Material Balances Chap. 2

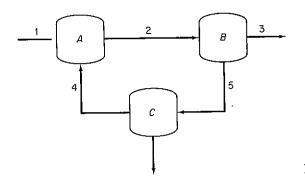


Figure E2.23

EXAMPLE 2.24 Recycle without Chemical Reaction

A distillation column separates $10,000 \, \text{kg/hr}$ of a 50% benzene-50% toluene mixture. The product D recovered from the condenser at the top of the column contains 95% benzene, and the bottoms W from the column contain 96% toluene. The vapor stream V entering the condenser from the top of the column is $8000 \, \text{kg/hr}$. A portion of the product from the condenser is returned to the column as reflux, and the rest is withdrawn for use elsewhere. Assume that the compositions of the streams at the top of the column (V), the product withdrawn (D), and the reflux (R) are identical because the V stream is condensed completely. Find the ratio of the amount refluxed to the product withdrawn (D).

Solution

This is a steady-state problem without reaction occurring.

Steps 1, 2, and 3 See Fig. E2.24 for the known data, symbols, and other information.

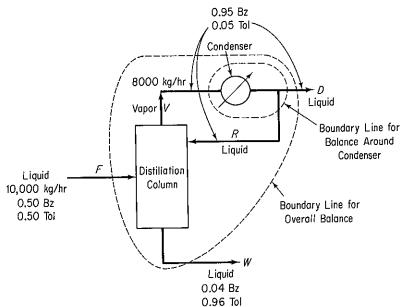


Figure E2.24

Step 4 Select a basis of 1 hr (equal to F = 10,000 kg).

Steps 5 and 6 All the compositions are known and three stream flows, D, W, and R, are unknown. No tie components are evident in this problem. Two component material balances can be made for the still and two for the condenser. Presumably three of these are independent; hence the problem has a unique solution. We can check as we proceed. A balance around either the distillation column or the condenser would involve the stream R. An overall balance would involve D and W but not R.

Steps 7, 8, and 9 What balances to select to solve for R is somewhat arbitrary. We will choose to use overall balances first to get D (and W), and then use a balance on the condenser to get R. Once D is obtained, R can be obtained by subtraction.

Overall Material balances:

Total material:

$$F = D + W$$

$$10,000 = D + W$$
 (a)

Component (benzene):

$$F\omega_F = D\omega_D + W\omega_w$$

$$10,000(0.50) = D(0.95) + W(0.04)$$
(b)

Solving (a) and (b) together, we obtain

$$5000 = (0.95)(10,000 - W) + 0.04W$$

$$W = 4950 \text{ kg/hr}$$

$$D = 5050 \text{ kg/hr}$$

Balance around the condenser:

Total material:

$$V = R + D$$

$$8000 = R + 5050$$

$$R = 2950 \text{ kg/hr}$$

$$\frac{R}{D} = \frac{2950}{5050} = 0.58$$
(c)

Would the benzene or toluene balances on the condenser yield additional information to that obtained from the total balance, Eq. (c)? Write the balances down and check to see if they are redundant with Eq. (c).

EXAMPLE 2.25 Recycle without Chemical Reaction

The manufacture of such products as penicillin, tetracycline, vitamins, and other pharmaceuticals, as well as photographic chemicals, dyes, and other fine organic compounds, usually requires separating the suspended solids from their mother liquor by centrifuging, and then drying the wet cake. A closed-loop system (see Fig. E2.25a) for centrifuge unloading, drying, conveying, and solvent recovery is comprised of equipment especially designed for handling materials requiring sterile and contamination-free conditions.

Given the experimental measurements on the pilot plant equipment outlined in Fig. E2.25a, what is the lb/hr of the recycle stream R?

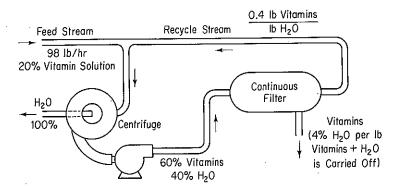


Figure E2.25a

Solution

Steps 1, 2, and 3 Figure E2.25a should be simplified with all the flows and compositions placed on it. Examine Fig. E2.25b. We computed the weight fraction of V in R from the data given in Fig. E2.25a. On the basis of 1 lb of water, the recycle stream contains (1.0 lb of $H_2O + 0.4$ lb of V) = 1.4 lb total. The recycle stream composition is

$$\frac{0.4 \text{ lb } V \quad 1 \text{ lb } H_2O}{1 \text{ lb } H_2O \quad 1.4 \text{ lb solution}} = 0.286 \text{ lb } V/\text{lb solution}$$

so that there is 0.714 lb H₂O/lb solution.

Step 4 Pick as a basis 1 hr so that F = 98 lb.

Steps 5 and 6 We have four unknown values of variables, W, C, P, and R, and can make two component material balances on each of two units of equipment; hence the problem has a unique solution.

Steps 7, 8, and 9 Probably the most efficient procedure in solving this problem is to make overall mass balances to calculate W and P, and then write mass balances about one of the units to calculate R.

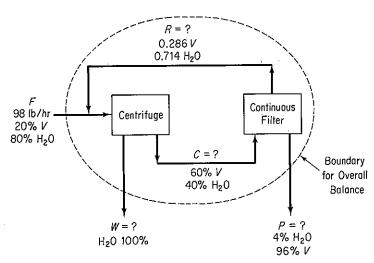


Figure E2.25b

Overall mass balances:

$$V: \qquad 0.20(98) = 0 \qquad + 0.96P \tag{a}$$

$$H_2O: 0.80(98) = (1.0)W + 0.04P$$
 (b)

Total:
$$98 = W + P$$
 (c)

Observe that V is a tie component so that P can be calculated directly in Eq. (a): P = 20.4 lb, and W can be calculated from Eq. (c).

$$W = 98 - 20.4 = 77.6 \text{ lb}$$

Steps 7, 8, and 9 (Continued) To determine the recycle stream R, we need to make a balance that involves the stream R. Either (a) balances around the centrifuge or (b) balances around the filter will do. The latter are easier to formulate since the mixing of R and F does not have to be calculated.

Total balance on filter:

$$C = R + P$$

$$C = R + 20.4$$
 (d)

Component V balance on filter:

$$C\omega_C = R\omega_R + P\omega_P$$

 $0.6C = 0.286R + 0.96(20.4)$ (e)

Solving Eqs. (d) and (e), we obtain R = 23.4 lb/hr.

Step 10 Check the value of R using a material balance around the centrifuge.

2.6-2 Recycle in Processes with Chemical Reaction

Now let us turn to recycle problems in which a chemical reaction occurs. Recall from Sec. 1.9 that not all of the limiting reactant necessarily reacts in a process. Do you remember the concept of conversion as discussed in Sec. 1.9? Two bases for conversion are used in describing a process; examine Fig. 2.18.

(a) Overall fraction conversion:

mass (moles) of reactant in fresh feed—mass (moles) of reactant in output of the overall process
mass (moles) of reactant in fresh feed

(b) Single-pass ("once-through") fraction conversion:

mass (moles) of reactant fed into the reactor—mass (moles) of reactant exiting the reactor

mass (moles) of reactant fed into the reactor

When the fresh feed consists of more than one material, the conversion must be stated for a single component, usually the limiting reactant, the most expensive reactant, or some similar compound.

Note the distinction between fresh feed and feed to the process. The feed to the process itself is made up of two streams, the fresh feed and the recycled material.

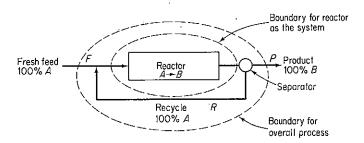


Figure 2.18 Recycle problem.

The gross product leaving the process is separated into two streams, the net product and the material to be recycled. In some cases the recycle stream may have the same composition as the gross product stream, while in other instances the composition may be entirely different depending on how the separation takes place and what happens in the process. Suppose that you are given the data that 30% of the A is converted to B on a single pass through the reactor, as illustrated in Fig. 2.18, and are asked to calculate the value of R, the recycle on the basis of 100 moles of fresh feed, F. We will make a balance for A with the reactor as the system.

Recall from Eq. (2.1) that for a specific chemical compound the steady-state material balance for a reactor is (the accumulation term in zero)

$$\begin{cases} \textbf{input} \\ \textbf{through} \\ \textbf{system} \\ \textbf{boundary} \end{cases} - \begin{cases} \textbf{output} \\ \textbf{through} \\ \textbf{system} \\ \textbf{boundary} \end{cases} + \begin{cases} \textbf{generation} \\ \textbf{within the} \\ \textbf{system} \end{cases} - \begin{cases} \textbf{consumption} \\ \textbf{within the} \\ \textbf{system} \end{cases} = 0$$
 (2.12)

Reactants are consumed and products are generated. If a reaction takes place within the system, you must be given (or look up) information about the reaction stoichiometry and extent of reaction. Or, perhaps the question is to calculate the extent of conversion given some of the process data. In any case, the fraction of feed converted to products is always an essential additional piece of information that helps determine values of the terms in Eq. (2.12).

Let us examine how to apply Eq. (2.12) for a recycle reactor such as shown in Fig. 2.18, in which A is converted to B. How much A exits the reactor itself? The unconverted A is 70% of the A that enters the reactor. No A occurs in the P stream. The system is the reactor and the basis is 100 moles of fresh feed. The A balance is

$$\frac{Input \ of \ A}{[(1.0)(100) + (1.0)R] - [(1.0)R + 0(P)] - [0.30(100 + R)]} = 0$$

or

$$0.70(100 + R) = R$$
moles of A unconverted moles of A leaving the reactor
 $R = 233 \text{ moles}$

Note that in Fig. 2.18 all the A was recycled for simplicity of illustration of the principle, but such may not be the case in general. Nevertheless, Eq. (2.12) still applies.

The single-pass (mole) balance on A provides the crucial information to evaluate R. Will an A balance, or total balance, for the overall process enable you to solve for R? Try one and see why not. What is the overall fraction conversion of A for the entire process? Does that information help you solve for R?

EXAMPLE 2.26 Recycle with a Reaction Occurring

Immobilized glucose isomerase is used as a catalyst in producing fructose from glucose in a fixed-bed reactor (water is the solvent). For the system shown in Fig. E2.26a, what percent conversion of glucose results on one pass through the reactor when the exit stream/recycle ratio in moles is equal to 8.33? The reaction is

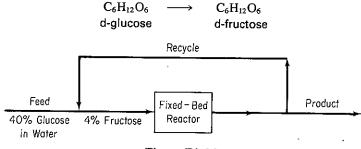


Figure E2.26a

Solution

We have a steady-state process with a reaction occurring.

Steps 1, 2, and 3 Figure E2.26b includes all the known and unknown values of the variables using appropriate notation (W stands for water, G for glucose, and F for fructose in the second position of the mass fraction subscripts). Note that the recycle stream and product stream have the same composition and consequently the same mass fraction symbols are used in the diagram for each stream.

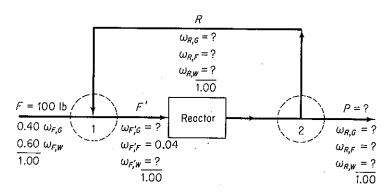


Figure E2.26b

Step 4 Pick as a basis F = 100 lb.

Steps 5 and 6 The sum of the mass fractions is one in each stream so that the unknown compositions can be picked to be $\omega_{F',G}$, $\omega_{R,G}$, $\omega_{R,W}$, and the unknown stream values are F' and P (R = P/8.33). Let f be the fraction conversion in the reactor. Three balances

each can be make about the mixing point 1, the reactor, and the separation point 2. Not all the balances will be independent, but sufficient independent balances should exist to solve this problem. We can check as we proceed with the calculations rather than going through an extensive analysis at the beginning.

Steps 7, 8, and 9 We will start with overall balances, as they are the easiest to write.

Overall:

Total:
$$100 = P$$

Consequently,

$$R = \frac{100}{8.33} = 12.0 \text{ lb}$$

No water is generated or consumed, hence

Water:
$$100 (0.60) = P(\omega_{R,W}) = 100\omega_{R,W}$$

 $\omega_{R,W} = 0.60$

We now have left three unknown values of the variables plus f.

Mixing Point 1:

Total:
$$100 + 12 = F' = 112$$

Glucose: $100(0.40) + 12(\omega_{R,G}) = 112(\omega_{F',G})$
Fructose: $0 + 12(\omega_{R,F}) = 112(0.04)$

oΓ

$$\omega_{R.F} = 0.373$$

Also, because
$$\omega_{R,F} + \omega_{R,G} + \omega_{R,W} = 1$$
,

$$\omega_{R,G} = 1 - 0.373 - 0.600 = 0.027$$

and then from the glucose balance,

$$\omega_{F',G} = 0.360$$

Reactor Plus Separator 2:

Total:
$$F' = 12 + 100 = 112$$
 (redundant equation)

Glucose:

$$\frac{In}{F'\omega_{F',G}} - \frac{Out}{(R+P)\omega_{R,G} - fF'\omega_{F',G}} = 0$$

$$112(0.360) - 112(0.027) - f(112)(0.360) = 0$$

$$f = 0.93$$

EXAMPLE 2.27 Recycle with a Reaction Occurring

Refined sugar (sucrose) can be converted to glucose and fructose by the inversion process.

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose d-Glucose d-Fructose

The combined quantity glucose/fructose is called inversion sugar. If 90% conversion of sucrose occurs on one pass through the reactor, what would be the recycle stream flow per 100 lb of sucrose solution entering the process shown in Fig. E2.27a? What is the concentration of inversion sugar (I) in the recycle stream and in the product stream? The concentrations of components in of the recycle stream and product stream are the same.

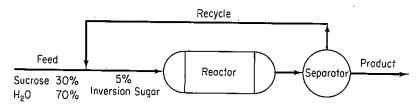


Figure E2.27a

Solution

Steps 1, 2, and 3 First we need to enter the concentrations and stream flows on the diagram. See Fig. E2.27b. (W stands for water, S for sucrose, and I for inversion sugar in the mass fraction subscripts.)

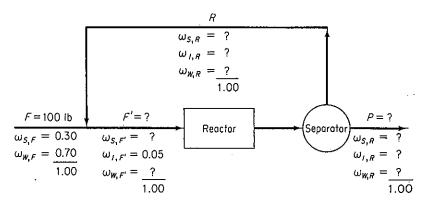


Figure E2.27b

Step 4

Basis:
$$F = 100 \text{ lb}$$

Steps 5 and 6 Keeping in mind that the sum of the mass fractions in each stream is unity, we have six unknown values of the variables, say $\omega_{S,F'}$, $\omega_{S,R}$, $\omega_{I,R}$, R, F', and P.

Steps 7, 8, and 9 Let us start with the necessary balances. Only the total balance in the overall balance is directly useful because the S and I balances involve the generation and consumption terms in Eq. (2.12).

Overall:

Total:
$$100 = P$$

Mixing Point:

Total:
$$100 + R = F'$$
 (a)

Sucrose:
$$100(0.30) + R\omega_{S,R} = F'\omega_{S,F'}$$
 (b)

Inversion:
$$0 + R\omega_{I,R} = F'(0.05)$$
 (c)

Reactor plus Separator To avoid calculating the reactor output stream properties, we will make the system the reactor plus the separator. First we need to calculate the pounds of water consumed in the reaction per pound of sucrose consumed in the reaction.

1 mole sucrose uses 1 mole water

$$\frac{1 \text{ mol } W \quad 1 \text{ mol } S}{1 \text{ mol } S} \quad \frac{18 \text{ lb } W}{1 \text{ mol } W} = 0.0526 \frac{\text{lb } W}{\text{lb } S}$$

Total: F' = R + P = R + 100 [redundant equation to (a)]

Water: Out Consumed (d)

$$F'(1 - 0.05 - \omega_{S,F'}) - (R + 100)(1 - \omega_{S,R} - \omega_{I,R}) - (F'\omega_{S,F'})(0.90)(0.0526) = 0$$
Sucrose:
$$\frac{In}{F'\omega_{S,F'} - (R + 100)\omega_{S,R} - (F'\omega_{S,F'})(0.90)} = 0$$
(e)

We have five independent equations (a)—(e) that can be solved for the five unknown values of the variables listed in steps 5 and 6; the value of P is given by the overall total materials balance. Either by successive substitution of Eqs. (a)—(e) into each other or by use of a computer program (see Sec. 2.7), you can find

$$R = 20.9 \text{ lb}$$

 $\omega_{LR} = \omega_{LP} = 0.279$

2.6-3 Bypass and Purge

Two additional commonly encountered types of process streams are shown in Fig. 2.19.

- (a) A bypass stream—one that skips one or more stages of the process and goes directly to another stage
- (b) A purge stream—a stream bled off to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream

A bypass stream is used to control the composition of a final exit stream from a unit by mixing the bypass stream and the unit exit stream in suitable proportions to obtain the desired final composition.

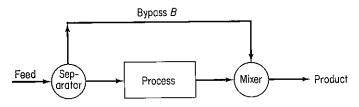


Figure 2.19a

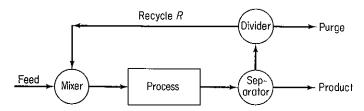


Figure 2.19b Recycle stream with purge.

As an example of the use of a purge stream, consider the production of NH₃. Steam reforming, with feedstock natural gas, LPG, or naphtha, is the most widely accepted process for ammonia manufacture. The route includes four major chemical steps:

Reforming:
$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Shift: $CO + H_2O \longrightarrow CO_2 + H_2$
Methanation: $CO + 3H_2 \longrightarrow H_2O + CH_4$
Synthesis: $3H_2 + N_2 \longrightarrow 2NH_3$

In the final stage, for the fourth reaction, the synthesis gas stream is approximately a 3:1 mixture of hydrogen to nitrogen, with the remainder about 0.9% methane and 0.3% argon.

Compressors step up the gas pressure from atmospheric to about 3000 psi—the high pressure that is needed to favor the synthesis equilibrium. Once pressurized and mixed with recycle gas, the stream enters the synthesis converter, where ammonia is catalytically formed at 400 to 500°C. The NH₃ is recovered as liquid via refrigeration, and the unreacted syngas is recycled.

In the synthesis step, however, some of the gas stream must be purged to prevent buildup of argon and methane. But purging causes a significant loss of hydrogen that could be used for additional ammonia manufacture, a loss that process designers seek to minimize.

Do you understand why the recycle process without a purge stream will cause an impurity to build up even though the recycle rate is constant? The purge rate is adjusted so that the amount of purged material remains below an acceptable specified economic level or so that the

$$\begin{cases} \text{rate of} \\ \text{accumulation} \end{cases} = 0 = \begin{cases} \text{rate of entering material} \\ \text{and/or production} \end{cases} - \begin{cases} \text{rate of purge} \\ \text{and/or loss} \end{cases}$$

Calculations for bypass and purge streams introduce no new principles or techniques beyond those presented so far. Two examples will make this clear.

EXAMPLE 2.28 Bypass Calculations

In the feedstock preparation section of a plant manufacturing natural gasoline, isopentane is removed from butane-free gasoline. Assume for purposes of simplification that the process and components are as shown in Fig. E2.28. What fraction of the butane-free gasoline is

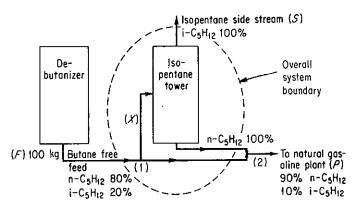


Figure E2.28

passed through the isopentane tower? Detailed steps will not be listed in the analysis and solution of this problem.

Solution

By examining the flow diagram you can see that part of the butane-free gasoline bypasses the isopentane tower and proceeds to the next stage in the natural gasoline plant. All the compositions are known. What kind of balances can we write for this process? We can write the following:

Basis: 100 kg feed

(a) Overall balances (each stream is designated by the letter F, S, or P):

Total material balance:

$$\frac{In}{100} = \frac{Out}{S+P} \tag{a}$$

Component balance (n-C₅), tie component:

$$\frac{In}{100(0.80)} = \frac{Out}{S(0) + P(0.90)}$$
 (b)

Consequently,

$$P = 100\left(\frac{0.80}{0.90}\right) = 88.9 \text{ kg}$$

 $S = 100 - 88.9 = 11.1 \text{ kg}$

The overall balances will not tell us the fraction of the feed going to the isopentane tower; for this we need another balance.

(b) Balance around isopentane tower. Let x = lb of butane-free gas going to isopentane tower and y be the $n-C_5H_{12}$ stream leaving the isopentane tower.

Total material balance:

$$\frac{In}{x} = \frac{Out}{11.1 + y} \tag{c}$$

Component $(n-C_5)$, a tie component:

$$x(0.80) = y \tag{d}$$

Consequently, combining (c) and (d),

$$x = 11.1 + 0.8x$$

x = 55.5 kg or the desired fraction is 0.555

Another approach to this problem is to make a balance at mixing points (1) or (2). Although there are no pieces of equipment at those points, you can see that streams enter and leave the junction.

(c) Balance around mixing point (2):

material into junction = material out

Total material:

$$(100 - x) + y = 88.9 (e)$$

Component (iso-C₅):

$$(100 - x)(0.20) + 0 = 88.9(0.10)$$
 (f)

Equation (f) avoids the use of y. Solving yields

$$20 - 0.2x = 8.89$$

x = 55.5 kg as before

EXAMPLE 2.29 Purge

Considerable interest exists in the conversion of coal into more convenient liquid products for subsequent combustion. Two of the main gases that can be generated under suitable conditions from insitu coal combustion in the presence of steam (as occurs naturally in the presence of groundwater) are H_2 and CO. After cleanup, these two gases can be combined to yield methanol according to the following equation

Figure E2.29 illustrates the process.

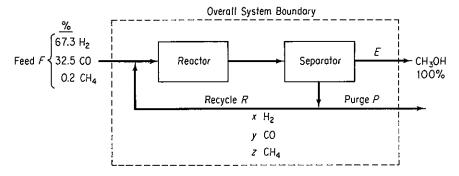


Figure E2.29

You will note in Fig. E2.29 that some CH₄ enters the process, but the CH₄ does not participate in the reaction. A purge stream is used to maintain the CH₄ concentration in the exit to the separator at no more than 3.2 mol%. The once-through conversion of the CO in the reactor is 18%.

Compute the moles of recycle, CH₃OH, and purge per mole of feed, and also compute the purge gas composition.

Solution

Steps 1, 2 and 3 Figure E2.29 is the sketch of the process. We will make balances about the whole process using the system designated by the dashed line, and also make a balance about the reactor plus separator to calculate the amount of recycle. Each of the stream flows has been labeled, and because the composition of the recycle and purge stream is not known, we have designated by x, y, and z, respectively, the mole fractions of H_2 , CO, and CH_4 . The ethanol stream is 100% CH_3 OH; the purge and recycle streams have the same compositions.

Step 4 Take a basis of 100 moles of feed.

Step 5 The unknown stream flows and mole fractions of the components are R, E, P, x, y, and z.

Step 6 We can make three independent elemental material balances for the overall process: H_2 , C, and O balances. A CO balance on the reactor plus separator will provide one additional balance. How can we obtain fifth and sixth balances so that the system of equations is determinate? One piece of information given in the problem statement that we have not used is the information about the upper limit on the CH_4 concentration in the purge stream. This limit can be expressed as $z \le 0.032$. Let us make

$$z = 0.032 \tag{a}$$

Another piece of information is the implicit balance,

$$x + y + z = 1 \tag{b}$$

Steps 7 and 8 The overall balances are (in moles):

H₂:
$$67.3 + 0.2(2) = E(2) + P(x + 2z)$$
 (c)

C:
$$32.5 + 0.2 = E(1) + P(y + z)$$
 (d)

O:
$$32.5 = E(1) + P(y)$$
 (e)

For a system composed of the reactor plus the separator (chosen to avoid calculating the unknown information about the reactor direct output), the CO balance is

$$\frac{In}{32.5 + Ry} - \frac{Out}{y(R+P)} = \frac{Consumed}{(32.5 + Ry)(0.18)}$$
 (f)

Would a H₂ balance on the reactor plus separator yield any additional information not given in Eq. (f)? The balance would be

H₂:
$$67.3 + Rx - x(R + P) = (67.3 + Rx)(0.18)$$
 (g)

Experienced engineers would say that the hydrogen balance is redundant. You can verify this conclusion by looking at the coefficient matrix of Eqs. (f) and (g):

$$0.82(32.5 + Ry) = (R + P)y = Ry + Py$$
$$0.82(67.3 + Rx) = (R + P)x = Rx + Px$$

or

$$0.82(32.5) = (0.18y)R + (y)P$$
$$0.82(67.3) = (0.18x)R + (x)P$$

What is the rank of

$$M = \begin{bmatrix} 0.18y & y \\ 0.18x & x \end{bmatrix}$$

The det [M] = 0.18yx - 0.18yx = 0, hence the rank of M is one, and Eqs. (f) and (g) are not independent.

Step 9 Equation (a) can be substituted into Eqs. (b)-(f) and the resulting five equations solved by successive substitution or by using one of the computer programs on the disk in the pocket in the back of this book. The resulting values obtained are (in moles)

E	CH₃OH	31.25
P	purge	6.25
R	recycle	705
x	H_2	0.768
у	co	0.200
z	CH₄	0.032

Step 10 Check to see that each of the balances (b)-(f) is satisfied.

Up to now we have discussed material balances of a rather simple order of complexity. If you try to visualize all the calculations that might be involved in even a moderate-sized plant, as illustrated in Fig. 2.4, the stepwise or simultaneous solution of material balances for each phase of the entire plant may seem to be a staggering task, but is a task that can be eased considerably by the use of computer codes as discussed in Sec. 2.7. Keep in mind that a plant can be described by a number of individual, interlocking material balances each of which, however tedious they are to set up and solve, can be set down according to the principles and techniques discussed in this chapter. In application there is always the problem of collecting suitable information and evaluating its accuracy, but this matter calls for detailed familiarity with any specific process and is not a suitable topic for discussion here. We can merely remark that some of the problems you will encounter have such conflicting data or so little useful data that the ability to perceive what kind of data are needed is the most important attribute you can bring to bear in their solution.

Self-Assessment Test

- 1. Explain what recycle and bypassing involve by means of words and also by a diagram.
- 2. Repeat for the term "purge."
- 3. If the components in the feed to a process appear in stoichiometric quantities and the subsequent separation process is complete so that all the unreacted reactants are recycled, what is the ratio of reactants in the recycle stream?