# Chapter 6. Understanding Process Conditions

**What You Will Learn**

- There are typical ranges for process temperatures and pressures.
- There should be a reason for operating outside these ranges.

In previous chapters, process flow diagrams (PFDs) were accepted without evaluating the technical features of the process. The process topology and process operating conditions were provided but were not examined. Economic evaluations were carried out, but without confirming that the process would operate as indicated by the flow diagram.

It is not uncommon to investigate process economics based upon assumed process performance. For example, in order to justify spending the capital to develop a new catalyst, the economics of a process using a hypothetical catalyst with assumed characteristics, such as no unwanted side reactions, might be calculated.

> **The ability to make an economic analysis of a chemical process based on a PFD is not proof that the process will actually work.**

In this chapter, you will learn how to analyze the reasons why the specific temperatures, pressures, and compositions selected for important streams and unit operations have been chosen. Stream specifications and process conditions are influenced by physical processes as well as economic considerations and are not chosen arbitrarily. The conditions used in a process most often represent an economic compromise between process performance and the capital and operating costs of the process equipment. Final selection of operating conditions should not be made prior to the analysis of the process economics. In this chapter, the focus is on analyzing process conditions that require special consideration. As an example, the question of why a reactor is run at 600°C instead of 580°C is not addressed, but rather the reasons are addressed why the reactor is not run at a much lower temperature, for example, 200°C. This type of analysis leads to the question of how process conditions are chosen and what the consequences are of changing these conditions.

## 6.1. Conditions of Special Concern for the Operation of Separation and Reactor Systems

Process streams are rarely available at conditions most suitable for reactor and separation units. Temperatures, pressures, and stream compositions must be adjusted to provide conditions that allow effective process performance. This is discussed in Chapter 2, where the generic BFD was introduced (see Figure 2.4[a]). This figure showed two feed preparation blocks: one associated with the reactor and the second with the separation section.

Two generalizations are provided to assist in analyzing and understanding the selection of process conditions.

- It is usually easier to adjust the temperature and/or pressure of a stream than it is to change its composition. In fact, often the concentration of a compound in a stream (for a gas) is a dependent variable and is controlled by the temperature and pressure of the stream.
- In general, pressures between 1 and 10 bar and temperatures between 40°C and 260°C do not

cause severe processing difficulties.

The rationale for the conditions given in the second generalization are explained below.

### 6.1.1. Pressure

There are economic advantages associated with operating equipment at greater than ambient pressure when gases are present. These result from the increase in gas density and a decrease in gas volume with increasing pressure. All other things being equal, in order to maintain the same gas residence time in a piece of equipment, the size of the equipment through which the gas stream flows need not be as large when the pressure is increased.

Most chemical processing equipment can withstand pressures up to 10 bar without much additional capital investment (see the cost curves in Appendix A). At pressures greater than 10 bar, thicker-walled, more expensive equipment is necessary. Likewise, operating at less than ambient pressure (vacuum conditions) tends to make equipment large and may require special construction techniques, thus increasing the cost of equipment.

**A decision to operate outside the pressure range of 1 to 10 bar must be justified.**

### 6.1.2. Temperature

There are several critical temperature limits that apply to chemical processes. At elevated temperatures, common construction materials (primarily carbon steel) suffer a significant drop in physical strength and must be replaced by more costly materials. This drop in strength with temperature is illustrated in Example 6.1.

### Example 6.1.

The maximum allowable tensile strengths for typical carbon steel and stainless steel at ambient temperature, 400°C, and 550°C are provided below (Walas [1]).

| Temperature | Tensile Strength of Material at Temperature Indicated (bar) | | |
| --- | --- | --- | --- |
| | Ambient | 400°C | 550°C |
| Carbon Steel (grade 70) | 1190 | 970 | 170 |
| Stainless Steel (Type 302) | 1290 | 1290 | 430 |

Determine the fractional decrease in the maximum allowable tensile strength (relative to the strength at ambient conditions) for the temperature intervals (a) ambient to 400°C and (b) 400°C to 550°C.

    a. Interval: ambient to 400°C:

      Carbon Steel: (1190–970)/1190 = 0.18

      Stainless Steel: (1290–1290)/1290 = 0.0

    b. Interval: 400°C to 550°C:

      Carbon Steel: (970–170)/1190 = 0.67

      Stainless Steel: (1290–430)/1290 = 0.67

Example 6.1 has shown that carbon steel suffers a loss of 18%, and stainless steel suffers no loss in tensile strength, when heated to 400°C. With an additional temperature increase of 150°C to 550°C,

stainless steel suffers a 67% loss while carbon steel suffers an additional 67% loss in strength. At operating temperatures of 550°C, carbon steel has a maximum allowable tensile strength of about 15% of its value at ambient conditions. For stainless steel, the maximum allowable strength at 550°C is about 33% of its ambient value. For this example, it is clear that carbon steel is unacceptable for service temperatures greater than 400°C, and that the use of stainless steel is severely limited. For higher service temperatures, more exotic (and expensive) alloys are required and/or equipment may have to be refractory lined.

**A decision to operate at greater than 400°C must be justified.**

Thus, if higher temperatures are specified, a justification must be found for the economic penalty associated with more complicated processing equipment, such as refractory-lined vessels or expensive materials of construction. In addition to the critical temperature of 400°C, there are temperature limits associated with the availability of common utilities for heating and cooling a process stream.

**Steam:** High-pressure steam between 40 and 50 bar is commonly available and provides heat at 250 to 265°C. Above this temperature additional costs are involved.

**Water:** Water from a cooling tower is commonly available at about 30°C (and is returned to the cooling tower at around 40°C). For utilities below this temperature, costs increase due to refrigeration. As the temperature decreases, the costs increase dramatically (see Table 8.3).

If cryogenic conditions are necessary, there may be an additional need for expensive materials of construction.

**A decision to operate outside the range of 40°C to 260°C, thus requiring special heating/cooling media, must be justified.**

## 6.2. Reasons for Operating at Conditions of Special Concern

When you review the PFD for different processes, you are likely to encounter conditions in reactors and separators that lie outside the temperature and pressure ranges presented in Section 6.1. This does not mean to say that these are "bad" processes, but rather that these conditions had to be used, despite the additional costs involved, to have the process operate effectively. These conditions, outside the favored temperature and pressure ranges, are identified as **conditions of special concern.**

When you encounter these conditions, you should seek a rational explanation for their selection. If no explanation can be identified, the condition used may be unnecessary. In this situation, the condition may be changed to a less severe one that provides an economic advantage.

A list of possible justifications for using temperature and pressure conditions outside the ranges given above are identified in Tables 6.1 through 6.3. The material provided in Tables 6.1 to 6.3 is based upon elementary concepts presented in undergraduate texts covering thermodynamics and reactor design.

**Table 6.1. Possible Reasons for Operating Reactors and Separators Outside the Temperature Ranges of Special Concern**

| Stream Condition | Process Justification for Operating at This Condition | Penalty for Operating at This Condition |
|---|---|---|
| High Temperature [$T > 250°C$] | **Reactors**<br>• Favorable equilibrium conversion for endothermic reactions<br>• Increase reaction rates<br>• Maintain a gas phase<br>• Improve selectivity<br>•<br>•<br><br>**Separators**<br>• Obtain a gas phase required for vapor-liquid equilibrium<br>•<br>• | • Use of special process heaters<br>• $T > 400°C$ requires special materials of construction<br>•<br>•<br>• |
| Low Temperature [$T < 40°C$] | **Reactors**<br>• Favorable equilibrium conversion for exothermic reactions<br>• Temperature-sensitive materials<br>• Improve selectivity<br>• Maintain a liquid phase<br>•<br>•<br>**Separators**<br>• Obtain a liquid phase required for vapor-liquid or liquid-liquid equilibrium<br>• Obtain a solid phase for crystallization<br>• Temperature-sensitive materials<br>•<br>• | • Uses expensive refrigerant<br>• May require special materials of construction for very low temperatures<br>•<br>•<br>• |

**Table 6.2. Possible Reasons for Operating Reactors and Separators Outside the Pressure Range of Special Concern**

| Stream Condition | Process Justification for Operating at This Condition | Penalty for Operating at This Condition |
|---|---|---|
| High Pressure ($P > 10$ bar) | **Reactors**<br>• Favorable equilibrium conversion<br>• Increase reaction rates for gas-phase reactions (due to higher concentration)<br>• Maintain a liquid phase<br>•<br>•<br><br>**Separators**<br>• Obtain a liquid phase for vapor-liquid or liquid-liquid equilibrium<br>•<br>• | • Requires thicker-walled equipment<br>• Requires expensive compressors if gas streams must be compressed<br>•<br>•<br>• |
| Low Pressure ($P < 1$ bar) | **Reactors**<br>• Favorable equilibrium conversion<br>• Maintain a gas phase<br>•<br>•<br><br>**Separators**<br>• Obtain a gas phase for vapor-liquid equilibrium<br>• Temperature-sensitive materials<br>•<br>• | • Requires large equipment<br>• Special design for vacuum operation<br>• Air leaks into equipment that may be dangerous and expensive to prevent<br>•<br>•<br>• |

**Table 6.3. Possible Reasons for Non-stoichiometric Reactor Feed Compositions of Special Concern**

| Stream Condition | Process Justification for Operating at This Condition | Penalty for Operating at This Condition |
|---|---|---|
| Inert Material in Feed to Reactor | • Acts as a diluent to control the rate of reaction and/or to ensure that the reaction mixture is outside the explosive limits (exothermic reactions)<br>• Inhibits unwanted side reactions<br>•<br>• | • Causes reactor and downstream equipment to be larger since inert takes up space<br>• Requires separation equipment to remove inert material<br>• May cause side reactions (material is no longer inert)<br>• Decreases equilibrium conversion<br>•<br>• |
| Excess Reactant | • Increases the equilibrium conversion of the limiting reactant<br>• Inhibits unwanted side reactions<br>•<br>• | • Requires separation equipment to remove excess reactant<br>• Requires recycle<br>• Added feed material costs (due to losses in separation and/or no recycle)<br>•<br>• |
| Product Present in Feed to Reactor | • Product cannot easily be separated from recycled feed material.<br>• Recycled product retards the formation of unwanted by-products formed from side reactions.<br>• Product acts as a diluent to control the rate of reaction and/or to ensure that the reaction mixture is outside the explosive limits, for exothermic reactions.<br>•<br>• | • Causes reactor and downstream equipment to be larger<br>• Requires larger recycle loop<br>• Decreases equilibrium conversion<br>•<br>• |

The rationale used to justify operating at temperatures that are of special concern and that are presented in Table 6.1 is given in the following list. The justification for entries in Tables 6.2 and 6.3 has a similar rationale.

For chemical reactors, possible justifications for operating at conditions of special concern are as follows.

1. **Favorable Equilibrium Conversion:** If the reaction is endothermic and approaches equilibrium, it benefits from operating at high temperatures. Le Chatelier's principle states that "for a reacting system at equilibrium, the extent of the reaction will change so as to oppose any changes in temperature or pressure." For an endothermic reaction, an increase in temperature tends to push the reaction equilibrium to the right (toward products). Conversely, low temperatures decrease the equilibrium conversion.

2. **Increase Reaction Rates:** All chemical reaction rates are strongly dependent upon temperature through an Arrhenius type equation:

$$k_{reaction} = k_0 e^{-\frac{E_{act}}{RT}} \qquad\qquad (6.1)$$

As temperature increases, so does the reaction rate constant, $k_{reaction}$, for both catalytic and noncatalytic reactions. Therefore, temperatures greater than 250°C may be required to obtain a high enough reaction rate in order to keep the size of the reaction vessel reasonable.

3. **Maintain a Gas Phase:** Many catalytic chemical reactions used in processes today require both reactants and products to be in the gas phase. For high-boiling-point materials or operations where high pressure is used, a temperature in excess of 400°C may be required in the reactor in order to maintain all the species in the vapor phase.

4. **Improve Selectivity:** If competing reactions (series, parallel, or a combination of both) occur and the different reactions have different activation energies, then the production of the desired product may be favored by using a high temperature. Schemes for competing reactions are covered in greater detail in many of the well known texts on chemical reaction engineering, as well as in Chapter 23.

For separators, the following item of justification is presented:

1. **Obtain a Vapor Phase for Vapor-Liquid Equilibrium:** This situation arises quite frequently when high-boiling-point materials need to be distilled. An example is the distillation of crude oil in which the bottom of the atmospheric column is typically operated in the region of 310°C to 340°C (590°F to 645°F).

You would benefit by spending time to acquaint yourself with the information presented in Tables 6.1 to 6.3 and to convince yourself that you understand the justifications given in these tables. These tables should not be considered an exhaustive list of possible reasons for operating in the ranges of special concern. Instead, they represent a starting point in analyzing process conditions. As you discover other explanations for reasons to operate equipment in the ranges of special concern you may wish to add them to Tables 6.1–6.3. Additional blank entries are provided for this purpose.

## 6.3. Conditions of Special Concern for the Operation of Other Equipment

Additional equipment (such as pumps, compressors, heaters, exchangers, and valves) produces the temperature and pressure required by the feed streams entering the reactor and separation sections. When initially choosing the stream conditions for the reactor and separator sections, it is worthwhile using certain guidelines or heuristics. These technical heuristics are useful guidelines for doing design. Comprehensive lists of heuristics are described and applied in Chapter 11. In this chapter, some of the more general guidelines that apply to streams passing through process equipment are presented. These are presented in Table 6.4. Some of these guidelines are explored in Example 6.2.

**Table 6.4. Changes in Process Conditions That Are of Special Concern for a Stream Passing through a Single Piece of Equipment**

| Type of Equipment | Change in Stream Condition Causing Concern | Justification or Remedy | Penalty for Operating Equipment in This Manner |
|---|---|---|---|
| 1. Compressors | $P_{out}/P_{in} > 3$ | **Remedy:** Use multiple stages and intercoolers. | High theoretical work requirement due to large temperature rise of gas stream. |
| | High-temperature inlet gas | **Remedy:** Cool the gas before compression. | High theoretical work requirement and special construction materials required. |
| 2. Heat Exchangers | $\Delta T_{lm} > 100°C$ | **Remedy:** Integrate heat better within process (see Chapter 15). <br><br>**Justification:** Heat integration not possible or not profitable. | Large temperature driving force means that valuable high-temperature energy is wasted. |
| 3. Process Heaters | $T_{out} < T_{steam\ available}$ | **Remedy:** Use high-pressure steam to heat process stream. <br><br>**Justification:** Heater may be needed during start-up. | Process heaters are expensive and unnecessary if heating can be accomplished by using an available utility. |
| 4. Valves | Large $\Delta P$ across valve | **Remedy:** For gas streams install a turbine to recover lost work. <br><br>**Justification:** <br>(a) Valve used for control purposes. <br>(b) Installation of turbine not profitable. <br>(c) Liquid is being throttled. | Wasteful expenditure of energy due to throttling. |
| 5. Mixers (Streams Mixing) | Streams of greatly differing temperatures mix | **Remedy:** Bring temperatures of streams closer together using heat integration. | Wasteful expenditure of high-temperature energy. |
| | Streams of greatly differing composition mix | **Justification:** <br>(a) Quenching of reaction products. <br>(b) Provides driving force for mass transfer. | Causes extra separation equipment and cost. |

**Example 6.2.**

It is necessary to provide a nitrogen stream at 80°C and a pressure of 6 bar. The source of the nitrogen is at 200°C and 1.2 bar. Determine the work and cooling duty required for three alternatives.

    a. Compress in a single compression stage and cool the compressed gas.

    b. Cool the feed gas to 80°C and then repeat Part (a).

    c. Repeat Part (b), except use two stages of compression with an intercooler.

d. Identify any conditions of special concern that occur.

Nitrogen can be treated as an ideal diatomic gas for this comparison. Use as a basis 1 kmol of nitrogen and assume that the efficiency, $\varepsilon$, of each stage of compression is 70%.

For ideal diatomic gas: $C_p = 3.5R$, $C_v = 2.5R$, $\gamma = C_p/C_v = 1.4$, $R = 8.314$ kJ/kmol K, and assuming an efficiency, $\varepsilon = 0.70$

$$\text{Equations used: } q = C_p \Delta T, \quad w = RT_{in}\gamma/(\gamma-1)[(P_{out}/P_{in})^{(\gamma-1)/\gamma} - 1]/\varepsilon,$$

$$T_{out} = T_{in}\left(1 + \frac{1}{\varepsilon}[(P_{out}/P_{in})^{(\gamma-1)/\gamma} - 1]\right)$$

Figure E6.2 gives the process flow diagrams for the three alternatives and identifies stream numbers and utilities.
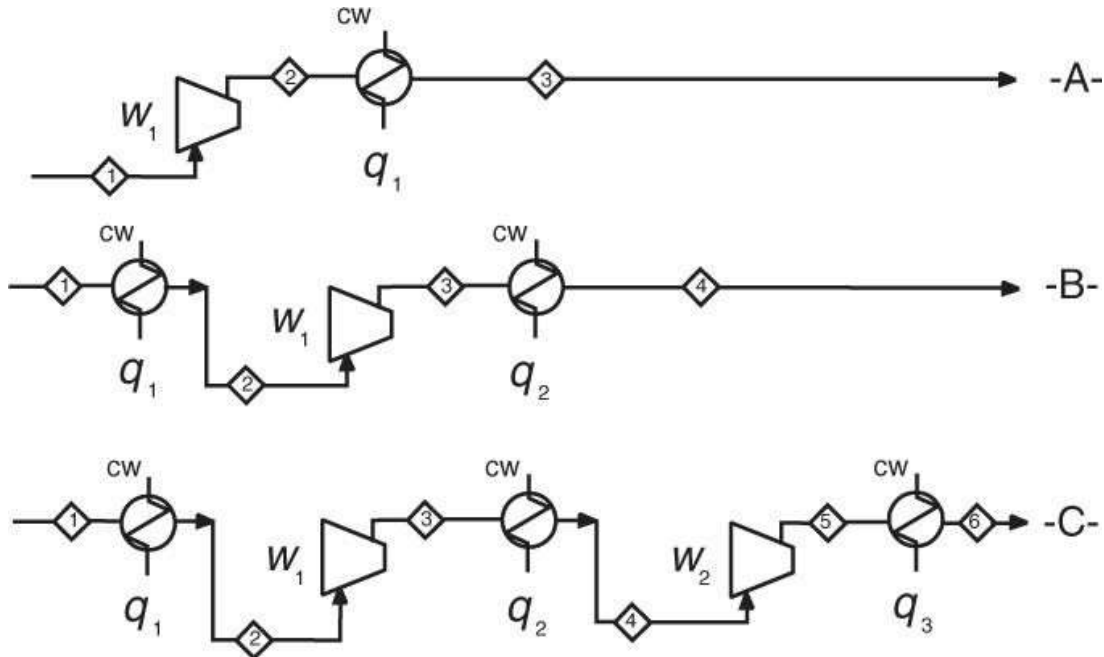


**Figure E6.2. Alternative Process Schemes for Compression of Nitrogen**

The results of the calculations for Parts (a), (b), and (c) are provided in Table E6.2, which shows stream conditions and utility requirements. To keep the calculations simple, the pressure drops across and between equipment have been ignored.

**Table E6.2. Flow Summary Table for Example 6.2 and Figure E6.2**

| Stream Number in Figure E6.2 | System -A- | | System -B- | | System -C- | |
|---|---|---|---|---|---|---|
| | $T(°C)$ | $P(bar)$ | $T(°C)$ | $P(bar)$ | $T(°C)$ | $P(bar)$ |
| 1 | 200 | 1.2 | 200 | 1.2 | 200 | 1.2 |
| 2 | 595 | 6.0 | 80 | 1.2 | 80 | 1.2 |
| 3 | 80 | 6.0 | 374 | 6.0 | 210 | 2.68 |
| 4 | — | — | 80 | 6.0 | 80 | 2.68 |
| 5 | — | — | — | — | 210 | 6.0 |
| 6 | — | — | — | — | 80 | 6.0 |

**Work: kJ/kmol**

| | | | | | | |
|---|---|---|---|---|---|---|
| $w_1$ | | 11,470 | | 8560 | | 3780 |
| $w_2$ | | — | | — | | 3780 |
| $w_{total}$ | | 11,470 | | 8560 | | 7560 |

**Heat: kJ/kmol**

| | | | | | | |
|---|---|---|---|---|---|---|
| $q_1$ | | 14,970 | | 3490 | | 3490 |
| $q_2$ | | — | | 8550 | | 3780 |
| $q_3$ | | — | | — | | 3780 |
| $q_{total}$ | | 14,970 | | 12,040 | | 11,050 |

**Part (d):** Alternative -A- requires a compressor exit temperature of 595°C, which is a condition of special concern. Note also that although the intermediate temperature of the gas (stream) in Alternative -B- was 374°C, because this stream is to be cooled there are no concerns about utility requirements.

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Example 6.2 showed three alternatives of differing complexity for achieving the same final conditions. The amount of work (*w*) and cooling utilities (*q*) required for each alternative were calculated. Based solely upon process complexity, Alternative -A- is the most desirable. However, this alternative has several disincentives that should be considered before final selection:

1. The highest electric utility demand and cost (assuming that the compressor is electrically driven)

2. The highest cooling utility demand and cost

3. A condition of special concern, that is, T > 400°C (see Table 6.1)

   *Note:* Compressors are high-speed rotating devices where the loss of material strength and thermal expansion is critical. It would be expected that the purchase cost of the compressor would undergo a quantum jump for high-temperature operations.

4. Exceeds the 3/1 pressure ratio provided as a guideline (see Table 6.4)

Alternative -B- is more complex than Alternative -A- because it requires an additional heat exchanger, but it avoids the condition of special concern in item 3. The result of using this extra exchanger is a significant decrease in utilities over Alternative -A-. As a result, it is likely that Alternative -B- would be preferred to Alternative -A-.

Alternative -C- requires an extra stage of compression and an additional cooler before the second compressor, something that is not required by Alternative -B-. However, Alternative -C- results in an additional savings in utilities over Alternative -B-.

The qualitative analysis given above suggests that both Alternatives -B- and -C- are superior to Alternative -A-. This conclusion is consistent with the two heuristics for compressors in Table 6.4: It is better to cool a hot gas prior to compressing it, and it is usually desirable to keep the compression ratio less than 3:1. Before a final selection is made, an economic analysis, which must include both the capital investment and the operating costs, should be carried out on each of the competing schemes. The equivalent annual operating cost (EAOC), described in Chapter 10, would be a suitable criterion to make such a comparison.

You should review the information given in Table 6.4 and convince yourself that you understand the rules, along with the penalties, remedies, and justifications, for operating equipment under these conditions. You may also be able to provide additional reasons why operating the equipment in this way would be justified. You should add these reasons to the list provided along with additional heuristics that are uncovered as you work problems and gain experience.

## 6.4. Analysis of Important Process Conditions

In this section, the focus is to analyze and to justify the conditions of special concern found in a process flow diagram. To help with this analysis, it is beneficial to prepare a process conditions matrix (PCM). In the PCM, all the equipment is listed vertically and the conditions of special concern are listed horizontally. Each unit is reviewed for conditions of special concern, and a check mark is used to identify which pieces of equipment have been identified. The PCM for the toluene hydrodealkylation process is shown in Table 6.5. The information for this PCM was obtained from Chapter 1, and you should verify that none of the areas of special concern have been missed.

**Table 6.5. Process Conditions Matrix for the PFD of the Toluene Hydrodealkylation Process Shown in Figure 1.5**

| Equipment | Reactors and Separators Tables 6.1–6.3 | | | | | Other Equipment Table 6.4 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | High Temp | Low Temp | High Pres. | Low Pres. | Non-Stoich. Feed | Comp | Exch. | Htr. | Valve | Mix |
| R-101 | X | | X | | X | | | | | |
| V-101 | | | | | | | | | | |
| V-102 | | | X | | | | | | | |
| V-103 | | | | | | | | | | |
| V-104 | | | | | | | | | | |
| T-101 | | | | | | | | | | |
| H-101 | | | | | | | | | | |
| E-101 | | | | | | | X | | | |
| E-102 | | | | | | | X | | | |
| E-103 | | | | | | | | | | |
| E-104 | | | | | | | | | | |
| E-105 | | | | | | | | | | |
| E-106 | | | | | | | | | | |
| C-101 | | | | | | | | | | |
| P-101 | | | | | | | | | | |
| P-102 | | | | | | | | | | |
| PCV on Stream 8 | | | | | | | | | X | |
| PCV on Stream from V-101 to V-103 | | | | | | | | | X | |

The special conditions identified in Table 6.5 are now considered and justified.

### 6.4.1. Evaluation of Reactor R-101

Three conditions of concern have been identified for the reactor. They are high temperature, high pressure, and non-stoichiometric feed conditions.

In order to understand why these conditions are needed, additional information about the toluene hydrodealkylation reaction is required. Table 6.6 provides additional but limited information. This information is divided into two groups.

**Table 6.6. Equilibrium and Reaction Kinetics Data for the Toluene Hydrodealkylation Process**

## Reaction Stoichiometry

$$C_6H_5CH_3 + H_2 = C_6H_6 + CH_4$$

toluene          benzene
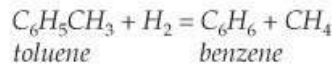
## Equilibrium Constant ($T$ is in units of K)

$$\ln(K_p) = 13.51 + \frac{5037}{T} - 2.073\ln(T) + 3.499 \times 10^{-4}T + 4.173 \times 10^{-8}T^2 + \frac{3017}{T^2}$$

## Heat of Reaction

$$\Delta H_{reaction} = -37{,}190 - 17.24T + 29.09 \times 10^{-4}T^2 + 0.6939 \times 10^{-6}T^3 + \frac{50{,}160}{T} \quad \frac{kJ}{kmol}$$

## At the Reaction Conditions of 600°C (873 K)

Equilibrium Constant, $K_p = 265$

Heat of Reaction, $\Delta H_{reaction} = -49{,}500 \quad \dfrac{kJ}{kmol}$
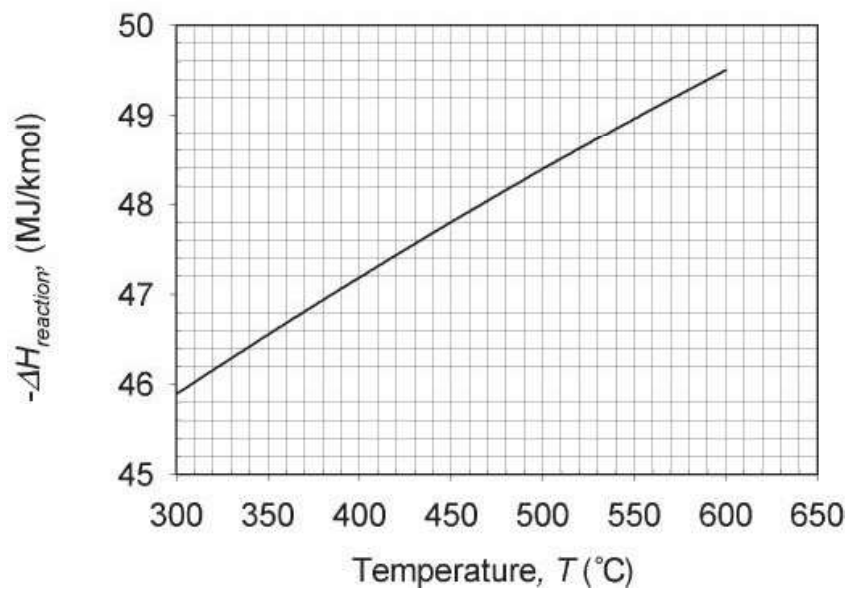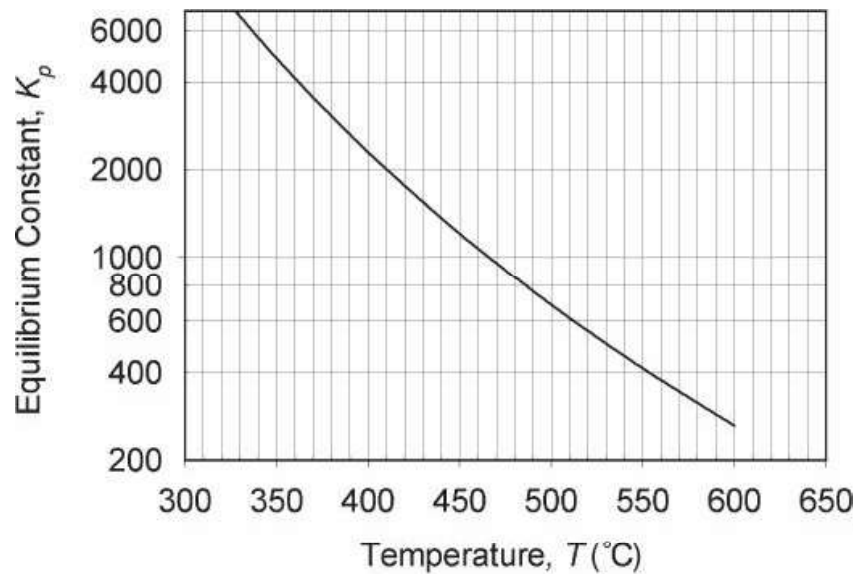
## Information on Reaction Kinetics

No side reactions

Reaction is kinetically controlled

**Thermodynamic Information:** This is information found in most chemical engineering thermodynamic textbooks:

a. Information required to perform energy balances, including heats of reaction and phase change, heat capacities, and so on

b. Information required to determine equilibrium conversion, including heats of formation, free energy of formation, and so on

Figure 6.1 is a plot of the heat of reaction and the equilibrium constant as a function of temperature, evaluated from the information provided in Table 6.6. From these plots it is evident that the chemical reaction is slightly exothermic, causing the equilibrium constant to decrease with temperature.

**Figure 6.1. Equilibrium Constant and Heat of Reaction as a Function of Temperature for the Toluene Hydrodealkylation Reaction**

**Reaction Kinetics Information:** This information is reaction specific and must be obtained experimentally. The overall kinetics may involve homogeneous and heterogeneous reactions both catalytic and noncatalytic. The expressions are often complex.

Before a process is commercialized, reaction kinetics information, such as space velocity and residence times, must be obtained for different temperatures and pressures from pilot plant studies. Such data are necessary to design the reactor. At this point, the specific details of the reactor design are not of interest, and hence specific kinetics expressions have not been included in Table 6.6 and are not necessary for the following analysis.

The analysis of the reactor takes place in two parts.

   a. Evaluation of the special conditions from the thermodynamic point of view. This assumes that

chemical equilibrium is reached and provides a limiting case.

    b. Evaluation of the special conditions from the kinetics point of view. This accounts for the limitations imposed by reaction kinetics, mass transfer, and heat transfer.

If a process is unattractive under equilibrium (thermodynamic) conditions, analysis of the kinetics is not necessary. For processes in which the equilibrium conditions give favorable results, further study is necessary. The reason for this is that conditions that favor high equilibrium conversion may be unfavorable from the standpoint of reaction kinetics.

**Thermodynamic Considerations.** The use of high-temperature, high-pressure, and non-stoichiometric feed conditions are considered separately.

**High-Temperature Concern (see Table 6.1).** Figure 6.1 provided the important information that the reaction is exothermic. Table 6.1 notes that for an exothermic reaction, the result of increasing temperature is a reduction in equilibrium conversion. This is confirmed by the plot of the equilibrium constant versus temperature given in Figure 6.1. The decrease in the equilibrium conversion is undesirable. The actual conversion for the HDA process is compared with the equilibrium conversion in Example 6.3.

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**Example 6.3.**

For the PFD presented in Figure 1.5,

    a. Calculate the actual conversion.

    b. Evaluate the equilibrium conversion at 600°C.

    Assuming ideal gas behavior: $K_p = (N_{benzene} N_{methane})/(N_{toluene} N_{hydrogen})$

    where $N$ represents the moles of each species at equilibrium.

    Information on the feed stream to the reactor from Table 1.5 (Stream 6 on Figure 1.5):

| | |
|---|---|
| Hydrogen | 735.4 kmol/h |
| Methane | 317.3 |
| Benzene | 7.6 |
| Toluene | 144.0 |
| Total | 1204.3 |

    c. Actual Conversion: Toluene in exit stream (Stream 9) = 36 kmol/h

    Conversion = (144 – 36)/144 = 0.75 (75%)

    d. Equilibrium Conversion at 600°C. From Table 6.6 at 600°C $K_p$ = 265

    Let $N$ = kmol/h of benzene formed

    $265 = [(N + 7.6)(N + 317.3)]/[(735.4 – N)(144 – N)]$

    $N = 143.6$

    Equilibrium Conversion = 143.6/144 = 0.997 (99.7%)

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The equilibrium conversion for the hydrodealkylation reaction remained high in spite of the high temperature. Although there is no real problem with using the elevated temperature in the reactor, it cannot be justified from a thermodynamic point of view.

**High-Pressure Concern (see Table 6.2).** From the reaction stoichiometry, it can be seen that there are equal numbers of reactant and product moles in the hydrodealkylation reaction. For this case, there

is no effect of pressure on equilibrium conversion. From a thermodynamic point of view there is no reason for the high pressure in the reactor.

**Non-stoichiometric Feed (see Table 6.3).** The component feed rates to the reactor (see Example 6.3) show that

1. Toluene is the limiting reactant.
2. Hydrogen is an excess reactant (more than 400% excess).
3. Methane, a reaction product, is present in significant amounts.

**Reaction Products (Methane) in Feed.** The presence of reaction product in the feed results in a reduction in the equilibrium conversion (see Table 6.3). However, Example 6.3 shows that at the conditions selected for the reactor, the equilibrium conversion remained high despite the presence of the methane in the feed.

**Excess Reactant (Hydrogen) in Feed.** The presence of excess reactants in the feed results in an increase in equilibrium conversion (see Table 6.3). Example 6.4 explores the effect of this excess hydrogen on conversion.

**Example 6.4.**

(Reference Example 6.3.) Reduce the amount of hydrogen in the feed to the reactor to the stoichiometric amount—that is, 144 kmol/h—and determine the effect on the equilibrium conversion at 600°C.

The calculations are not shown. They are similar to those in Example 6.3(b). The total moles of hydrogen in the feed were changed from 735.4 kmol/h to the stoichiometric value of 144 kmol/h.

The results obtained were $N = 128.8$ kmol/h, equilibrium conversion = 0.895 (89.5%).

Example 6.4 reveals that the presence of the large excess of hydrogen had a noticeable effect on the equilibrium conversion.

It is concluded that thermodynamic considerations do not explain the selection of the high temperature, the high pressure, and the presence of reaction products in the feed. The presence of a large excess of hydrogen is the only positive effect predicted by thermodynamics.

**Consideration of Reaction Kinetics.** The information on reaction kinetics is limited in this chapter. A more detailed description of the kinetics rate expression will be given in a case study in Chapter 23, and the predictions made in this chapter with this limited information will be investigated further. However, you will find that a great deal of understanding can be extracted from the limited information presented here.

From the information provided in Table 6.6 and Chapter 1 the following is known:

1. The reaction takes place in the gas phase.
2. The reaction is kinetically controlled.
3. There are no significant side reactions.

**High-Temperature Concern (see Table 6.1).** In a region where the reaction kinetics control, the reaction rate increases rapidly with temperature, as Example 6.5 illustrates.

**Example 6.5.**

The activation energy for the rate of reaction for the hydrodealkylation of toluene is equal to 148.1 kJ/mol (Tarhan [2]). What is the reaction rate at 600°C relative to that at 400°C?

$$\text{Ratio of Reaction Rates} = \exp[-E/R\{1/T_2 - 1/T_1\}]$$
$$= \exp[148100/8.314\{1/673 - 1/873\}] = 430$$

The size of a reactor would increase by nearly three orders of magnitude if the reaction were carried out at 400°C (the critical temperature for materials selection, Table 6.1) rather than 600°C. Clearly the effect of temperature is significant.

Most reactions are not kinetically controlled as is the case here. In most cases the rate is controlled by heat or mass transfer considerations. These are not as sensitive to temperature changes as chemical reaction rates. For more detail, see Chapter 23.

**High-Pressure Concern (see Table 6.2).** For gas-phase reactions, the concentration of reactants is proportional to the pressure. For a situation where the reaction rate is directly proportional to the concentration, operation at 25 bar rather than at 1 bar would increase the reaction rate by a factor of 25 (assuming ideal gas behavior). Although it is not known that the rate is directly proportional to the concentration, it can be predicted that the effect of pressure is likely to be substantial, and the reactor size will be substantially reduced.

**Non-stoichiometric Feed (see Table 6.3).** The reactor feed contains both excess hydrogen and the reaction product methane.

**Methane in the Feed.** The effect of methane is to reduce the reactant concentrations. This decreases the reaction rate and represents a negative impact. The methane could possibly reduce the formation of side products, but there is no information to suggest that this is the case.

**Excess Hydrogen in the Feed.** The large amount of excess hydrogen in the feed ensures that the concentration of hydrogen will remain large throughout the reactor. This increases the reaction rate. Although there is no information provided regarding the decision to maintain the high hydrogen levels, it may be linked to reducing the formation of side products.

With the exception of the presence of methane product in the feed, the high-temperature operation, the excess hydrogen, and the elevated pressure all support an increase in reaction rate and a reduction in reactor volume. This suggests that the catalyst is not "hot"—that is, the catalyst is still operating in the reaction-controlled regime and mass transfer effects have not started to intrude. For these conditions, the manipulation of temperatures and pressures is essential to limit the reactor size.

There is a significant economic penalty for using more than 400% excess hydrogen in the reactor feed. The raw material cost of hydrogen would be reduced significantly if excess hydrogen were not used. The fact that this large excess is used in spite of the economic penalty involved suggests that the hydrogen plays an important role in the prevention of side products. The concept of selectivity is discussed further in Chapter 23.

The presence of methane in the feed has not yet been resolved. At best it behaves as an inert and occupies volume that must be handled downstream of the reactor, thus making all the equipment larger and more expensive. This question is considered in more detail in Example 6.6.

**Example 6.6.**

It has been proposed that the hydrogen/methane stream is handled in the same manner as was the toluene/benzene stream. Recall that the unreacted toluene was separated from the benzene product and then recycled. It is proposed that the methane be separated from the hydrogen. The methane would then become a process by-product and the hydrogen would be recycled. Discuss this proposal using the arguments provided in Tables 6.1 and 6.2.

To use distillation for the separation of methane from hydrogen, as was used with the toluene/benzene, requires a liquid phase. For methane/hydrogen systems, this requires extremely high pressures together with cryogenic temperatures.

If the hydrogen could be separated from the methane and recycled, then the reactor feed would not contain significant quantities of methane, and the large excess of hydrogen could be maintained without the steep cost of excess hydrogen feed. Note that the overall conversion of hydrogen in the process is only 37%, whereas for toluene it is 99%.

Alternative separation schemes that do not require a liquid phase (e.g., a membrane separator) should be considered. The use of alternative separation technologies is addressed further in Chapter 12.

### 6.4.2. Evaluation of High-Pressure Phase Separator V-102

This vessel separates toluene and benzene as a liquid from the noncondensable gases hydrogen and methane. The reactor product is cooled and forms a vapor and a liquid stream that are in equilibrium. The vapor-liquid equilibrium is that at the temperature and pressure of the stream entering V-102. From Tables 6.1 and 6.2, it can be concluded that the lower temperature (38°C) was provided to obtain a liquid phase for the vapor-liquid equilibrium. The pressure was maintained to support the formation of the liquid phase. Because the separation can be accomplished relatively easily at high pressure, it is worthwhile maintaining V-102 at this high pressure.

### 6.4.3. Evaluation of Large Temperature Driving Force in Exchanger E-101

There is a large temperature driving force in this exchanger, because the heating medium is at a temperature of approximately 250°C, and the inlet to the exchanger is only 30°C. This is greater than the 100°C suggested in Table 6.4. This is an example of poor heat integration, and a closer look at improving this will be taken in Chapter 15 (also see the case study presented in Chapter 30).

### 6.4.4. Evaluation of Exchanger E-102

Stream 9 is cooled from 654°C to 40°C using cooling water at approximately 35°C. Again this is greater than the 100°C suggested in Table 6.4, and the process stream has a lot of valuable energy that is being wasted. Again, a lot of money can be saved by using heat integration (see Chapter 15).

### 6.4.5. Pressure Control Valve on Stream 8

The purpose of this control valve is to reduce the pressure of the stream entering the fuel gas line from 23.9 bar to 2.5 bar. This reduction in pressure represents a potential loss of useful work due to the throttling action of the valve. Referring to Table 6.4, it can be seen that when a gas is throttled, work can be recovered by using a turbine, although this may not be economically attractive. The operation of this valve is justified because of its control function.

### 6.4.6. Pressure Control Valve on Stream from V-102 to V-103

The purpose of this valve is to reduce the pressure of the liquid leaving V-102. This reduction in pressure causes some additional flashing and recovery of dissolved methane and hydrogen from the toluene/benzene mixture. The flashed gas is separated in V-103 and sent to the fuel gas line. The

purpose of this valve is to control the pressure of the material fed to the distillation column T-101. Because the stream passing through the valve is essentially all liquid, little useful work could be recovered from this stream.

This completes the review of the conditions of special concern for the toluene hydrodealkylation process.

## 6.5. Summary

In this chapter, you learned to identify process conditions that are of special interest or concern in the analysis of the PFD. A series of tables was presented in which justifications for using process conditions of special concern were given. The process conditions matrix (PCM) was introduced for the toluene hydrodealkylation process and all the equipment in which process conditions of special concern existed were identified. Finally, by comparing the process conditions from the PFD to those given in the tables, an analysis was made as to why these conditions were selected for the process and where improvements could be made.

**What You Should Have Learned**

- The preferred pressure range in a chemical process is 1–10 bar.
- The preferred temperature range in a chemical process is 40°C–260°C.
- Operating above 400°C requires justification.
- There are reasons for operating outside these ranges, and there are many examples in the chemical process industry.
- There are financial consequences of operating outside these ranges, such as the need for refrigeration, the inability to use steam for heating, and the need for more expensive materials of construction.

## References

1. Walas, S. M., *Chemical Process Equipment: Selection and Design* (Stoneham, MA: Butterworth, 1988).
2. Tarhan, M. O., *Catalytic Reactor Design* (New York: McGraw-Hill, 1983).

## Short Answer Questions

1. State two common criteria for setting the pressure of a distillation column.
2. Suggest two reasons each why distillation columns are run *above* or *below* ambient pressure. Be sure to state clearly which explanation is for above and which is for below ambient pressure.
3. Suggest two reasons why reactors are run at elevated pressures and/or temperatures. Be sure to state clearly which explanation is for elevated pressure and which is for elevated temperature.
4. Give two reasons why operation of a process at greater than 250°C is undesirable. Give one reason each why one would operate a distillation column and a reactor at a temperature greater than 250°C.
5. Define a "condition of special concern." Define two such conditions, and state one possible justification for each.
6. In the food and drug industries, many processes used to produce new active ingredients (drugs) or to separate and purify drugs and foods occur at vacuum conditions and often at low

temperatures (less than room temperature). What is it about these types of products that requires that these conditions of special concern be used?

## Problems

7. For the separation of a binary mixture in a distillation column, what will be the effect of an increase in column pressure on the following variables?

   a. Tendency to flood at a fixed reflux ratio

   b. Reflux ratio for a given top and bottom purity at a constant number of stages

   c. Number of stages required for a given top and bottom purity at constant reflux ratio

   d. Overhead condenser temperature

8. In a new chemical process, a reboiler for a tower requires a heating medium at 290°C. Two possible solutions have been suggested: (a) Use high-pressure steam superheated to 320°C, and (b) use saturated steam at 320°C. Suggest one disadvantage for each suggestion.

9. As the ambient temperature and humidity increase, the temperature at which cooling water (cw) can be supplied to any piece of equipment increases. For example, in the winter, cw may be available at 27°C whereas in midsummer it may rise to 34°C. How, if at all, does this affect the pressure at which a distillation column operates (assuming that the overhead condenser uses cooling water as the heat exchange utility)?

10. It is desired to produce a hot vapor stream of benzene to feed a reactor for a certain petrochemical process. The benzene is available from an off-site storage facility at 1 atm pressure and ambient temperature (assume 25°C), and the reactor requires the benzene to be at 250°C at 10 atm. Two possible process schemes are being considered to heat and pressurize the feed: (1) Pump the liquid benzene to pressure and then vaporize it in a heat exchanger, and (2) vaporize the benzene first and then compress it to the desired pressure. Answer the following:

    a. Discuss qualitatively which scheme (if either) is better.

    b. Confirm your answer to Part (a) by comparing the costs using both schemes to feed 1000 kg/h of benzene to the reactor. (Assume that the cost of heating is $15/GJ and that electricity costs $0.06/kWh.)

11. One way to produce very pure oxygen and nitrogen is to separate air using a distillation process. For such a separation determine the following:

    a. Find the normal boiling point (at 1 atm pressure) of nitrogen and oxygen.

    b. For a distillation column operating at 1 atm pressure, what would be the top and bottom temperatures and top and bottom compositions of a distillation column that separates air into nitrogen and oxygen? (For this problem, you may assume that air contains only nitrogen and oxygen and that pure components leave at the top and bottom of the column.)

    c. At what pressure can oxygen and nitrogen be liquefied at ambient temperature (say, 40°C)?

    d. What does the answer to Part (c) tell you about the potential to distill air at ambient conditions?

12. The production of ammonia (a key ingredient for fertilizer) using the Haber process takes place at temperatures of around 500°C and pressures of 250 atm using a porous iron catalyst according the following highly exothermic synthesis reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.4 \text{ kJ/mol}$$
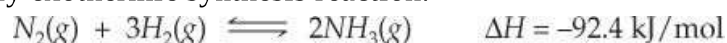
Give possible reasons for the high temperature and pressure used for this reaction.

13. Consider the ammonia process in Problem 6.12. For the given conditions, the maximum single-pass conversion obtained in the reactor is about 15–20%. Explain how the temperature and pressure should be adjusted to increase this conversion and the penalties for making these changes.

14. For the production of drying oil shown as Project B.4 in Appendix B, do the following:

    a. Construct a process conditions matrix (PCM) for the process, and determine all conditions of special concern.

    b. For each condition of special concern identified in Part (a), suggest at least one reason why such a condition was used.

    c. For each condition of special concern identified in Part (a), suggest at least one process alternative to eliminate the condition.

15. For the styrene production process given in Project B.3 in Appendix B, do the following:

    a. Construct a process conditions matrix (PCM) for the process, and determine all conditions of special concern.

    b. Explain the reasons for using the conditions of special concern in the reactor.

    c. Suggest any process alternatives for Part (b).