter appears to have the best combination of properties such as oxygen content, octane number, energy content, and cost, the former can be manufactured using ethanol according to:

$$C_2H_5OH + iso\text{-butene} \rightleftharpoons ETBE$$
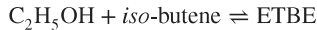
Because ethanol can be manufactured from biomass, it is potentially more acceptable to the environment.

(a) Rework Example 6.1 for this process.

(b) Is reactive distillation promising for combining the reaction and separation operations? If so, suggest a distribution of chemicals using a reactive distillation operation.

6.3 For the ammonia process in Example 6.4, consider operation of the reactor at 932°F and 400 atm. Use a simulator to show how the product, recycle, and purge flow rates, as well as the mole fractions of argon and methane vary with the purge-to-recycle ratio. How do the power requirements for compression vary, assuming 3 atm pressure drop in the reactor and 1 atm pressure drop in the heat exchanger?

6.4 *Revamp of a toluene hydrodealkylation process.* This problem considers some waste-minimization concepts involving **recycle to extinction** - a heuristic for process synthesis. However, in this exercise, when this heuristic is applied, analysis using process simulation is carried out. For this reason, we advise the reader to solve this exercise after studying Chapter 7 and possibly after solving Exercises 7.2 to 7.4, which simulates sections of the toluene hydrodealkylation process. Our operating toluene hydrodealkylation unit, shown in Figure 6.18, involves the hydrogenation of toluene to benzene and methane. An equilibrium side reaction produces a small quantity of biphenyl. To be more competitive and to eliminate waste, the process needs to be studied for a possible revamp. The customer for our small production of biphenyl

has informed us that it will not renew its contract with us, and we have no other prospective buyer for biphenyl. Also, a membrane separator company believes that if we install their equipment, we can reduce our makeup hydrogen requirement. Make preliminary process design calculations with a simulator to compare the following two alternatives, and advise me of the technical feasibility of the second alternative and whether we should consider such a revamp further. For your studies, you will have to perform mainly material balance calculations. You will not make detailed distillation calculations, and liquid pumps need not be modeled. For the second alternative, calculate the required area in square feet of the membrane unit and determine if it is reasonable.

Alternative 1. Do no revamp and use the biphenyl for its fuel value.

Alternative 2. Eliminate operation of the toluene column and recycle the biphenyl (with the toluene) to extinction. This should increase the yield of benzene. Also, install a membrane separation unit to reduce hydrogen consumption.

Current plant operation: The current plant operation can be adequately simulated with CHEMCAD, using the equipment models indicated in the flow diagram. Alternatively, any other simulator can be used with appropriate models. Note that the flow diagram of the process includes only the reactor, separators, and recycle-gas compressor. The plant operating factor is 96% (8,410 hr/yr). The feedstock is pure toluene at a flow rate of 274.2 lbmol/hr, which is fixed for both alternatives, because any additional benzene that we can make can be sold. The makeup hydrogen is 95 mol% hydrogen and 5 mol% methane. Our reactor outlet conditions are 1,000°F and 520 psia. The hydrogen-to-toluene molar ratio in the feed to the reactor must be 4 to prevent coke formation. The toluene conversion is 70%. The biphenyl in the reactor effluent is the chemical equilibrium amount. The flash drum conditions are 100°F at 500 psia. The flash vapor is not separated into hydrogen and methane but is purged to limit methane buildup in the recycle gas. The purge gas, which has fuel value, is 25% of the vapor leaving the flash vessel. Perfect separations can be assumed for the three columns. Based on this information, you can obtain the current plant material balance.
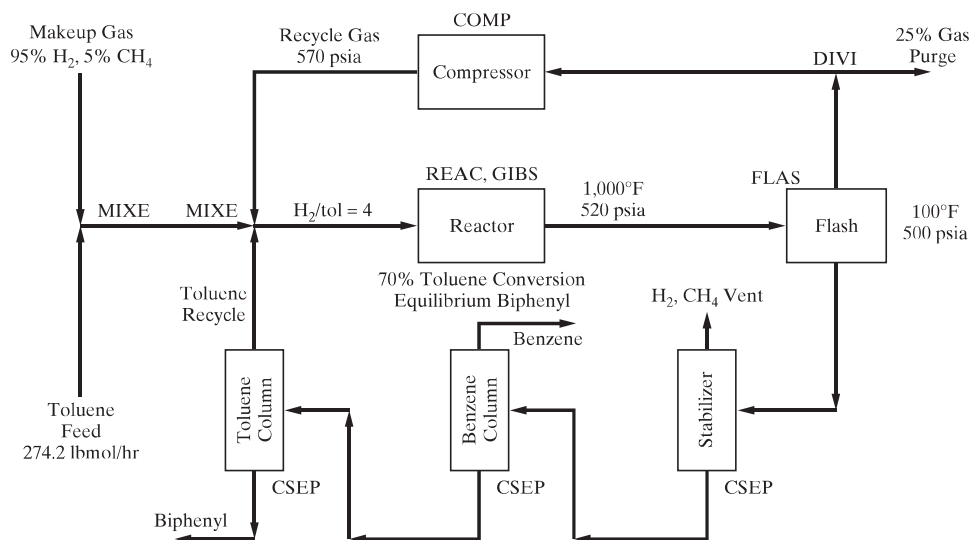

Figure 6.18 Flowsheet for the toluene hydrodealkylation process.

Alternative 1. Simulate the current plant operation. Note that the process has two recycle loops that must be converged. The SRK equation of state is adequate for *K*-values and enthalpies. From your converged material balance, summarize the overall component material balance in pounds per year (i.e., process feeds and products).

Alternative 2. Eliminate the toluene column and rerun the simulation. Because the biphenyl will be recycled to extinction, the benzene production should increase. Replace the stream divider, which divides the flash vapor into a purge and a gas recycle, with a membrane separation unit that can be modeled with a CSEP (black-box separator) unit.

For Alternative 2, the vendor of the membrane unit has supplied the following information:

Hydrogen will pass through the membrane faster than methane. Vapor benzene, toluene, and biphenyl will not pass through the membrane.

The hydrogen-rich permeate will be the new recycle gas. The retentate gas will be used for fuel.

Tests indicate that the purity of the hydrogen-rich permeate gas will be 95 mol% with a hydrogen recovery of 90%. However, the pressure of the permeate gas will be 50 psia, compared to 500 psia for the recycle gas in the current plant operation. A pressure of 570 psia is required at the discharge of the recycle-gas compression system. Thus, a new compressor will be needed.

Run the revamped process with the simulator. From your converged material balance, summarize the overall component material balance in pounds per year (i.e., process feeds and products).

The membrane unit is to be sized by hand calculations on the basis of the hydrogen flux through the membrane. Tests by the vendor using a nonporous cellulose acetate membrane in a spiral-wound module indicate that this flux is 20 scfh (60°F and 1 atm) per square foot of membrane surface area per 100 psi hydrogen partial-pressure driving force. To determine the driving force, take the hydrogen partial pressure on the feed side of the membrane as the arithmetic average between the inlet and the outlet (retentate) partial pressures. Take the hydrogen partial pressure on the permeate side as that of the final permeate.

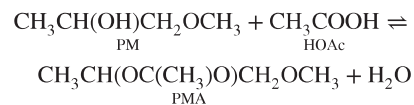Summarize and discuss your results in a report and make recommendations concerning cost studies.

6.5   For the reaction system:

$$A + B \xrightarrow{k_1} C + A \xrightarrow{k_3} E$$
$$\searrow^{k_2} D + A \nearrow^{k_4}$$
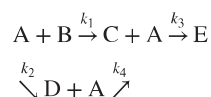
select an operating temperature that favors the production of C. The pre-exponential factor and activation energy for the reactions are tabulated as follows:

Rxtn	k_0 (m^6/kmol$^2 \cdot$ s)	E (kJ / kmol)
1	3.7×10^6	65,800
2	3.6×10^6	74,100
3	5.7×10^6	74,500
4	1.1×10^7	74,400

6.6   Propylene glycol mono-methyl-ether acetate (PMA) is produced by the esterification of propylene glycol mono-methyl ether (PM) in acetic acid (HOAc):

$$\underset{\text{PM}}{CH_3CH(OH)CH_2OCH_3} + \underset{\text{HOAc}}{CH_3COOH} \rightleftharpoons$$
$$\underset{\text{PMA}}{CH_3CH(OC(CH_3)O)CH_2OCH_3} + H_2O$$

Conventionally, the reaction takes place in a fixed-bed reactor followed by the recovery of PMA from water, and unreacted PM and HOAc. Prepare a potential distribution of chemicals for a reactive distillation process with the feed at 203°F and 1 atm.

6.7   For the following reactions, determine the maximum or minimum temperatures of the reactor effluents assuming:

(a) Complete conversion

(b) Equilibrium conversion

The reactants are available in stoichiometric proportions at the temperature and pressure indicated.

	T_0 (°F)	P (atm)
a. $C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$	1,200	38.7
b. $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$	77	1.0
c. $CO + \frac{1}{2}O_2 \rightarrow CO_2$	77	1.0
d. $C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$	932	26.0

Also, find the heats of reaction at the conditions of the reactants.

6.8   For Example 6.9, use a simulator to graph the effluent temperature of the methanol reactor as a function of the H$_2$/CO ratio.

6.9   For Example 6.10, use a simulator to graph the effluent temperature of the methanol reactor as a function of the dodecane flow rate.

6.10   Divide the methanol reaction operation in Example 6.6 into five consecutive stages in series. Feed the CO reactant entirely into the first operation at 25°C and 1 atm. Divide the H$_2$ reactant into five cold shots and vary the temperature of H$_2$ before dividing it into cold shots. Assuming that the reaction operations are adiabatic, determine the maximum temperature in the flowsheet as a function of the temperature of the cold shots. How does this compare with the adiabatic reaction temperature?

6.11   Repeat Exercise 6.10 using intercoolers instead of cold shots and an unknown number of reaction stages. The feed to the first reactor is at 25°C and 1 atm. Throughout the reactors, the temperature must be held below 300°C. What is the conversion of CO in the first reactor? How many reaction stages and intercoolers are necessary to operate between 25 and 300°C?

6.12   *Alternatives for preparing a feed.* A process under design requires that 100 1bmol/hr of toluene at 70°F and 20 psia be brought to 450°F and 75 psia. Develop at least three flowsheets to accomplish this using combinations of heat exchangers, liquid pumps, and/or gas compressors. Discuss the advantages and disadvantages of each flowsheet, and make a recommendation as to which flowsheet is best.