

APPENDIX B

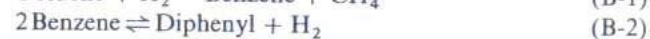
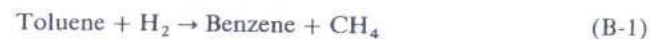
HDA CASE STUDY

The design of a process to produce benzene by the hydroalkylation of toluene has been discussed in numerous chapters in this text. The purpose of this appendix is simply to collect and present a set of sample calculations for this case study. This problem is a modified version of the 1967 AIChE Student Contest problem.*

LEVEL 0: INPUT INFORMATION

The definition of the problem was given in Example 4.1-1. The information of importance is as follows:

Reactions:



Reaction conditions: Reactor inlet temperature = 1150°F (to get a high enough rate) and reactor pressure = 500 psia.

Selectivity: Moles being produced per mole of toluene converted = S

* See J. J. McKetta, "Encyclopedia of Chemical Processing and Design," vol. 4, Dekker, New York, 1977, p. 182.

TABLE B-1
Selectivity of HDA process

S	0.99	0.985	0.977	0.97	0.93
x	0.5	0.60	0.70	0.75	0.85

From the 1967 AIChE Student Contest Problem. See J. J. McKetta, "Encyclopedia of Chemical Processing and Design," vol. 4, Dekker, New York, 1977, p. 182.

The 1967 AIChE Student Contest problem presents the selectivity data given in Table B-1. If we plot the data as $\ln(1 - S)$ versus $\ln(1 - x)$, so that we make the data as sensitive as possible, we obtain the results shown in Fig. B-1.

1. Now, if we fit an equation to the data and rearrange the results, we obtain

$$S = 1 - \frac{0.0036}{(1 - x)^{1.544}} \quad (\text{B-3})$$

Conditions: Gas phase, no catalyst.

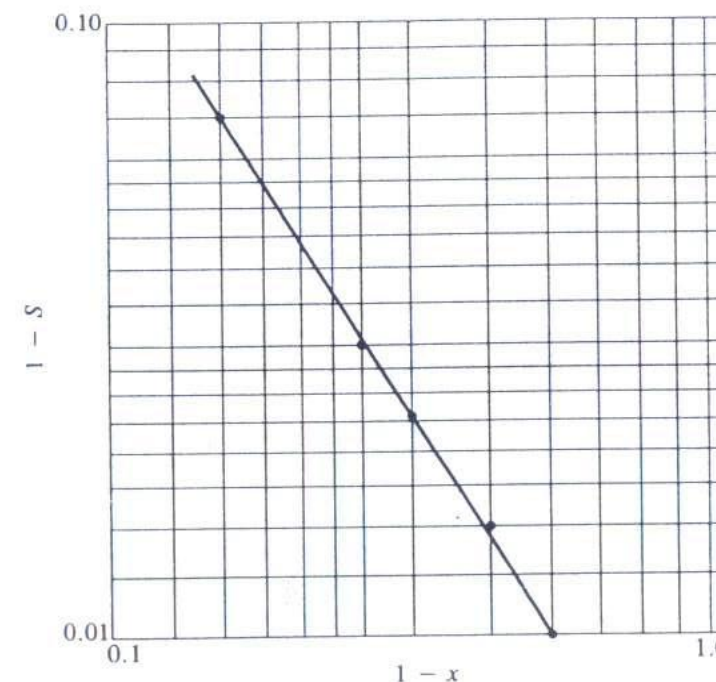


FIGURE B-1
Selectivity of the HDA process.

2. Production rate = 265 mol/hr of benzene.

3. Product purity:

$$x_D \geq 0.9997$$

4. Raw materials: Pure toluene at ambient conditions; 95% H₂, 5% CH₄ at 100°F, 550 psia.

5. Constraints: H₂/aromatics = 5 at reactor inlet (to prevent coking); reactor outlet temperature ≤ 1300°F (to prevent hydrocracking reactions); quench reactor effluent to 1150°F (to prevent coking).

6. Other plant and site data are given where needed.

LEVEL-1 DECISION: BATCH VERSUS CONTINUOUS

Choose a continuous process.

LEVEL-2 DECISIONS: INPUT-OUTPUT STRUCTURE

See Examples 5.1-2, 5.2-1, and 5.3-1.

1. Purify feed streams: The toluene feed stream is pure; do not purify the hydrogen feed stream because the methane impurity is small. Also, methane is a by-product of the reactions, and the separation of gases is expensive.

2. Reversible by-products: Diphenyl is a by-product formed by a reversible reaction. Thus, we can either recover diphenyl from the process or let it build up to its equilibrium level in a recycle loop. If we remove the diphenyl, we have a selectivity loss of toluene to produce the diphenyl. However, if we recycle the diphenyl, we can avoid the selectivity loss, but we must oversize all of the equipment in the recycle loop to accommodate the recycle flow of diphenyl. We guess that it is cheaper to recover the diphenyl.

3. Recycle and purge: Since a reactant (hydrogen) and both a feed impurity (methane) and a reaction by-product (methane) boil lower than propylene, we will need a gas recycle and a purge stream; i.e., we want to recycle the hydrogen, but the methane will build up in the recycle loop so that it must be purged. A membrane separation process, which could be used to separate the hydrogen and methane, might be less expensive than the loss of hydrogen in a purge stream. Unfortunately, however, no design procedure or cost correlation is available for membrane separators, and so we base our first design on a gas recycle and purge stream.

4. Excess reactants: Since neither O₂ from air nor H₂O is a reactant there are no excess reactants.

TABLE B-2
Component destinations

Component	NBP, °F	Destination
H ₂	-423	Gas recycle and purge
CH ₄	-259	Gas recycle and purge
Benzene	776.2	Primary product
Toluene	231.1	Recycle
Diphenyl	496.4	By-product

5. Number of product streams: The component boiling points and destinations are given in Table B-2. The H₂ and CH₄ are lumped as one product stream, and the benzene and diphenyl are two additional product streams. Thus, the flowsheet is given in Fig. 5.1-2.

6. Material balances and stream costs: Let

$$P_B = 265 \text{ mol/hr benzene} \quad x = 0.75 \quad y_{PH} = 0.4 \quad (\text{B-4})$$

$$S = 1 - \frac{0.0036}{(1 - x)^{1.544}} = 0.9694 \quad (\text{B-3})$$

Fresh feed toluene:

$$F_F = \frac{P_B}{S} = \frac{265}{0.9694} = 273.4 \text{ mol/hr} \quad (\text{B-5})$$

Diphenyl produced:

$$\begin{aligned} P_D &= P_B(1 - S)/2S \\ &= 265(1 - 0.9694)/2(0.9694) = 4.18 \end{aligned} \quad (\text{B-6})$$

Extents:

$$\text{Extent 1} = 273.4 \quad \text{Extent 2} = 4.18 \quad (\text{B-7})$$

Makeup gas:

$$\text{H}_2: \quad y_{FH}F_G - \frac{P_B}{S} + \frac{P_B(1 - S)}{2S} = y_{PH}P_G \quad (\text{B-8})$$

$$\text{CH}_4: \quad (1 - y_{FH})F_G + \frac{P_B}{S} = (1 - y_{PH})P_G \quad (\text{B-9})$$

Add these expressions to obtain

$$P_G = F_G + P_B \frac{1 - S}{2S} \quad (\text{B-10})$$

Combine Eqs. B-8 and B-10:

$$F_G = \frac{P_B[1 - (1 - y_{PH})(1 - S)/2]}{S(y_{FH} - y_{PH})} \quad (\text{B-11})$$

$$= \frac{265[1 - (1 - 0.4)(1 - 0.9694)/2]}{0.9694(0.95 - 0.4)} = 492.5$$

$$P_G = 492.5 + \frac{265(1 - 0.9694)}{2(0.9694)} = 496.7 \quad (\text{B-12})$$

Excess H_2 :

$$F_E = y_{PH} F_G = 0.4(492.5) = 197.0$$

$$H_2 \text{ Reacted} = \frac{P_B}{S} - \frac{P_B}{2S}(1 - S) \quad (\text{B-13})$$

$$= 273.4 - 4.18 = 269.2$$

Stream costs:

$$\text{Value of Benzene} = \$0.85/\text{gal} = \$9.04/\text{mol} = C_B \quad (\text{B-14})$$

$$\text{Toluene} = \$0.50/\text{gal} = \$6.40/\text{mol} = C_T \quad (\text{B-15})$$

(assuming a captive internal price)

$$H_2 \text{ Feed} = \$1.32/\text{mol} = C_{H_2} \quad (\text{B-16})$$

Heat values:

$$H_2 = 0.123 \times 10^6 \text{ Btu/mol} = \Delta H_{C,H} \quad (\text{B-17})$$

$$CH_4 = 0.383 \times 10^6 \text{ Btu/mol} = \Delta H_{C,M} \quad (\text{B-18})$$

$$\text{Benzene} = 1.41 \times 10^6 \text{ Btu/mol} = \Delta H_{C,B} \quad (\text{B-19})$$

$$\text{Toluene} = 1.68 \times 10^6 \text{ Btu/mol} = \Delta H_{C,T} \quad (\text{B-20})$$

$$\text{Diphenyl} = 2.69 \times 10^6 \text{ Btu/mol} = \Delta H_{C,D} \quad (\text{B-21})$$

(We assume that the fuel value of diphenyl is \$5.38/mol.)

Economic potential:

$$EP = C_B P_B - C_T F_F + C_F \{ \Delta H_{C,D} P_D + [\Delta H_{C,H} y_{PH} + \Delta H_{C,M} (1 - y_{PH})] P_G \} \quad (\text{B-22})$$

We can use this relationship and the expressions above to prepare Fig. 5.3-1.

Level-2 Alternatives

We made several decisions concerning the structure of the flowsheet, and if we had made different decisions, we would have changed the flowsheet. If we list the

process alternatives as we develop a design, it is easier to review these decisions after we complete a base-case design. The alternatives at level 2 are as follows.

1. Remove the CH_4 from the H_2 feed stream—This is probably not desirable because we produce CH_4 as a by-product anyway.
2. Recycle the diphenyl rather than removing it—With this approach we avoid any selectivity loss of toluene to diphenyl, but we must oversize all the equipment in the diphenyl-recycle loop to accommodate the equilibrium flow of diphenyl.
3. Recover some H_2 from the purge stream — We must determine whether the H_2 recovery is justified by determining the cost of the recovery system.

LEVEL-3 DECISIONS: RECYCLE STRUCTURE OF THE FLOWSHEET

Design Decisions

The design decisions for the recycle structure were discussed in Example 6.1-2. These are briefly reviewed now:

1. Only one reactor is required (the reactions take place at the same temperature and pressure).
2. There are two recycle streams—a gas recycle (and purge) of $H_2 + CH_4$ and a liquid toluene-recycle stream.
3. We must use a 5/1 hydrogen-to-aromatics ratio at the reactor inlet according to the problem statement.
4. A gas-recycle compressor is required.

Before we can decide on the reactor heat effects, we must calculate the recycle material balances. The recycle flowsheet is shown in Fig. 6.2-1.

Recycle Material Balances

The recycle material balances were developed as Eqs. 6.2-2 and 6.2-10. Toluene to reactor:

$$F_T = \frac{F_{FT}}{x} = \frac{P_B}{S_X} \quad (\text{B-23})$$

$$= \frac{265}{0.9694(0.75)} = 365$$

Recycle gas:

$$R_G = \frac{P_B}{S y_{PH}} \left(\frac{M}{x} - \frac{y_{FH}}{y_{FH} - y_{PH}} \right) \quad (\text{B-24})$$

$$= \frac{265}{0.9694(0.4)} \left(\frac{5}{0.75} - \frac{0.95}{0.95 - 0.4} \right) = 3376$$

Reactor Heat Effects

The reactor heat effects were discussed in Examples 6.3-1 and 6.3-3. The reactor heat load is

$$Q_R = \Delta H_R F_{FT} = \Delta H_R P_B / S$$

$$= -21,530 \left(\frac{265}{0.9694} \right) = 5.836 \times 10^6 \text{ Btu/hr} \quad (\text{B-25})$$

and the adiabatic exit temperature is given by

$$Q_R = \Delta H_R \frac{P_B}{S}$$

$$= \{7.16F_G + [7y_{FH} + 10.1(1 - y_{PH})]R_G + 48.7F_T\}(T_{R,\text{out}} - 1150)$$

$$T_{R,\text{out}} = 1150 + \frac{21,530 P_B / S}{7.16F_G + (10.1 - 3.1y_{PH})R_G + 48.7P_B / Sx}$$

$$= 1150 + \frac{21,530(265/0.9694)}{7.16(492.5) + [10.1 - 3.1(0.4)]3376 + 48.7(265)/[0.9694(0.75)]}$$

$$= 1265 \quad (\text{B-26})$$

These results are shown in Fig. 6.3-1, and we find that we expect that an adiabatic reactor will be acceptable.

Recycle Compressor Costs

The reactor pressure is given as 500 psia. We guess that the pressure at the phase splitter is 465 psia and that the recycle compressor must increase the pressure to 555 psia. This allows a pressure drop of 90 psi through the gas-recycle loop. We need to assess the sensitivity of our design to changes in this guess.

The design equation for a gas compressor is

$$\text{hp} = \left(\frac{3.03 \times 10^{-5}}{\gamma} \right) P_{\text{in}} Q_{\text{in}} \left[\left(\frac{P_{\text{out}}}{P_{\text{in}}} \right)^{\gamma} - 1 \right] \quad (\text{B-27})$$

Using Table 6.5-1, we can write

$$\gamma = 0.29y_{FH} + 0.23(1 - y_{FH}) = 0.254 \quad (\text{B-28})$$

Also,
$$\left(\frac{P_{\text{out}}}{P_{\text{in}}} \right)^{\gamma} = \left(\frac{555}{465} \right)^{0.254} = 1.046 \left(= \frac{T_2}{T_1} \right) \quad (\text{B-29})$$

and for our first design we assume that this value is constant. The gas density at 100°F and 465 psia, given an ideal gas, is

$$\rho_m = \left(\frac{1 \text{ mol}}{359 \text{ ft}^3} \right) \left(\frac{460 + 32}{460 + 100} \right) \frac{465}{14.7} = 0.0774 \text{ mol/ft}^3 \quad (\text{B-30})$$

and the inlet pressure is

$$P_{\text{in}} = 465 \text{ lb/in.}^2 (144 \text{ in.}^2/\text{ft}^2) = 6.70 \times 10^4 \text{ lb/ft}^2 \quad (\text{B-31})$$

The volumetric flow rate is

$$Q_{\text{in}} = \frac{R_G(\text{mol/hr})}{(\rho_m \text{ mol/ft}^3)(60 \text{ min/hr})} = \frac{R_G}{60\rho_m} \quad (\text{B-32})$$

Then since

$$R_G = \frac{273}{0.4} \left(\frac{5}{0.75} - \frac{0.95}{0.95 - 0.41} \right) = 3371 \text{ mol/hr} \quad (\text{B-33})$$

$$Q_{\text{in}} = \frac{3371}{60(0.0774)} = 727 \text{ ft}^3/\text{min} \quad (\text{B-34})$$

Also,
$$\text{hp} = \frac{3.03 \times 10^{-5}}{0.254} (6.70 \times 10^4)(727)(1.046 - 1) = 267 \quad (\text{B-35})$$

and the brake horsepower is

$$\text{bhp} = \frac{267}{0.8} = 334 \quad (\text{B-36})$$

Guthrie's correlation (Appendix E.1) gives

$$\text{Install. Cost} = \frac{\text{M\&S}}{280} (517.5) (\text{bhp})^{0.82} (2.11 + F_c) \quad (\text{B-37})$$

If M&S = 792 and $F_c = 1.0$ (a centrifugal compressor), and introducing a capital charge factor of $\frac{1}{3}$ yr to put the installed cost on an annual basis, we find that

$$\text{Compressor Cost} = \left(\frac{792}{280} \right) (517.5) (334) \frac{0.82(3.11)}{3} = \$177,800/\text{yr} \quad (\text{B-38})$$

For optimization calculations, we can write

$$\text{Comp. Cost} = \left(\frac{R_G}{3371} \right)^{0.82} \left[\frac{(555/465)^{\gamma} - 1}{1.046} \right]^{0.82} \quad (\text{B-39})$$

The operating cost is based on a motor efficiency (compressor plus motor) of 0.8 and a power cost of \$0.045/kwhr:

$$\text{Ann. Cost} = \left(\frac{334 \text{ hp}}{0.8}\right) \left(\frac{1 \text{ kw}}{1.341 \text{ hp}}\right) \left(\frac{0.045}{\text{kw hr}}\right) \left(8150 \frac{\text{hr}}{\text{yr}}\right) = \$114,000/\text{yr} \quad (\text{B-40})$$

We can also write this expression as

$$\text{Power Cost} = 114,000 \left(\frac{R_G}{3371}\right) = \$33.81 R_G/\text{yr} \quad (\text{B-41})$$

Reactor Cost

The kinetics for the primary reaction have been discussed by Silsby et al.* and by Zimmerman and York.† Since the amount of diphenyl produced is very small, we base the reactor design only on the primary reaction. (However, a kinetic model for the by-product reaction is available in Hougen and Watson.‡) So

$$r = -k(T)(H)^{1/2} \quad (\text{B-42})$$

$$\text{where } k = 6.3 \times 10^{10} (\text{g} \cdot \text{mol}/\text{L})^{-1/2} (\text{s}^{-1}) \exp \left[\frac{-52,000 \text{ cal}/(\text{g} \cdot \text{mol})}{RT_R} \right] \quad (\text{B-43})$$

Since there is a large excess of hydrogen, we assume that $H^{1/2}$ is a constant. Also, we assume that we can estimate the reactor volume based on isothermal operation, although we will base the isothermal reactor temperature on a mean value between the reactor inlet and outlet temperatures $T_R = (1150 + 1265)/2 = 1208$. Thus, we write the reactor volume V_R as

$$V_R = \frac{F \ln [1/(1-x)]}{k \rho_m} \quad (\text{B-44})$$

where the molar density at the reactor conditions (assuming an ideal gas) is

$$\rho_m = \left(\frac{1}{359} \frac{\text{mol}}{\text{ft}^3}\right) \left(\frac{460 + 32}{460 + T_R}\right) \left(\frac{500}{14.7}\right) = 0.0279 \text{ mol}/\text{ft}^3 \quad (\text{B-45})$$

* R. I. Silsby and E. W. Sawyer, *J. Appl. Chem.*, 6: 347 (August 1956); W. D. Betts, F. Popper, and R. I. Silsby, *J. Appl. Chem.*, 7: 497 (September 1957).

† C. C. Zimmerman and R. York, *I&EC Proc. Des. Dev.*, 3: 254 (July 1964).

‡ O. A. Hougen and K. M. Watson, *Chemical Process Principles: Part III, Kinetics and Catalysis*, Wiley, New York, 1947, p. 875.

where $T_R = (1150 + 1265)/2 = 1207$. From Eqs. B-42 and B-43

$$\begin{aligned} kH^{1/2} &= 6.3 \times 10^{10} \left(\frac{\text{g} \cdot \text{mol}}{\text{L}}\right)^{1/2} \left[\left(\frac{1 \text{ g} \cdot \text{mol}}{454 \text{ lb} \cdot \text{mol}}\right) \left(\frac{28.32 \text{ L}}{\text{ft}^3}\right)\right]^{-1/2} \\ &\times \left[0.4(0.0279) \frac{\text{mol}}{\text{ft}^3}\right]^{1/2} \exp \left[\frac{-52,000(1.8)}{1.987(1685)}\right] \\ &= 2.522 \times 10^4 [0.4(0.0279)]^{0.5} \exp \left[\frac{-93,600}{1.987(1667)}\right] = 0.0142 \text{ s}^{-1} \end{aligned} \quad (\text{B-46})$$

Then, from Eq. B-44,

$$V_R = \frac{(492.5 + 2048 + 364)(\text{mol}/\text{hr}) \ln [1/(1 - 0.75)]}{(0.0142 \text{ s}^{-1})(3600 \text{ s}/\text{hr})(0.0279 \text{ mol}/\text{ft}^3)} = 4090 \text{ ft}^3 \quad (\text{B-47})$$

If we assume a cylindrical reactor with $L_R/D_R = 6$, then

$$V_R = \frac{\pi D_R^3}{4} \quad L_R = \frac{\pi}{4} (6D_R^3) \quad (\text{B-48})$$

$$\text{and thus,} \quad D_R = 9.52 \text{ ft} \quad L_R = 56.96 \text{ ft} \quad (\text{B-49})$$

The inlet and outlet temperatures for the reactor are 1150°F and 1265°F, which is very high, and therefore we will add 6 in. of insulation on the inside of the reactor to try to keep the inside wall temperature below 900°F. The addition of this insulation requires that we add another foot to the diameter of our reactor shell, and to be somewhat conservative we let

$$D_R = 10 \text{ ft} \quad L_R = 60 \text{ ft} \quad (\text{B-50})$$

Then, from Guthrie's correlation for pressure vessels,

$$\begin{aligned} \text{Ann. Cost} &= \left(\frac{792}{282}\right) (101.9)(10^{1.066})(60^{0.82}) \frac{2.18 + 3.67 + 1.6}{3} \\ &= \$239,254/\text{yr} \end{aligned} \quad (\text{B-51})$$

We neglect the cost of the insulation in our first estimate of the reactor cost, hoping that the additional cost associated with oversizing the reactor will compensate for the insulation.

Economic Potential

By subtracting the annualized reactor cost and both the annualized capital and the operating cost of the compressor from the stream costs (i.e., the level-2 economic potential, Eq. B-22), we can calculate the economic potential at level 3 as a function of the design variables (conversion and purge composition); see Fig. 6.7-1. We note that there is an optimum value for both conversion and purge composition. Of course, these optima are not the true optima because we have not considered the separation costs or the heat exchanger costs yet. However, we do

note that the range of the design variables where profitable operation is possible has been significantly reduced. Since the process is still profitable, we continue to the next level.

LEVEL 4: SEPARATION SYSTEM

Now we add the details of the separation system. To determine the general structure of the separation system, we must decide which of the flowsheets shown in Figs. 7.1-2 through 7.1-4 is applicable. The reactor effluent is at 1265°F and therefore is all vapor. Then, providing we obtain a phase split at 100°F and 465 psia, the flowsheet given in Fig. 7.1-4 will be correct.

We can use either the Hadden and Grayson method given in Sec. C.1 or a FLOWTRAN program to find the K_i values for the flash drum. The flash calculations were discussed in Sec. 7.1, and as shortcut expressions we use these: Light components, $K_i > 10$:

$$l_i = \frac{f_i \sum f_j}{K_i \sum f_i} \quad v_i = f_i \left(1 - \frac{\sum f_j}{K_i \sum f_i} \right) \quad (\text{B-52})$$

Heavy components, $K_j < 0.1$:

$$l_j = f_j \left(1 - \frac{K_j \sum f_i}{\sum f_j} \right) \quad v_j = \frac{K_j f_j \sum f_i}{\sum f_j} \quad (\text{B-53})$$

With these expressions, we calculate the vapor and liquid flows leaving the flash drum (see Table B-3)

$$\sum f_i = 1549 + 2323 = 3872 \quad \sum f_j = 265 + 91 + 4 = 360 \quad (\text{B-54})$$

From these results, we see that we obtain a reasonable phase split. However, a significant amount of benzene leaves with the flash vapor. Some of this benzene will be lost in the purge stream, and the remainder will be recycled with the gas stream. From the reactions in Eqs. B-1 and B-2, we would expect that some of this recycled benzene will be converted to diphenyl. However, our selectivity correlation, Eq. B-3, does not indicate that there will be any loss.

We suspect that the data given in Table B-1 were for a pure toluene feed, so that no loss would be apparent. Hence, from the information available it is not possible to estimate the benzene loss, and we should ask the chemist or the pilot

TABLE B-3
Flash calculations

Component	f_i or f_j	K_i or K_j	v	l
H ₂	1549	99.07	1547	2
CH ₄	2323	20.00	2312	11
Benzene	265	0.0104	29.6	235.4
Toluene	91	0.00363	3.6	87.4
Diphenyl	4	0.000008	0	4

plant group to run some additional experiments (which is why we want to undertake the conceptual design study very early in the life of a project). The value of the benzene in the flash vapor stream, assuming that all of it is lost, is

$$\begin{aligned} \text{Potential Benzene Loss} &= (29.6 \text{ mol/hr})(\$9.04/\text{mol})(8150 \text{ hr/yr}) \\ &= \$2.18 \times 10^6/\text{yr} \end{aligned} \quad (\text{B-55})$$

which is very large. Thus, there is a great incentive for undertaking the experiments.

As an alternative, we could attempt to increase the pressure of the flash drum. Since $P_T y_i = \gamma_i P_i^\circ x_i$, we often can obtain a reasonable estimate of the effect of pressure by using the expression

$$P_T K_i = \text{Constant} \quad (\text{B-56})$$

so that increasing the pressure will decrease the K value for benzene and will decrease the amount of benzene in the flash vapor. Since the number of moles is conserved in the reactions, Eqs. B-1 and B-2, pressure does not appear to affect the reaction rate or the equilibrium. However, the possibility of coke formation or hydrocracking reactions (both of which were mentioned as the causes of some constraints in the problem formulation) again makes it essential to undertake additional experiments before we undertake a design at a higher pressure.

Rather than get bogged down in details about the benzene-recycle loss or pressure effects, we go ahead and complete a first design. In particular, if the process is not profitable in any event, so that we decide not to proceed to a final design, then we do not want to waste money on experiments developing a data base for a plant that we are not going to build.

LEVEL 4a: VAPOR RECOVERY SYSTEM

If we are going to include a vapor recovery system, we must decide on the location (flash vapor, purge stream, or gas recycle) and the type of recovery system (absorption, condensation, adsorption, or membrane system). In the discussion above, we estimated the value of the total amount of benzene leaving in the flash vapor. If it should be acceptable to recycle benzene, we still must estimate the benzene and toluene loss in the purge stream, to see whether we should place a recovery system on this purge stream. The flash vapor flows of benzene and toluene are given in Table B-3, the purge flow is given by Eq. B-10, and the gas-recycle flow is given by Eq. B-33. Thus, the fraction of the flash vapor that leaves as purge is

$$\text{Fraction Purged} = \frac{P_G}{P_G + R_G} = \frac{496}{496 + 3376} = 0.128 \quad (\text{B-57})$$

The benzene and toluene losses are then

$$\begin{aligned} \text{Benzene in Purge} &= 0.128(29.6) = 3.79 \text{ mol/hr} \\ \text{Toluene in Purge} &= 0.128(3.6) = 0.461 \end{aligned} \quad (\text{B-58})$$

and the values of these streams are (see Eq. B-54)

$$\begin{aligned}\text{Benzene Loss} &= (\$9.04/\text{mol})(3.79 \text{ mol/hr})(8150 \text{ hr/yr}) = \$279,200/\text{yr} \\ \text{Toluene Loss} &= (\$6.40/\text{mol})(0.461 \text{ mol/hr})(8150 \text{ hr/yr}) = \$24,000/\text{yr}\end{aligned}\quad (\text{B-59})$$

Now we must guess whether the addition of a benzene and toluene recovery system on the purge stream can be justified. However, if the costs of the liquid separation system and the heat-exchanger network are sufficiently large that the process loses money (and we decide not to build it), we do not want to spend much effort on the design of a vapor recovery system. Thus, tentatively, we accept this purge loss, although we might return to this problem later. (For example, we could use the toluene feed as the solvent in an absorber.)

LEVEL 4b: LIQUID SEPARATION SYSTEM

From the results of the flash calculation (see Table B-2), we have an estimate of the amount of H_2 and CH_4 dissolved in the flash liquid. If we assume that we recover all the benzene, then the feed to the liquid separation system is

$$\begin{aligned}\text{Feed: } \text{H}_2 &= 2 & \text{CH}_4 &= 11 & \text{Benzene} &= 235.4 & \text{Toluene} &= 87.4 \\ & & \text{Diphenyl} &= 4 \text{ mol/hr}\end{aligned}\quad (\text{B-60})$$

Level-4b Decisions

The decisions we must make concerning the liquid separation system include

1. How should the light ends be removed if they might contaminate the product?
2. What is the best destination of the light ends?
3. Do we recycle components that form azeotropes with the reactants?
4. What separations can be made by distillation?
5. What sequence of columns should we use?
6. How should we accomplish separations if distillation is not feasible?

We discuss most of these decisions below. However, no azeotropes are formed with the reactants and distillation separations are easy for all the components, so that items 2 and 6 are not considered.

LIGHT ENDS. If we recovered all the benzene as well as the H_2 and CH_4 overhead in a product column, the product purity would be

$$x_D = \frac{235.4}{2 + 11 + 235.4} = 0.948 \quad (\text{B-61})$$

which is well below our product purity requirement of $x_D = 0.9997$. Of course, some toluene must leave in this stream.

If we attempt to drop the pressure to 50 psia and flash off the H_2 and CH_4 , we can obtain a rough estimate of the K values by using Eq. B-56 (it would be better to

TABLE B-4
Low-pressure flash

Component	f_i or f_j	K_i or K_j	v	l
H_2	2	921	1.95	0.05
CH_4	11	186	9.51	1.49
Benzene	235.4	0.0906	0.85	234.55
Toluene	87.4	0.0337	0.11	82.29
Diphenyl	4	0.000074	0	0

use the Hadden and Grayson correlations given in Sec. C.1 for such a large pressure change). Thus, we obtain the K values and the component flows from Table B-4:

$$\sum f_i = 2 + 11 = 13 \quad \sum f_j = 235.4 + 87.4 + 4.0 = 326.8 \quad (\text{B-62})$$

Now if we recover all the H_2 , CH_4 , and benzene, we find that

$$x_D = \frac{234.55}{234.55 + 0.05 + 1.49} = 0.9935 \quad (\text{B-63})$$

which is still less than our desired purity of $x_D = 0.9997$ (even if we neglect the toluene in this stream). Moreover, there is a fairly large benzene loss from this low-pressure flash; i.e., from Eq. B-59

$$\text{Benzene Loss} = (\$483,000/\text{yr}) \left(\frac{0.85}{3.76} \right) = \$109,200/\text{yr} \quad (\text{B-64})$$

Hence, our estimates indicate that we probably will need a stabilizer to obtain a product stream with the required purity (a pasteurization section on the product column might be acceptable, and we list this as an alternative).

If we recover the light ends (H_2 and CH_4) in a stabilizer, then we would normally send these light ends to the vapor recovery system to recover any benzene or toluene that leaves with this stream (or to any unit that recovers and recycles some of the hydrogen from the purge stream). However, since we have not included any units of this type (at least at this time), we would probably send the light ends to the fuel supply.

COLUMN SEQUENCING. To use a stabilizer column to remove the H_2 and CH_4 from the benzene product, we normally pressurize this column to make it easier to condense the overhead and thereby to obtain an adequate amount of reflux. That is, the H_2 and CH_4 are removed as a vapor stream from the reflux drum after a partial condenser, but it is necessary to take some benzene overhead to provide an adequate amount of liquid reflux. From Table B-3 the K value of benzene is fairly high at 50 psia, so that we might set the stabilizer pressure at 150 psia, or so.

If we use a column sequence that does not remove the light ends in the first column, then every column that totally condensed the H_2 and CH_4 in the overhead would have to be operated at high pressure. Thus, the capital cost probably would

be greater than if we had removed the light ends in the first column. Similarly, operation of several columns at high pressure increases the bubble points of the bottoms streams, so that a higher-pressure steam might be required to drive the reboilers. For these reasons, we assume that it is cheapest to remove the light ends in the first column.

When we then consider the separation of benzene (234.5 mol/hr), toluene (87.4 mol/hr), and diphenyl (4 mol/hr), almost all the heuristics (i.e., lightest first, most plentiful first, favor equimolar splits—but not the easiest first or save difficult, high-purity splits until last), favor the direct sequence. Hence, for our base-case design we will choose the lightest first sequence to evaluate. However, complex columns might provide a cheaper separation system.

Now we want to estimate the sizes and the costs of the columns. Since the recycle column, i.e., the toluene-diphenyl split, involves only a binary mixture, we consider the design of this column first. Similarly, we consider the design of the product column before we consider that of the stabilizer. We design both of the recycle and product columns to operate at slightly above ambient pressure because it is easy to condense both toluene and benzene with cooling water at this pressure.

TOLUENE COLUMN. From a plot of the vapor pressures of toluene and diphenyl, we find that the slopes of the vapor-pressure curves for these two components are somewhat different. This result, according to the Clausius-Clapeyron equation, implies that the heats of vaporization of the two compounds are different, which in turn implies that the common assumption of equal molal overflow in the column will not be correct. We could correct for this difference in latent heats by introducing a fictitious molecular weight for one of the components and then using the McCabe-Thiele procedure to design the column. However, for our preliminary calculations we ignore this potential difficulty.

From the vapor-pressure data, we find that

$$\alpha_{\text{top}} = \frac{760}{7.4} = 102.7 \quad \alpha_{\text{bottom}} = \frac{10,000}{405} = 24.7 \quad (\text{B-65})$$

This is a large variation in α , as well as a very large temperature gradient across the column, that is, $110.6^\circ\text{C} = 231^\circ\text{F}$ at the top versus $254.9^\circ\text{C} = 492^\circ\text{F}$ at the bottom. Thus, we expect that some of the simplified design procedures, such as Fenske's equation, Gilliland's correlation, or Smoker's equation, which we often use to estimate column designs, may give misleading predictions. Nevertheless, we might be able to get some idea of the column design with these shortcut design procedures if we choose a conservative estimate of α_{av} . For this reason we let $\alpha = 25$.

Given no losses of aromatics anywhere in the process (which, of course, is not really consistent with our other calculations, but the error is small), the feed rate to the toluene column is 87.4 mol/hr of toluene and 4 mol/hr of diphenyl, so that

$$x_F = 87.4/(87.4 + 4) = 0.956 \quad (\text{B-66})$$

Thus, the feed composition of toluene is quite high.

If we recover 99.5% of the toluene overhead and 99.5% of the diphenyl in the bottoms, then we find that

$$d_T = 0.995(87.4) = 87.1 \quad d_D = 0.005(4) = 0.021 \quad (\text{B-67})$$

$$\text{and} \quad x_D = \frac{87.1}{87.1 + 0.021} = 0.9996 \quad (\text{B-68})$$

$$\text{Also,} \quad w_T = 0.005(87.4) = 0.438 \quad w_D = 0.995(4) = 0.398 \quad (\text{B-69})$$

$$\text{and} \quad x_B = \frac{0.438}{0.438 + 0.398} = 0.095 \quad (\text{B-70})$$

Assuming a saturated-liquid feed, Underwood's equation for minimum reflux

$$R_m = \frac{1}{\alpha - 1} \left[\frac{x_D}{x_F} - \frac{\alpha(1 - x_D)}{1 - x_F} \right] \quad (\text{B-71})$$

$$\text{gives} \quad R_m = \frac{1}{25 - 1} \left[\frac{0.9997}{0.956} - \frac{25(1 - 0.9997)}{1 - 0.956} \right] \quad (\text{B-72})$$

$$= \frac{1}{24} (1.0456 - 0.227) = 0.0347 \quad (\text{B-73})$$

which is very low; the feed composition is very high, and α is very large. With a very low value of reflux such as this, we should also consider the use of only a stripping column as an alternative. However, we continue with the design, and we let

$$R \approx 1.5R_m = 1.5(0.0347) = 0.05 \quad (\text{B-74})$$

According to Fenske's equation, the minimum number of theoretical trays at total reflux needed for the separation is about

$$N_m = \frac{\ln [x_D/(1 - x_D)][(1 - x_w)/x_w]}{\ln \alpha} = \frac{\ln [(0.9996/0.0004)(0.905/0.095)]}{\ln 25} = 3.13 \quad (\text{B-75})$$

We can obtain an estimate of the number of theoretical trays required at the operating reflux ratio by using Gilliland's approximation

$$N_T = 2N_m = 6.2 \quad (\text{B-76})$$

The overall plate efficiency is given by O'Connell's correlation, Eq. A2-72. For a quick estimate we assume that $\mu_F = 0.3$, and we write that

$$E_o \approx \frac{0.5}{(0.3\alpha)^{0.25}} = 0.302 \quad (\text{B-77})$$

Then the actual number of required trays is

$$N = \frac{6.2}{0.30} = 21.6 \approx 22 \quad (\text{B-78})$$

For a 2-ft tray spacing and an additional 15 ft at the ends, the tower height is

$$H = 2(22) + 15 = 59 \approx 60 \text{ ft} \quad (\text{B-79})$$

The tower cross-sectional area can be estimated by using Eq. A.3-12

$$A = 2.124 \times 10^{-4} \sqrt{M(T_b + 460)} V \quad (\text{B-80})$$

and we want to base the design on the bottom of the tower, i.e., the diphenyl, where $M = 154$ and $T_b = 492^\circ\text{F}$. The vapor rate is written as

$$V = L + D = (R + 1)D = 1.05(87.1 + 0.021) = 91.73 \quad (\text{B-81})$$

and the area becomes

$$A = 2.124 \times 10^{-4} \sqrt{154(492 + 460)} (91.7) = 7.5 \text{ ft}^2 \quad (\text{B-82})$$

The column diameter is

$$D = \sqrt{\frac{4A}{\pi}} = 2.7 \approx 3 \text{ ft} \quad (\text{B-83})$$

Now we can use Guthrie's correlation to find the cost

$$\text{Ann. Cost} = \left(\frac{792}{280}\right) (101.9) (3^{1.066}) (60^{0.802}) \left(\frac{3.18}{3}\right) = \$26,300/\text{yr} \quad (\text{B-84})$$

TOLUENE COLUMN CONDENSER AND COOLING WATER. A condenser heat balance gives

$$Q_C = \Delta H_v V = U_C A_C \Delta T_m = w_c C_p (120 - 90) \quad (\text{B-85})$$

and if $\Delta H_v = 14,400 \text{ Btu/mol}$, $U_C = 100 \text{ Btu/(hr} \cdot \text{ft}^2 \cdot ^\circ\text{F)}$, and $T_b = 231^\circ\text{F}$, then

$$\Delta T_m = \frac{120 - 90}{\ln [(231 - 90)/(231 - 120)]} = 125^\circ\text{F} \quad (\text{B-86})$$

$$\text{Thus,} \quad A_C = \frac{14,400(91.7)}{100(125)} = 105 \text{ ft}^2 \quad (\text{B-87})$$

and the annual cost is

$$\text{Ann. Cost} = \left(\frac{792}{280}\right) (101.9) (105^{0.65}) \left(\frac{3.29}{3}\right) = \$6500/\text{yr} \quad (\text{B-88})$$

Also, the cooling-water costs are

$$\text{Ann. Cost} = \left(\frac{\$0.06}{1000 \text{ gal}}\right) \left(\frac{1 \text{ gal}}{8.34 \text{ lb}}\right) \left[\frac{14,400(91.7) \text{ lb}}{30 \text{ hr}}\right] \left(8150 \frac{\text{hr}}{\text{yr}}\right) = \$2600/\text{yr} \quad (\text{B-89})$$

TOLUENE COLUMN REBOILER AND STEAM. A heat balance for the reboiler gives

$$Q_R = \Delta H_v \bar{V} = U_R A_R \Delta T_m = W_s \Delta H_s \quad (\text{B-90})$$

The area then becomes

$$A_R = \frac{19,600 (91.7)}{11,250} = 160 \text{ ft}^2 \quad (\text{B-91})$$

and the cost is

$$\text{Ann. Cost} = \left(\frac{792}{280}\right) (101.9) (160^{0.65}) \left(\frac{3.29}{3}\right) = \$8600/\text{yr} \quad (\text{B-92})$$

The boiling point of diphenyl is 492°F , and so we must use 1000-psi steam (or some high-pressure level) in the reboiler. Of course, we could use 420-psi steam if we operated the tower under a vacuum, so that the boiling point of diphenyl was reduced to about 420°F (which would allow a ΔT of 30°F). However, since the costs associated with this column are reasonably small up to this point, we use 1000-psi steam. Then the steam costs are

$$\text{Ann. Cost} = \left(\frac{\$2.25}{1000 \text{ lb}}\right) \left[\frac{19,600(91.7) \text{ lb}}{667.5 \text{ hr}}\right] \left(8150 \frac{\text{hr}}{\text{yr}}\right) = \$49,6000/\text{yr} \quad (\text{B-93})$$

This cost is fairly high, so that we might want to examine some alternatives later.

BENZENE COLUMN. Again assuming perfect separations and no losses, we see that the flow rate to the benzene column contains 235.4 mol/hr of benzene, 87.4 mol/hr of toluene, and 4 mol/hr of diphenyl. Since the diphenyl flow rate is so small, we assume that we could obtain a reasonable estimate of the column design if we lump it together with the toluene. Then

$$x_F = \frac{235.4}{235.4 + 91.4} = 0.720 \quad (\text{B-94})$$

In addition, our product specification for benzene requires that the purity be 99.97%, and we want to recover 99.5% of the benzene overhead. With these restrictions

$$d_B = 0.995(235.4) = 234.2 \quad d_T = 234.2 \left(\frac{1 - 0.9997}{0.9997}\right) = 0.07 \quad (\text{B-95})$$

$$\text{and} \quad w_B = 235.4 - 234.2 = 1.2 \quad w_T = (87.4 + 4 - 0.07) = 92.33$$

so

$$x_w = 0.013 \quad (\text{B-96})$$

From the vapor-pressure data we find that $\alpha_{nv} \approx 2.5$, and then Eq. B-71 gives

$$R_m \approx \frac{1}{(\alpha - 1)x_F} = \frac{1}{(2.5 - 1)0.72} = 0.926 \quad (\text{B-97})$$

Hence

$$R \approx 1.2R_m = 1.2(0.926) = 1.11 \quad (\text{B-98})$$

Also, from Eq. B-75,

$$N_m = \frac{\ln [(0.9997/0.0003)(0.987/0.013)]}{\ln 2.5} = 13.6 \quad (\text{B-99})$$

Then, by Gilliland's approximation

$$N_T \approx 2N_m = 2(13.6) = 27.2 \quad (\text{B-100})$$

For α values in the range of 2 to 3, E_0 is insensitive to α (see Eq. A.2-72), and therefore we can guess that $E_0 = 0.5$. Hence, the total number of trays required is

$$N \approx \frac{27.2}{0.5} = 54.4 \approx 55 \quad (\text{B-101})$$

and the column height (allowing 15 ft at the ends) is

$$H = 2(55) + 15 = 125 \text{ ft} \quad (\text{B-102})$$

The cross-sectional area of the column is given by Eq. B-80, where we evaluate the area at the bottom of the column and V is given by Eq. B-81. Hence,

$$A = (2.124 \times 10^{-4}) \sqrt{92(231 + 460)} [(1.11 + 1)(234.2 + 0.07)] = 19.73 \quad (\text{B-103})$$

and the diameter is

$$D = \sqrt{\frac{4A}{\pi}} = \sqrt{4 \left(\frac{19.73}{\pi} \right)} = 5.01 \text{ ft} \quad (\text{B-104})$$

Then, from Guthrie, the cost is

$$\begin{aligned} \text{Ann. Cost} &= \left(\frac{792}{280} \right) (101.9)(125^{1.066})(5.01^{0.802}) \left(\frac{3.18}{3} \right) \\ &= \$81,300/\text{yr} \end{aligned} \quad (\text{B-105})$$

BENZENE COLUMN CONDENSER AND COOLING WATER. A heat balance on the condenser gives

$$Q_C = \Delta H_V V = U_C A_C \Delta T_m = w_c C_p (120 - 90) \quad (\text{B-106})$$

With $\Delta H_V = 13,300$, $U_C = 100$, and

$$\Delta T_m = \frac{120 - 90}{\ln[(177 - 90)/(177 - 120)]} = 70.9 \quad (\text{B-107})$$

we find that

$$A_C = \frac{13,300(1.11 + 1)(234.2 + 0.07)}{100(70.9)} = 928 \text{ ft}^2 \quad (\text{B-108})$$

and the cost is

$$\begin{aligned} \text{Ann. Cost} &= \left(\frac{792}{280} \right) (101.3)(928^{0.65}) \left(\frac{3.29}{3} \right) \\ &= \$26,700/\text{yr} \end{aligned} \quad (\text{B-109})$$

Also, the cooling-water cost is

$$\begin{aligned} \text{Ann. Cost} &= \left(\frac{\$0.06}{1000 \text{ gal}} \right) \left(\frac{1 \text{ gal}}{8.34 \text{ lb}} \right) \left[\frac{13,300(494.7)}{30} \frac{\text{lb}}{\text{hr}} \right] \left(8150 \frac{\text{hr}}{\text{yr}} \right) \\ &= \$12,900/\text{yr} \end{aligned} \quad (\text{B-110})$$

BENZENE COLUMN REBOILER AND STEAM COSTS. A reboiler heat balance gives

$$Q_R = \Delta H_V \bar{V} = U_R A_R \Delta T_R = W_S \Delta H_S \quad (\text{B-111})$$

so that with $\Delta H_V = 14,400$, $\bar{V} = V$, and $U_R \Delta T_R = 11,250$, then

$$A_R = \frac{14,400(494.7)}{11,250} = 708 \text{ ft}^2 \quad (\text{B-112})$$

and the cost is

$$\begin{aligned} \text{Ann. Cost} &= \left(\frac{792}{280} \right) (101.3)(708^{0.65}) \left(\frac{3.29}{3} \right) \\ &= \$20,800/\text{yr} \end{aligned} \quad (\text{B-113})$$

Moreover, the steam cost is given by

$$\begin{aligned} \text{Ann. Cost} &= \left(\frac{\$1.65}{1000 \text{ lb}} \right) \left[\frac{14,400(494.7) \text{ lb}}{933.7 \text{ hr}} \right] \left(8150 \frac{\text{hr}}{\text{yr}} \right) \\ &= \$102,600/\text{yr} \end{aligned} \quad (\text{B-114})$$

STABILIZER. The design of the stabilizer is not as simple as that for the other columns. First, it is very difficult to find reliable thermodynamic data for mixtures of hydrogen and methane with aromatics. The variety of points that could be used on the Hadden and Grayson charts (see Sec. C.1) illustrates this difficulty.

In addition, the mixture of hydrogen and methane that we desire to remove from the top of the column is essentially noncondensable, so to obtain a sufficient amount of liquid for reflux, we must allow some benzene to go overhead. However, as we saw in the purge-loss calculation (Eq. B-59), even small flows of benzene are quite valuable. Therefore, we want to pressurize the stabilizer column, both to minimize the benzene loss from the partial condenser and to be able to use normal cooling water in this condenser. Of course, as we increase the operating pressure, we increase the capital costs of the column, of the condenser, and of the reboiler because the wall thickness must be increased. Hence, we anticipate that there will be an optimum operating pressure for the column.

To fix the operating pressure of the stabilizer, we might start by examining the behavior of the flash drum when $K_i < 0.1$ for benzene. For example, by considering the value listed in Table B-3 for benzene, we might initially guess that we want $K_B = 0.02$. Then, from the Hadden and Grayson correlation (Sec. C.1), the pressure of the flash drum has to be 280 psia to condense the overhead at 100°F, and it is not even possible to condense the overhead at 130°F. Similarly, if we let $K_B = 0.05$, we find that the pressure is 80 psia at 100°F and 165 psia at 130°F, so the pressure calculation is very sensitive.

Now, to determine the importance of choosing values of K_B that are very small, i.e., in the range from 0.02 to 0.05, we must estimate the value of the benzene that is lost with the vapor leaving the flash drum. We expect that the values of K_{H_2} and K_{CH_4} will be very large compared to unity, and so we expect that the liquid in the flash drum will be essentially pure benzene. Then the equilibrium relationship when $x_B \approx 1.0$ gives

$$y_B = K_B x_B \approx K_B \quad (\text{B-115})$$

From Table B-3, we expect the hydrogen and methane flows leaving in the stabilizer overhead to be about 2 and 11 mol/hr, respectively, so

$$y_B = K_B = \frac{n_B}{2 + 11 + n_B} \quad (\text{B-116})$$

$$\text{or} \quad n_B = \frac{13K_B}{1 - K_B} \quad (\text{B-117})$$

If $K_B = 0.05$, then the benzene loss calculated from this expression is about 0.7 mol/hr, and from Eq. B-59 the value of the benzene loss is

$$\text{Ann. Loss} = 9.04(0.7)8150 = \$51,600/\text{yr} \quad (\text{B-118})$$

which is fairly large. Of course, this loss is compensated, at least in part, by the fuel value of the benzene in the overhead stream.

After examining the sensitivity of the benzene loss from the flash drum of the stabilizer, we decided to choose $K_B = 0.04$ with a condensing temperature of 115°F, so that for our first design the operating pressure of the stabilizer is 150 psia. At these conditions

$$K_{H_2} = 185 \quad K_{CH_4} = 36 \quad (\text{B-119})$$

and the benzene loss is

$$n_B = \frac{13(0.04)}{1.0 - 0.04} = 0.54 \quad (\text{B-120})$$

$$\text{and} \quad \text{Ann. Loss} = 9.04(0.54)8150 = \$39,800/\text{yr} \quad (\text{B-121})$$

The distillate flows are then

$$d_{H_2} = 2 \quad d_T = 11 \quad d_B = 0.54 \quad (\text{B-122})$$

$$\text{so that} \quad x_{D,H_2} = 0.148 \quad x_{D,CH_4} = 0.812 \quad X_{D,B} = 0.040 \quad (\text{B-123})$$

We can simplify the design calculations if we lump all the aromatics and consider them to be benzene, so that the benzene feed rate to the column becomes (see Table B-3) $235.4 + 87.4 + 4 = 326.8$ mol/hr. Hence, the feed rate is

$$F = 2 + 11 + 326.8 = 379.8 \text{ mol/hr} \quad (\text{B-124})$$

and the feed composition is

$$x_{H_2} = 0.0055 \quad x_{CH_4} = 0.0324 \quad x_B = 0.961 \quad (\text{B-125})$$

With this assumption, the effluent from the bottom of the tower will be essentially pure benzene boiling at 150 psia. Then from the Hadden and Grayson correlations for $K_B = 1.0$ and $P = 150$ psia, we find that the temperature is 360°F. However, we expect that the presence of the toluene and diphenyl will increase this boiling point, thus we guess that the bottoms temperature is about 400°F. Also, at 150 psia and 400°F, we find that

$$K_{H_2} = 70 \quad K_{CH_4} = 36 \quad (\text{B-126})$$

Now, from Eqs. B-119 and B-125 we can estimate the α values:

$$\text{Top:} \quad \alpha_{H_2} = \frac{185}{0.04} = 4600 \quad \alpha_{CH_4} = \frac{36}{0.04} = 900 \quad (\text{B-127})$$

$$\text{Bottom:} \quad \alpha_{H_2} = \frac{70}{1} = 70 \quad \alpha_{CH_4} = \frac{36}{1} = 36$$

Clearly to introduce an assumption of constant relative volatility would be rather "shaky" but all the shortcut design procedures rely on this assumption. Hence, for our first design we assume that α_i is constant, but we use the smallest possible value, Eq. B-127 at the bottom, in our calculations.

Underwood's expression for the minimum reflux rates for binary separations should give us a conservative estimate for multicomponent separations, so

$$R_m = \frac{1}{\alpha - 1} \left[\frac{x_{D,C_1}}{x_{F,C_1}} - \alpha_{C_1-B} \frac{x_{D,B}}{x_{F,B}} \right] \quad (\text{B-128})$$

$$= \frac{1}{36 - 1} \left[\frac{0.812}{0.0324} - 36 \left(\frac{0.04}{0.961} \right) \right] = 0.689 \quad (\text{B-129})$$

Then, for an operating reflux, we choose

$$R \approx 1.5(0.689) \approx 1.033 \quad (\text{B-130})$$

We estimate the minimum number of trays by using Fenske's equation, which we write as

$$N_m = \frac{\ln [(x_{C_1}/x_B)_D (x_B/x_{C_1})_w]}{\ln \alpha_{C_1-B}} \quad (\text{B-131})$$

If $(x_B/x_{C_1})_w = 10^{-6}$, then

$$N_m = \frac{\ln [(0.812/0.04) 0.719 / (6.62 \times 10^{-5})]}{\ln 36} = 3.4 \quad (\text{B-132})$$

Then, from Gilliland's approximation

$$N_T = 2N_m = 6.8 \quad (\text{B-133})$$

Using Eq. B-79 to estimate the overall plate efficiency (note that we are not certain that $\mu_F = 0.3$ centipoise at high pressures) gives

$$E_o = \frac{0.5}{[0.3(36)]^{0.25}} = 0.276 \quad (\text{B-134})$$

so that the total number of required trays is about

$$N = \frac{6.86}{0.276} = 24.6 \quad (\text{B-135})$$

and the column height is

$$H = 2(25) + 15 = 65 \text{ ft} \quad (\text{B-136})$$

The vapor rate is

$$V = (R + 1)D \approx (1.033 + 1)(2 + 11 + 0.54) \approx 27.5 \quad (\text{B-137})$$

and the tower diameter is (for an ideal gas)

$$A = 0.000214 \left[78(400 + 460) \left(\frac{15}{150} \right) \right]^{1/2} (27.5) = 0.478 \quad (\text{B-138})$$

and the column diameter is

$$D = \sqrt{\frac{4A}{\pi}} = 0.8 \text{ ft} \approx 1 \text{ ft} \quad (\text{B-139})$$

Unfortunately, this diameter is less than the allowable minimum value of 1.5 ft, so we should consider the possibility of using a packed tower. However, clearly we have based our design on a number of questionable assumptions, so at some point we must undertake a more careful analysis. Nevertheless, our primary focus at this time should be the processing costs of the total plant, rather than an accurate design of the stabilizer, and since we do not expect that the stabilizer will be very expensive, we estimate the cost

$$\text{Ann. Cost} = \left(\frac{792}{280} \right) (101.3)(65^{1.066})(1^{0.802}) \left(\frac{2.18 + 1.15}{3} \right) = \$5400/\text{yr} \quad (\text{B-140})$$

STABILIZER CONDENSER AND COOLING WATER. A heat balance for the condenser gives

$$Q_C = \Delta H_V V = U_C A_C \Delta T_m = w_c C_p (t_{\text{out}} - 90) \quad (\text{B-141})$$

Since we are condensing the overhead at 115°F, we cannot allow the temperature of the cooling water to increase from 90 to 120°F. Thus, for our first design we assume that $t_{\text{out}} = 100^\circ\text{F}$. Then

$$\Delta T_m = \frac{100 - 90}{\ln [(115 - 90)/(115 - 100)]} = 19.6 \approx 20^\circ\text{F} \quad (\text{B-142})$$

We let $U_C = 100 \text{ Btu}/(\text{hr} \cdot \text{ft}^2 \cdot ^\circ\text{F})$, and we assume that $\Delta H_{H_2} = 389$ and $\Delta H_{CH_4} = 3520 \text{ Btu/mol}$. Hence

$$A_c = \frac{[389(\frac{2}{13}) + 3520(\frac{11}{13})]27.5}{(100)(20)} = 41.8 \text{ ft}^2 \quad (\text{B-143})$$

and the cost is

$$\text{Ann. Cost} = \left(\frac{792}{280} \right) (101.3)(41.8^{0.65}) \left(\frac{3.29}{3} \right) = \$3600/\text{yr} \quad (\text{B-144})$$

Also, the cost of cooling water is

$$\text{Ann. Cost} = \left(\frac{\$0.06}{1000 \text{ gal}} \right) \left(\frac{1 \text{ gal}}{8.34 \text{ lb}} \right) \left[\frac{83,600 \text{ lb}}{1(100 - 90) \text{ hr}} \right] \left(8150 \frac{\text{hr}}{\text{yr}} \right) = \$500/\text{yr} \quad (\text{B-145})$$

STABILIZER REBOILER AND STEAM. The reboiler heat balance is

$$Q_R = \Delta H_V \bar{V} = U_R A_R \Delta T_R = W_S \Delta H_S \quad (\text{B-146})$$

We assume that $\bar{V} = V$ and $\Delta H_V = \Delta H_v$, so that

$$A_R = \frac{13,300(27.5)}{11,250} = 32.5 \text{ ft}^2 \quad (\text{B-147})$$

and the cost is

$$\text{Ann. Cost} = \left(\frac{792}{280} \right) (101.3)(32.5^{0.65}) \left(\frac{3.29}{3} \right) = \$3000/\text{yr} \quad (\text{B-148})$$

The boiling point of the bottoms is about 400°F, so we use 420-psia steam in the reboiler. Then, using the values in Sec. E.1, we find that the cost is

$$\text{Ann. Cost} = \left(\frac{\$2}{1000 \text{ lb}} \right) \left[\frac{13,300(27.5) \text{ lb}}{775.6 \text{ hr}} \right] \left(8150 \frac{\text{hr}}{\text{yr}} \right) = \$7700/\text{yr} \quad (\text{B-149})$$

LEVEL-4 ECONOMIC POTENTIAL. To calculate the economic potential at level 4, we subtract the annualized capital costs of the columns, condensers, and reboilers, as well as the steam and cooling-water costs, from the values of the level-3 economic potential. In addition, we must subtract the purge losses of benzene and toluene (as well as any recycle losses, but we may take fuel credit for the benzene and toluene in the purge and the stabilizer overhead). The results are shown in Fig. 7.3-13, and we see that the range of the design variables corresponding to profitable operation has been dramatically reduced.

Of course, with a different process alternative, the profitability might be increased. However, we want to complete the design before we examine any alternatives.

LEVEL-4 ALTERNATIVES. There are numerous alternatives that we could consider at level 4. A vapor recovery system might prove to be profitable on either the

flash vapor (if we incur recycle losses) or the purge stream. Absorption, condensation, adsorption, or a membrane recovery system could be used as this vapor recovery process.

There are also numerous alternatives for the distillation system. Since the reflux ratios are so small for both the stabilizer and the recycle column, we might be able to use just stripping columns, i.e., no rectifying sections. Similarly, since both the CH_4 -benzene and the toluene-diphenyl splits are very easy, we should consider the possibility of using pasteurization sections to decrease the number of columns. However, we defer an attempt to evaluate the costs of these alternatives until we have evaluated the heat-exchanger network for our base-case design.

LEVEL 5: HEAT-EXCHANGER NETWORK

The procedure for designing a heat-exchanger network was presented in Chap. 8. To develop the data we need for this procedure, we must calculate the temperature-enthalpy curves for each process stream. We would recommend that normally this information be developed with the use of a CAD package such as FLOWTRAN, particularly for processes where mixtures exhibit a phase change (i.e., a set of flash calculations is needed along the length of an exchanger to calculate the T - H profile). Similarly, for cases where a phase change takes place at high pressures, it is usually simpler to use a CAD package to calculate the physical properties required than it is to use handbooks and empirical correlations. The use of FLOWTRAN for these calculations is discussed in Chap. 12.

APPENDIX C

DESIGN DATA

C.1 HYDROCARBON VAPOR-LIQUID EQUILIBRIA*

Use Figs. C.1-1 and C.1-2 for compounds with lower boiling points than heptane, and use Table C.1-1 with the graphs for compounds or cuts with higher boiling points than heptane.

* Taken from S. T. Hadden and H. G. Grayson, "New Charts for Hydrocarbon Vapor-Liquid Equilibria," *Hydrocarb. Proc. and Petrol. Refiner*, **40**: 91, 207 (September 1961).