# 8 [4] Fundamentals of Material Balance (Reactive Systems)

*"It was obvious—to me at any rate—that the answer was to why an enzyme is able to speed up a chemical reaction by as much as 10 million times. It had to do this by lowering the energy of activation—the energy of forming the activated complex. It could do this by forming strong bonds with the activated complex, but only weak bonds with the reactants or products."*

Linus Pauling

*"Every sentence I utter must be understood not as an affirmation but as a question."*

Niels Bohr

*Humanity stands . . . before a great problem of finding new raw materials and new sources of energy that shall never become exhausted. In the meantime we must not waste what we have, but must leave as much as possible for coming generations.*

Svante Arrhenius

## 8.1 Chapter Purpose and Strategy

In both chemical and bioprocess engineering, the material balance of reactive systems is very important. According to the American Institute of Chemical Engineers (AIChE), two of the main achievements of chemical engineering are the synthesis of ammonia and the production of antibiotics on an industrial scale. As was shown and discussed in Chap. 4, in 1908, Professor Fritz Haber filed for a patent on the "synthesis of ammonia from its elements," and as we will see and discuss in Chap. 10, U.S. companies with strong governmental support began producing penicillin in 1943 and on a larger scale in 1945. These two great achievements involve reactive systems.

In our view, having completed Chap. 7, you have already learned the main concepts in material balance, and we purposely left reactive systems for this chapter. As you will see, using the same approach as that proposed, analyzed, and discussed in Chap. 7 (Fig. 7.15), you will be ready to take on and solve most, if not all, material balances for reactive systems. So why did we leave reactive systems for this chapter? As stated previously, our aim in writing this book is to teach you some concepts and various subjects step by step. We would like to reinforce the concept of teaching as discovery, i.e., furnishing you with the tools and then, through examples, facilitating your process of discovery. Perhaps you've already noticed that at the beginning of Chap. 7, we mentioned and explained the concepts of side stream and recycle, but we intentionally did not explain why they are used in processing. Then, for example, the recycle concept was presented in problem 10 (Sect. 7.9), and

R. Simpson and S.K. Sastry, *Chemical and Bioprocess Engineering: Fundamental Concepts for First-Year Students*, DOI 10.1007/978-1-4614-9126-2_8,

then a similar problem 11 (Sect. 7.9) without recycle was analyzed, and finally in its solution (step V) we presented a discussion on the advantages and disadvantages of recycling in a process stream. But at this point, independently of our discussion, maybe you have already "discovered" at least some of the advantages and disadvantages of a recycle stream. (Did you?)

But the main reason to leave reactive systems for this chapter is because it includes some additional characteristics. Everything that we have learned about approaching and solving material balance problems is useful and necessary. But for reactive systems we need to discuss the issue of material balance in a reactor. An important feature is the advantage of the use of mole instead of mass. Why? As you recall from chemistry, the relative quantities of reagents and products in a chemical reaction are given by the stoichiometry. For example:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2\ H_2O$$

The first thing to notice is that this a balanced equation. In addition, the stoichiometry indicates that one molecule (or 1 [mol]) of $CH_4$ (methane) reacts with two molecules (or 2 [mol]) of $O_2$ to form one molecule (or 1 [mol]) of $CO_2$ and two molecules (or 2 [mol]) of $H_2O$.

Later, we will revisit the concept of a balanced equation and its implications.

## 8.2 Why Reactive Systems Are Relevant to Material Balance

### 8.2.1 Chemical Process

Chemical reactors are the heart of processing plants. Unlike all the other unit operations, it is in the reactor where the molecules that make up the raw materials undergo profound changes, transforming into valuable commercial products. Chemical changes occur only in the reactor. Other operations involve the preparation of raw materials to feed the reactor or to separate and purify the products.

But this process of chemical transformation is often very complex. In addition, it creates valuable commercial products and generates other products that may be of lesser value, undesirable, or even in some cases harmful to humans and the environment. In this situation, the engineer must be able to evaluate the performance of the reactor and answer questions such as how efficient the transformation of raw materials into valuable products is. Also, what type of products are being generated? What fraction of the raw materials degrades into noncommercial products? Which will be treated by expensive processes of separation? And to what extent are contaminants occurring that cannot be disposed of in the environment?

The most important available tool of an engineer to properly design and evaluate the operation of reactive processes is material balance. This is an accounting process; unlike nonreactive processes, it involves generating terms (positive or negative). Some molecules disappear and new molecules emerge from those consumed. This accounting process is often complicated because there are many possible reactions. For example, the combination of carbon monoxide (CO) with hydrogen ($H_2$) can yield methanol, methane, or higher alcohols, even hydrocarbons (Fischer–Tropsch reaction). It all depends on the type of catalyst used.

The global chemical industry generates approximately 50,000 different products, on every scale imaginable, ranging from highly specific products measurable in grams to commodities or basic products for heavy industry (petrochemical, mining), measured in thousands of tons annually. Whatever the size or complexity of the process, the material balance provides the framework to guide engineers in their work.

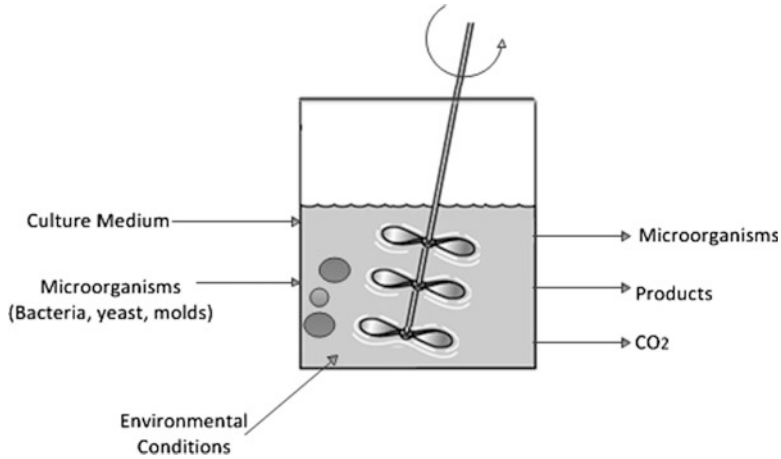


**Fig. 8.1** Schematic representation of a fermentation process

### 8.2.2 Bioprocess

A bioprocess refers to any operation involving the transformation of a given substrate into products by the action of microorganisms or their derivatives, such as enzymes. Bioprocesses are generally conducted in reactors (e.g., bioreactors, fermenters) charged with a substrate or raw material and microorganisms to generate products. Figure 8.1 shows a schematic representation of a fermentation bioprocess.

For the bioprocess to be successful, microorganisms must be given optimal conditions for their development and growth. These conditions include the culture medium with the necessary nutrients and optimal environmental conditions (e.g., temperature, pH, agitation, oxygen). The objective of the bioprocess will depend on the desired product, which can be an organic compound or biomass (microorganisms). In most cases, the focus will be on the generation of a desired compound, e.g., ethanol, organic acids, and antibiotics. Some examples of industrial bioprocesses include the production of yogurt, beer, wine, antibiotics, bread, biological processes of wastewater treatment, and composting.

In this context, the operation of a bioprocess, like a chemical reaction, is related to heat transfer (heating/cooling), mass transfer (e.g., diffusion), kinetics, and energy balances. Considering the reactor (bioreactor) as the system under study it will be necessary to analyze changes in the different properties over time and space. It is indisputable that viewing these changes and expressing them in mathematical terms is vital for formulating material balance equations with respect to time for what enters (substrate material) and "reacts" inside the reactor (microorganisms/biomass), and what leaves the reactor. Therefore, a schematic representation is as follows (Fig. 8.2).

Translating the preceding scheme into a mass balance equation for microorganisms or a substrate, we obtain

$$\begin{aligned}&\text{Input} - \text{Output} \pm \text{Transformation}(\text{generation}/\text{consumption})\\&\quad = \text{Accumulation}(\text{Deaccumulation})\end{aligned} \tag{8.1}$$

As was discussed in Chap. 7, we will face problems under steady-state conditions, but now we will be adding a term to take into account the transformation occurring inside the reactor or bioreactor:

$$\text{Input} - \text{Output} \pm \text{Transformation}(\text{generation}/\text{consumption}) = 0 \tag{8.2}$$

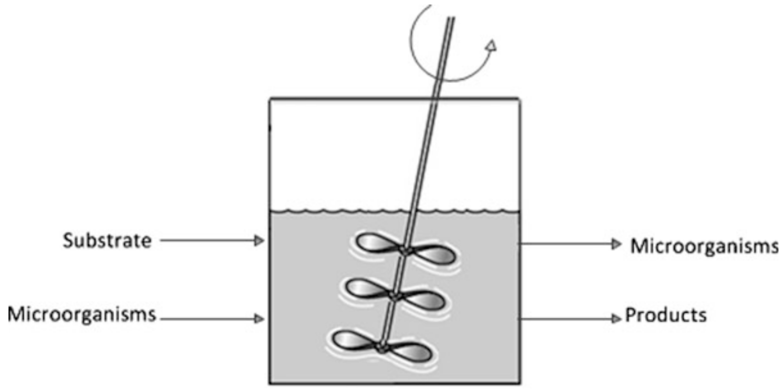


**Fig. 8.2** Bioreactor

But do not get confused; the total mass balance remains the same as in (7.5):

$$\text{Total input mass} - \text{Total output mass} = 0. \quad (8.3)$$

## 8.3 Particularities of Material Balance on Reactive Systems

### 8.3.1 Material Balance Equations for Reactive Systems (Steady-State and Continuous Operation)

As mentioned previously, matter is neither created nor destroyed, but it is conserved. The law of conservation of matter postulates that the amount of material before and after a process is strictly the same. What the law of conservation of matter implies is that, beyond transformations, matter is always conserved. In other words, atoms react with each other as substances, but atoms are neither created nor destroyed.

Formulation of a general mass balance for a reactive and open system under steady-state conditions (process unit):

**Total mass balance**
Referring to Fig. 8.3, the total mass balance under steady state can be written as follows:

$$\text{Total input mass} - \text{Total output mass} = 0. \quad (8.4)$$

Thus,

$$\left(\sum_{i=1}^{i=n} \dot{m}_i\right)_{\text{in}} - \left(\sum_{j=1}^{j=k} \dot{m}_j\right)_{\text{out}} = 0, \quad (8.5)$$

where $\left(\dot{m}_i\right)_{\text{in}}$ is the mass flow rate of stream $i$ entering the system (mass/time), and $\left(\dot{m}_j\right)_{\text{out}}$ is the mass flow rate of stream $j$ leaving the system (mass/time).

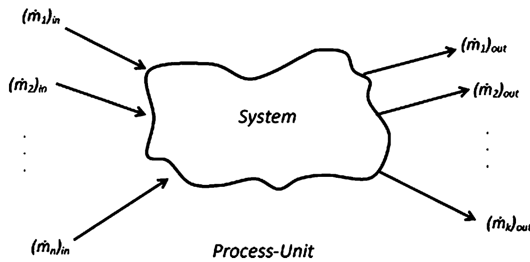


**Fig. 8.3** General material balance for a reactive and open system under steady-state conditions

**Mass balance for each component**

It is important to note that in a reactive system, the mass for each component is not necessarily conserved (although the total mass is conserved!). As for nonreactive systems, we can write one mass balance for each component. If we have $p$ components, then we can formulate $p$ equations. Writing the mass balance for some specific component $r$, we obtain

$$\left(\sum_{i=1}^{n} x_{ri}\,\dot{m}_i\right)_{\text{in}} - \left(\sum_{j=1}^{m} x_{rj}\,\dot{m}_j\right)_{\text{out}} + (m_r)_{\text{reaction}} = 0 \tag{8.6}$$

where $x_{ri}$ is the mass fraction of component $r$ in stream $i$; $x_{rj}$ is the mass fraction of component $r$ in stream $j$; and $(m_r)_{\text{reaction}}$ is the mass of component $r$ generated or consumed due to the reaction (this term could be positive, negative, or 0 depending on whether component $r$ is a reagent, a product, or not part of the reaction).

The first term in (8.6) represents the addition of the masses of component $r$ in all input streams. In the same way, the second term represents all the masses of component $r$ leaving the system. Finally, the third term represents the amount of component $r$ that was generated or consumed due to the reaction. If component $r$ is not part of the reaction, then the third term in (8.6) is 0.

As with nonreactive systems, we can write one total mass balance and, in addition, one mass balance for each component (1, 2, . . ., $p$). Since we have $p$ components, we are able to write $p + 1$ equations in total, but **ONLY *p* of them are independent!** Why? For example, if we sum up all the material balance equations formulated for each component, we will discover that the result is equal to the total mass balance.

**Remember, the number of independent equations is equal to the number of components in the process unit (system).**

As mentioned earlier, we have an extra term due to the reaction among compounds. Before addressing problems of material balance in reactive systems, it is necessary to briefly analyze chemical reactions and understand why the use of molar units is much more pertinent and convenient than the use of mass units for material balances in a reactor.

## 8.3.2 Stoichiometry

As mentioned earlier, in a balanced equation, the relative quantities of reagents and products are given in molecular or molar bases:

$$aA + bB \rightarrow cC. \tag{8.7}$$

As depicted in (8.7), $a$ moles of compound A react with $b$ moles of compound B to generate $c$ moles of compound C. If we feed the reactor with $a$ moles of A and $b$ moles B, then we can state that the feed is a stoichiometric mixture. Remember that the equation should be balanced, but what is a balanced equation? For example, is the following equation for formaldehyde ($CH_2O$) production balanced?

$$CH_3OH + O_2 \rightarrow CH_2O + H_2O. \tag{8.8}$$

No, because the number of atoms per element must be the same on both sides of the equation. In (8.8), we have one carbon atom on each side and four atoms of hydrogen on each side but three atoms of atomic oxygen on the left-hand side and just two on the right-hand side. Thus, the equation is not balanced. Balancing (8.8), we obtain

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CH_2O + H_2O.$$

Or, amplifying both sides of the equation, we get

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O. \tag{8.9}$$

**Warm-Up Example 1**. Acetylene is a gas that can be obtained by treating calcium carbide with $H_2O$ according to the following reaction:

$$CaC_2 + H_2O \rightarrow C_2H_2 + Ca(OH)_2. \tag{8.10}$$

(a) Is the equation balanced? Why or why not? (b) How many moles of acetylene can be produced with 1 [kg] of calcium carbide?

First, to answer question (a), we need to verify whether the number atoms per element is the same on each side of (8.10).

Calcium atoms, one per side

Carbon atoms, two per side

Atoms of atomic hydrogen, two on the left and four on the right

Atoms of atomic oxygen, one on the left and two on the right

Thus the equation is not balanced.

So a balanced equation for the production of acetylene is

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2, \tag{8.11}$$

where there is one calcium atom on each side, two carbon atoms one each side, four atoms of atomic hydrogen on the left and four on the right, and two atoms of atomic oxygen on the left and two on the right.

Now, with (8.11) balanced, we can answer question (b). The balanced equation indicates that 1 [mol] of calcium carbide produces 1 [mol] of acetylene.

Moles of calcium carbide = mass of calcium carbide/molecular weight of calcium carbide = 1,000 [g]/64 [g/mol] = 15.625 [mol]. Given that, according to (8.11), to produce 1 [mol] acetylene requires 1 [mol] calcium carbide; therefore, with 15.625 [mol] calcium carbide we can produce 15.625 [mol] acetylene.

### 8.3.3 Limiting and Excess Reagents and Reaction Conversion

According to the stoichiometry of a reaction, you can determine the exact number of moles of reagents A and B that are necessary to produce, say, product C. If the reaction stoichiometry is

$$5A + 3B \rightarrow 4C, \tag{8.12}$$

then in (8.12) you need 5 [mol] of A and 3 [mol] of B to produce 4 [mol] of C, or, in general, the moles of A and the moles of B must be in a proportion of 5/3 to have a stoichiometric mixture (stoichiometry ratio, SR). If all the reagents are fed in as the stoichiometry indicates, no reagent will be limiting or in excess in the reaction.

**Warm-Up Example 2**. What happens if you are feeding, for example, 6 [mol] of A and 3 [mol] of B in reaction (8.12)? Then reagent A is in excess (more than the required amount) and, in addition, we can say that reagent B is limiting. As seen in this example, we can deduce

$$\text{If the molar ratio } (A/B) \begin{array}{l} > 5/3, \text{then compound A is in excess} \\ = 5/3 \text{ then compounds A and B are in a stoichiometric mixture} \\ < 5/3, \text{then compound B is in excess} \end{array} \tag{8.13}$$

**Excess**
In warm-up example 2, we stated that compound A was in excess, but can we quantify its excess? Yes. How? By defining the fractional excess as

$$\textbf{Fractional excess} = (\text{Moles fed} - \text{Moles needed})/\text{Moles needed}. \tag{8.14}$$

Then, in warm-up example 2, we can calculate the excess of reagent A.
Fractional excess of reagent will be A = (6 − 5)/5 = 0.2 (20 %).

**Conversion**
If we have a stoichiometric mixture and all the reagents are consumed (disappear), then we have 100 % conversion. In this case, when we have a stoichiometric mixture, the conversion could be calculated with any of the reagents. On the other hand, if the mixture it is not stoichiometric, then the conversion must be calculated with the limiting reagent.

$$\textbf{Fractional conversion} = (\text{Moles of limiting compound reacted})/(\text{Moles of limiting compound fed}) \tag{8.15}$$

**Warm-Up Example 3**. 6 [mol] of A and 4 [mol] of B are fed to a reactor. The stoichiometry of the reaction is

$$2A + 3B \rightarrow 4C \tag{8.16}$$

If the conversion is 60 %, how many moles of C are produced?

First, we need to determine whether A or B is the limiting reagent. According to the stoichiometry, for each mole of A we need 1.5 [mol] of B, so for 6 [mol] of A, 9 [mol] of B are needed. Therefore, the limiting reagent is B. In addition, the conversion is 60 %. Therefore, from (8.15):

$$\text{Fractional conversion} = \text{Moles of B reacted}/\text{Moles of B fed} = 0.6 = \text{Moles of B reacted}/4.$$

Thus, 2.4 [mol] of B reacted. Given that for each mole of B that reacted we obtain 4/3 [mol] of C (8.16), then for 2.4 [mol] of B, we obtain 3.2 [mol] of C.

## 8.4 Material Balance in Reactors and Bioreactors

As was said and proven through examples, we will use moles as units for each stream and, in addition, we have designed a strategy specially to help you write down the equations when doing a material balance on a reactor. Warm-up examples 4 and 5 are typical chemical processes and are presented to show an easy, straightforward, and graphical way to manage material balances in a chemical reactor. Then, warm-up examples 6 and 7 are classical examples of bioprocess problems. In either case, the emphasis is not in the process itself, but in reinforcing your capabilities to manage material balance problems with reactions. As was stated previously, as you are being trained to take on and solve material balance problems on reactive systems you will be, somehow, unconsciously discovering the work of chemical and bioprocess engineers. In the next section (Sect. 8.5), we will revisit the strategy and procedure on approaching and solving material balance problems. For now, the focus is on the particularities of the material balance of chemical reactors and bioreactors (fermenters).

### 8.4.1 Typical Material Balance Problems in Chemical Processes

As has been stressed throughout the book, and particularly in the previous chapter, a correct procedure is, again, essential to solving material balance problems for reactive systems. Warm-up examples 4 and 5 focus on managing material balances for reactors.

**Warm-Up Example 4**. A reactor is fed with a mixture of oxygen ($O_2$) and propane ($C_3H_8$). Oxygen is in excess and the conversion of the reaction is 70 %. At the output of the reactor, the presence of 21 [mol] of $CO_2$ and 40 [mol] of $O_2$ has been analytically determined. (a) What is the fractional excess of oxygen? (b) How many moles of propane were fed to the reactor? (c) What is the molar composition of the output stream?

First, we need to write down the balanced equation for the reaction between oxygen and propane:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O. \tag{8.17}$$

Second, we will develop a table (Table 8.1) that simulates what is happening in the reactor, i.e., a column listing all compounds (reagents and products) and then columns for input moles, reaction moles, and output moles, where $x$ is the moles of the limiting reagent (in this case propane) and $y$ is the excess moles of oxygen.

**Table 8.1** Simulation of the reaction for the mixture of $O_2$ and $C_3H_8$ (propane) where $O_2$ is in excess and the fractional conversion is 70%

| Compound | Input moles | Reaction moles | Output moles |
|---|---|---|---|
| $O_2$ | $5x + y$ | $0.7(5x) = 3.5x$ | $(5x + y) - 3.5x = 1.5x + y$ |
| $C_3H_8$ | $x$ | $0.7x$ | $x - 0.7x = 0.3x$ |
| $CO_2$ | – | – | $0.7x \times 3 = 2.1x$ |
| $H_2O$ | – | – | $0.7x \times 4 = 2.8x$ |

**Table 8.2** Completed data for the reaction of $O_2$ and $C_3H_8$ (propane)

| Compound | Input moles | Reaction moles | Output moles | Molar composition (%) |
|---|---|---|---|---|
| $O_2$ | 75 | 35 | 40 | 43.47 |
| $C_3H_8$ | 10 | 7 | 3 | 3.26 |
| $CO_2$ | – | – | 21 | 22.83 |
| $H_2O$ | – | – | 28 | 30.44 |
| | | | Total = 92 | 100 % |

**Understanding the content of Table 8.1**

Input moles. According to the stoichiometry, for each mole of $C_3H_8$ we need 5 [mol] oxygen. If we assigned $x$ for the moles of propane, then for $O_2$ we need $5x$ plus the y moles in excess, thus $5x + y$.

Reaction moles. Given that $O_2$ is in excess, $C_3H_8$ is the limiting reagent, and given that the conversion is 70 % (fractional conversion = 0.7), according to (8.15),

Fractional conversion = *Moles of limiting compound reacted/Moles of limiting compound fed* = 0.7; therefore the moles of limiting compound reacted = $0.7x$, and by stoichiometry $5(0.7x) = 3.5x$ moles of $O_2$ will react.

Output moles. To get the output column for reagents, subtract the reaction column from the input column. To calculate the moles of products, it is necessary to see how much reagent reacts and follow the relationship given by the stoichiometry. For example, according to (8.18), for each mole of $C_3H_8$ we get 3 [mol] $CO_2$, so for $0.7x$ mol $C_3H_8$ that reacted, we get $2.1x$ mol $CO_2$. In the same way, we get $2.8x$ mol $H_2O$ at the output.

According to the problem statement, at the output we get 21 [mol] $CO_2$ and 40 [mol] $O_2$. Thus,

$2.1x = 21$; $x = 10$ [mol] and

$1.5x + y = 40$; $y = 25$ [mol].

Completing the table, we can answer question (c) (Table 8.2).

(a) What is the fractional excess of oxygen? According to (8.14):

$$\text{Fractional excess of } O_2 = (75 - 50)/50 = 0.5(50\ \%).$$

(b) How many moles of propane were fed to the reactor? $x = 10$ [mol] propane.

**Warm-up example 5**. A reactor is fed with 100 [kg] of A and 150 [kg] of B, and the conversion of the reaction is 75 % (fractional conversion = 0.75). (a) What is the molecular weight of C? (b) How many moles of C are obtained at the output stream? (c) What is the molar composition at the output of the reactor?

ADDITIONAL DATA: $MW_A = 20$ [g/mol]; $MW_B = 30$ [g/mol].

$$3A + 2B \rightarrow 4C \tag{8.18}$$

**Table 8.3** Simulation of the reaction of compounds A and B

| Compound | Input moles | Reaction moles | Output moles |
|---|---|---|---|
| A (limiting reagent) | 5 | $5 \times 0.75 = 3.75$ | $5 - 3.75 = 1.25$ |
| B (in excess) | 5 | $(10/3) \times 0.75 = 2.5$ | $5 - 2.5 = 2.5$ |
| C (product) | – | – | $3.75 \times (4/3) = 5$ |

**Table 8.4** Completed data for the reaction of compounds A and B in mass units

| Compound | Input mass [g] | Reaction mass [g] | Output mass [g] |
|---|---|---|---|
| A (limiting reagent) | $5 \times 20 = 100$ | $5 \times 0.75 \times 20 = 75$ | $100 - 75 = 25$ |
| B (in excess) | $5 \times 30 = 150$ | $(10/3) \times 0.75 \times 30 = 75$ | $150 - 75 = 75$ |
| C (product) | – | – | $5 \times 30 = 150$ |
| Total | 250 | | 250 |

**Table 8.5** Molar composition at the out of the reactor

| Compound | Input moles | Reaction moles | Output moles | Molar composition at output [%] |
|---|---|---|---|---|
| A (limiting reagent) | 5 | 3.75 | 1.25 | 14.3 |
| B (in excess) | 5 | 2.5 | 2.5 | 28.6 |
| C | – | – | 5 | 57.1 |
| Total | | | 8.75 | 100 |

**Solution**

(a) According to the stoichiometry given in (8.18), 3 [mol] of A (mass of A = 60 [g]) and 2 [mol] of B (mass of B = 60 [g]) gives 4 [mol] of C. Given that mass is conserved, 120 [g] of reagent should produce 120 [g] of product (100 % conversion). Thus, the molecular weight of C should be

$$MW_C \times 4 = 120\ [g], \text{ then } MW_C = 30\ [g/mol].$$

(b) Here, we will focus on a strategy for analyzing the material balance for the reactor.

First, we will express the mass of A and B in moles (kg mol); thus,
Moles of A = 100 [kg]/20 = 5 [kg mol] and moles of B = 150 [kg]/30 = 5 [kg mol].

Second, we need to determine whether the fed mixture is stoichiometric. As depicted in (8.18), the stoichiometric ratio is 3/2 (moles of A/moles of B). As shown in (8.13), in this case, we can conclude that the feed ratio is not stoichiometric ($5/5 \neq 3/2$) and, in addition, because $5/5 < 3/2$, B is in excess and A is limiting the reaction. Therefore, if we are feeding 5 [kg mol] of A, according to the stoichiometry, we need $(2/3) \times 5$ [kg mol] of B, then 10/3 [kg mol] of B are needed to react with 5 [kg mol] of A. As mentioned earlier, the conversion of the reaction is referred to the limiting reagent (A in this case), then in the reactor:

<u>Material balance for reactors</u>

As shown in warm-up example 4, a practical way to deal with material balances for a reactor is to construct a table (Table 8.3). From now on, all the material balances for reactors will be done using this procedure.

**5 [kg mol] of compound C are obtained at the output stream**

**Checking the mass balance**. Because mass is conservative, all the mass entering the reactor should be equal to all the mass leaving it. Thus (Table 8.4),

To answer question (c) we will complete the table adding the molar composition at the output (Table 8.5):

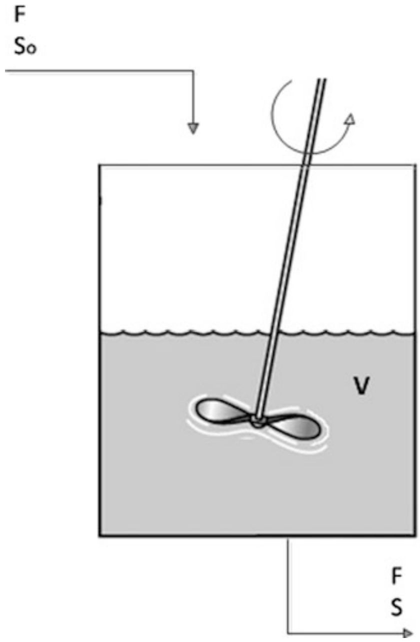


**Fig. 8.4** Continuous stirred-tank reactor (CSTR)

### 8.4.2 Typical Material Balance Problems in Bioprocesses

**Warm-up example 6**. A continuous stirred-tank reactor (CSTR) of volume $V$ is fed with a stream of $F$ L/h and with a substrate concentration of $S_0$ [kg/L]. The transformation speed of the substrate within the reactor is directly proportional to its concentration ($-kS$), where $k$ has units of 1/h. If we can assume that the concentration of the substrate at the output stream is equal to the concentration within the reactor, and the reactor is operated under steady state (Fig. 8.4), then express the substrate concentration at the output stream ($S$) as a function of known variables ($F$, $V$, $k$, and $S_0$).

**Solution**
Again, the focus is to analyze what is happening in the reactor, in this case a bioreactor. In addition, the data related to the reactions (substrate transformation) are given in mass units. Thus:

<u>Mass balance for substrate</u>

$$F[\text{L/h}] \times S_0(\text{kg/L}) - F[\text{L/h}] \times S(\text{kg/L}) - V(\text{L}) \times k(1/\text{h}) \times S(\text{kg/L}) = 0. \tag{8.19}$$

Therefore, the substrate concentration at the output stream as a function of $F$, $S_0$, $V$, and $k$ is

$$S = \frac{FS_0}{F + Vk}. \tag{8.20}$$

**Warm-up example 7**. A clever young chemical engineering student is proposing that you analyze the previous problem, but this time instead of using one reactor of volume $V$, he is suggesting using two reactors of volume $V/2$ each. He is clever, but not as well prepared as you, and so he asks you to investigate two alternatives, to maximize the disappearance of the substrate, as follows: (a) Use both reactors in parallel. (b) Use both reactors in series. (c) What would your recommendation be and

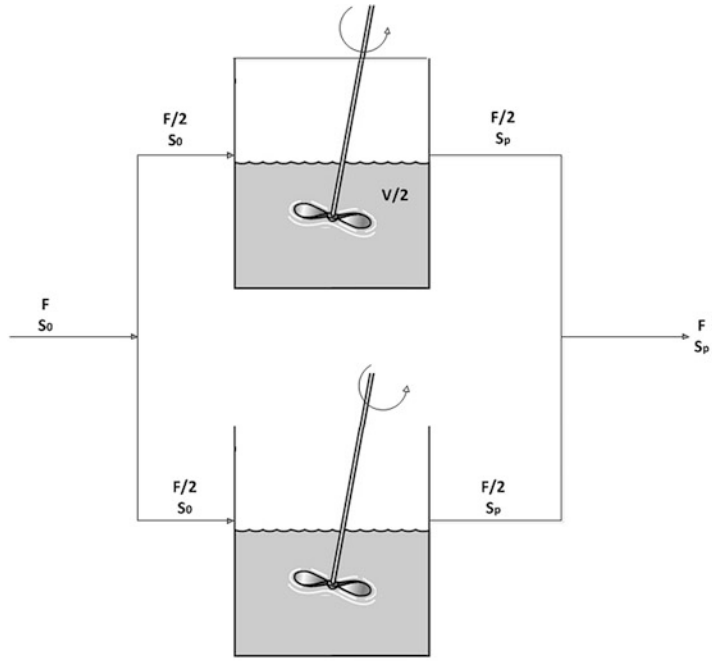


**Fig. 8.5** Continuous stirred-tank reactor (CSTR)

why? (d) How would you compare the best arrangement between (a) and (b) with the previous problem (warm-up example 6)?

**Solution**

(a) First, we will create a schematic representation for two bioreactors ($V/2$ each) operating in parallel (Fig. 8.5):

**Mass balance for substrate in each bioreactor**

*Bioreactor $B_1$*

$$\frac{F}{2}S_0 - \frac{F}{2}S_P - \frac{V}{2}kS_P = 0 \tag{8.21}$$

*Bioreactor $B_2$*

$$\frac{F}{2}S_0 - \frac{F}{2}S_P - \frac{V}{2}kS_P = 0 \tag{8.22}$$

Then in both bioreactors we get the same output concentration as follows: $S_P = \frac{FS_0}{F+Vk}$; the same answer as in the previous problem (one bioreactor of volume $V$).

(b) First, we will create a schematic representation for two bioreactors ($V/2$ each) operating in series (Fig. 8.6):

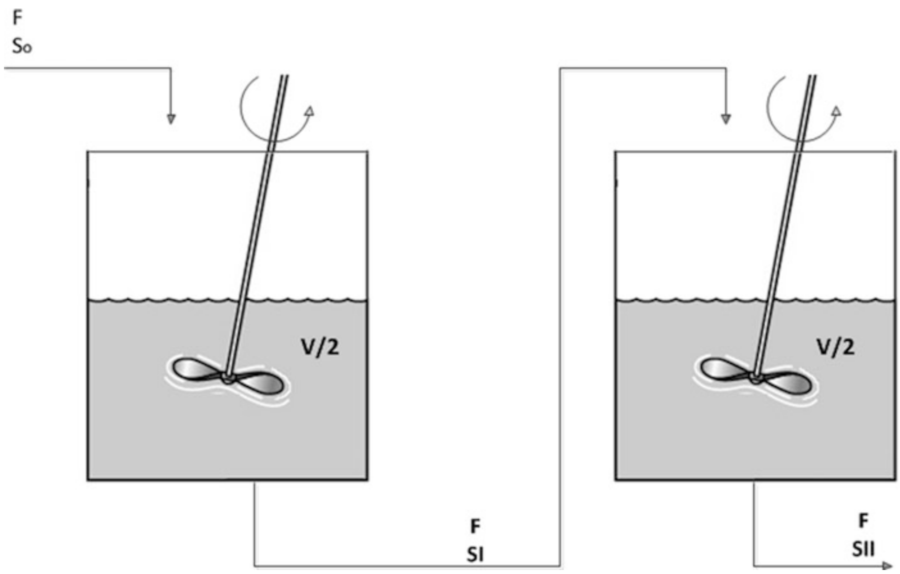


**Fig. 8.6** Two continuous stirred-tank reactors operated in series

*Bioreactor* $B_1$

$$FS_0 - FS_{\mathrm{I}} - \frac{V}{2}kS_{\mathrm{I}} = 0 \tag{8.23}$$

Then

$$S_{\mathrm{I}} = \frac{FS_0}{F + \frac{V}{2}k}. \tag{8.24}$$

*Bioreactor* $B_2$

$$FS_I - FS_{\mathrm{II}} - \frac{V}{2}kS_{\mathrm{II}} = 0. \tag{8.25}$$

Then, substituting (8.24) in (8.25) and rearranging we get

$$S_{\mathrm{II}} = \frac{F^2S_0}{\left[F + \frac{V}{2}k\right]^2}. \tag{8.26}$$

(c) Given that the object is to maximize the disappearance of the substrate, we need to compare $S_{\mathrm{P}}$ with $S_{\mathrm{II}}$ and see which of these two concentrations is lower.

We rewrite $S_{\mathrm{P}}$ as follows:

$$S_{\mathrm{P}} = \frac{F^2S_0}{F[F + Vk]}. \tag{8.27}$$

Now, compare $S_P$ with $S_{II}$ to see which of the two has a larger denominator.

Denominator of $S_P$

$$F[F+Vk]=F^2+FVk. \tag{8.28}$$

Denominator of $S_{II}$

$$\left[F+\frac{V}{2}k\right]^2=F^2+F\frac{V}{2}K+F\frac{V}{2}K+\left(\frac{V}{2}k\right)^2=F^2+FVk+\left(\frac{V}{2}k\right)^2. \tag{8.29}$$

Given that all parameters are greater than 0 and the denominator of $S_{II}$ has an additional term, $S_{II}$ is less than $S_P$.

The recommendation is to use two bioreactors in series.

(d) Two reactors of volume $V/2$ each in series is better than two reactors in parallel and better than one bioreactor of volume $V$.

**Corollary** *In warm-up examples 4 and 5 (chemical reactors), we had information about stoichiometry and conversion, and the proposed procedure was to construct a table to take into account the moles entering the reactor, moles reacting, and the moles leaving the reactors (reagents and products). This is a convenient procedure and facilitates the material balance in the reactor. On the other hand, in the bioreactor problems, we had information about the disappearance of the substrate (kinetics), and in that case it was easier just to formulate the mass balance like (8.6).*

To keep the subject as simple as possible, we have intentionally avoided kinetics. Our aim has been to teach you just a few concepts and keep challenging you; in addition, we have been using this simple, but hopefully effective, learning strategy to familiarize you with chemical and bioprocess engineering.

To further familiarize you with chemical reactors and bioreactors and to solve problems with the strategy proposed, analyzed, and revised in Chap. 7, in the next section (Sect. 8.5) we will solve three more problems of chemical processes and bioprocesses.

## 8.5 Formulating and Solving Material Balance Equations in Reactive Systems (Steady-State and Continuous Operation)

In Chap. 7, Sect. 7.8 ("Designing and structuring a general procedure to formulate and solve material balance problems"), we developed a detailed explanation of a general strategy for solving material balance problems for nonreactive systems. Here, we will use strictly the same strategy, although we need to take into account some particularities of the reactive systems. First, it is highly advisable to analyze the material balance with moles instead of mass. Second, we will have additional unknowns, for example, the reaction stoichiometry, reaction conversion, and molecular weights of the compounds. These new variables should be considered when doing an analysis of the degrees of freedom. Conceptually, the analysis of the degrees of freedom is the same, with the only consideration that it will be appropriate to take into account new types of variable (e.g., stoichiometry, reaction conversion).

Section 8.6 is dedicated to putting into practice the strategy developed in Chap. 7 (for details please return to Sect. 7.8.2.1 on the procedure description and analysis) but now applied to material balance for reactive systems.

## 8.6 Solved Problems

1. **Reactor with recycle [4]**. The system depicted in Fig. 8.7 shows a simplified scheme of a reactor-separator system that includes a recycle stream. Compounds A and B are fed to the reactor to produce compound C according to the following stoichiometric reaction:

$$A + B \rightarrow C,$$

where the molecular weights of compounds A and B are 30 and 20 [g/mol], respectively.
The system was designed to produce 1,000 [kg/h] of compound C. According to the experimental data, recorded at the laboratory, the reaction has a conversion of 60 % and the molar fraction of compound A in the feed stream of the reactor is 0.4. In addition, output stream 3 only contains compound C, and stream 4 (the recycle stream) only contains compounds A and B. (a) What is the molar composition of the fresh stream (1)? (b) What is the molar composition of the recycle stream?

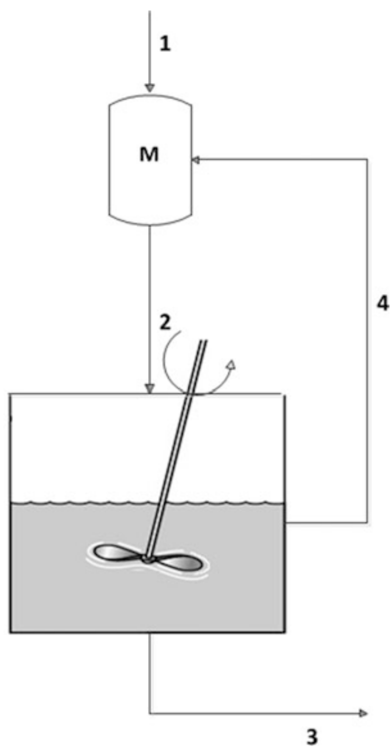


**Fig. 8.7** Reactor with recycle

**Solution**

**Step I**

**Reading and understanding**

As was mentioned, we will follow the same strategy that was developed for material balance for nonreactive systems. Some slight differences are that here we will use moles instead of mass, and the material balance through the reactor will be done developing the table that was presented in warm-up example 4.

**Step II**

**Flow diagram, variable definition and codification, and inclusion of all available data**

Figure 8.8 includes all the information given in the problem statement.

$F_1$: Molar flow rate of feed stream to system [kg mol/h]
$X_{A1}$: Molar fraction of compound A in feed stream
$F_2$: Molar flow rate of feed stream to reactor [kg mol/h]
$X_{A2}$: Molar fraction of compound A in feed stream to reactor
$F_3$: Molar flow rate of output stream of system [kg mol/h]
$F_4$: Molar flow rate of recycle stream [kg mol/h]
$X_{A4}$: Molar fraction of compound A in recycle stream
$\chi_R$: Conversion of reaction

Thus, the total number of variables is 8 (NV = 8).

**STEP III**

**Analysis of degrees of freedom in process**

As depicted in Fig. 8.8, we can carry out a material balance for the mixture of the fresh stream and the recycle stream (two material balances) and three material balances on the reactor. Thus,

$$\text{NMB} = 5.$$

In addition, we have three specified variables, the output stream (1,000 [kg/h]), the conversion of the reaction (60 %), and the molar fraction of compound A in the feed stream to the reactor ($X_{A2} = 0.4$). Thus,

$$\text{NSV} = 3.$$

Therefore, given that NR = 0, the degrees of freedom of the system are

$$\text{DF} = \text{NV} - (\text{NMB} + \text{NSV} + \text{NR}) = 8 - (5 + 3 + 0). \text{ Thus, DF} = 0.$$

Now the problem can be quantitatively formulated and solved.

**STEPS IV and V**

**Mathematical formulation, including all available data and solution, results, analysis, and discussion**

First, to express $F_3$ as a molar rate, we need to calculate the molecular weight of compound C. According to the stoichiometry, 1 [mol] of A (30 [g]) plus 1 [mol] of B (20 [g]) generates 1 [mol] of C (which should be 50 [g] of C). Given that

$$\text{Moles} = \text{Mass/MW, 1 [mol] of C} = \text{50 [g] of C/MW}_C\text{; MW}_C = 50 \text{ [g/mol]} = 50 \text{ [kg/kg mol]},$$
$$F_3 = 1{,}000 \text{ [kg/h]}/50 \text{ [kg/kg mol]} = 20 \text{ [kg mol/h]}.$$

Material balance for reactor ($R$)

Before creating a table, we need to determine which compound is limiting the reaction. Given that the stoichiometry establishes that for 1 [mol] of A, 1 [mol] of B is necessary, and considering that the molar fraction of A in the feeding stream of the reactor is 0.4, A is the limiting reagent.

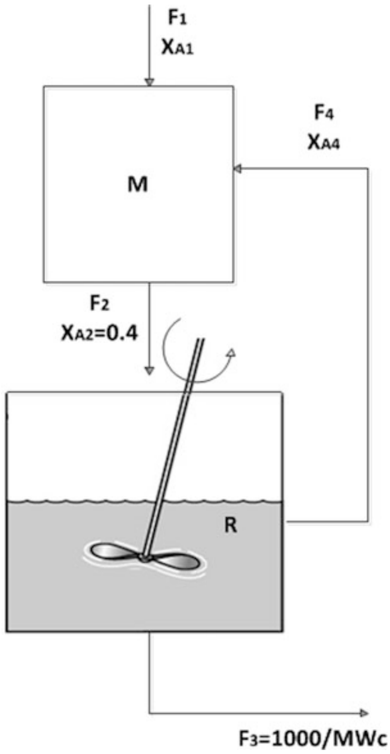


**Fig. 8.8** Reactor with recycle including all variables and available data

First, remember that the conversion of the reaction is 60 % (0.6 fractional conversion). In addition, the output of C is 20 [kg mol/h]. Thus, from Table 8.6,

$$F_2 = 83 \text{ [kg mol/h]}.$$

Now completing Table 8.6, we get the following table.

From Table 8.7, we can infer that $F_4 = 43$ [kg mol/h] and

$$X_{A4} = 13.34/43.34 = 0.31.$$

Material balance for fresh stream and recycle (*M*)

Mole balance for compound A:

$X_{A1} \times F_1 + X_{A4} \times F_4 - X_{A2} \times F_2 = 0$, substituting the available data:

$$X_{A1} \times F_1 + 0.31 \times 43 - 0.4 \times 83 = 0 \tag{8.30}$$

Total mole balance:

$F_1 + F_4 - F_2 = 0$, substituting the available data:

$F_1 + 43 - 83 = 0$, then $F_1 = 40$ [kg mol/h], and substituting $F_1$ in (8.30), we get $X_{A1} = 0.50$.

(a) $X_{A1} = 0.50$, so the molar fraction of B is also 0.50.

(b) $X_{A4} = 0.31$, so the molar fraction of B is 0.69 (1 − 0.31).

As shown in this example, the procedure developed in Chap. 7 can be fully utilized for material balances for reactive systems.

**Table 8.6** Simulation of the reaction of compounds A and B

| Compound | Input [kg mol/h] | Reaction [kg mol/h] | Output [kg mol/h] |
|---|---|---|---|
| A | $0.4F_2$ | $0.6(0.4F_2)$ | $0.16F_2$ |
| B | $0.6F_2$ | $0.6(0.4F_2)$ | $0.36F_2$ |
| C | | | $0.6(0.4F_2) = 20$ |

**Table 8.7** Completed data for the reaction of compounds A and B

| Compound | Input [kg mol/h] | Reaction [kg mol/h] | Output [kg mol/h] |
|---|---|---|---|
| A | 33 | 20 | 13 |
| B | 50 | 20 | 30 |
| C | | | 20 |

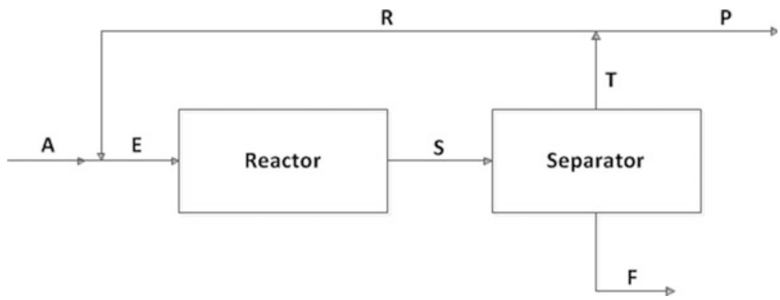


**Fig. 8.9** Process for formaldehyde production

**Table 8.8** The weight-by-weight composition at the output of the reactor (stream S)

| Compound | % w/w |
|---|---|
| $CH_3OH$ | 25 |
| $O_2$ | 14 |
| $CH_2O$ | 23 |
| $H_2O$ | 38 |

**Table 8.9** The weight-by-weight composition in stream F

| Compound | % w/w |
|---|---|
| $CH_3OH$ | 4.6 |
| $CH_2O$ | 24.4 |
| $H_2O$ | 71.0 |

2. **Formaldehyde production [8]**. Formaldehyde ($CH_2O$) can be obtained through the reaction of methanol ($CH_3OH$) and oxygen ($O_2$) according to

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O$$

The reaction has a conversion of 40 %, oxygen is fed in excess, and the process scheme is presented in Fig. 8.9.

The weight-by-weight composition at the output of the reactor (stream S) is as follows (Table 8.8).

In addition, the weight-by-weight composition in stream F is as follows (Table 8.9).

205 [lb/h] of $O_2$ are leaving the purge (*P*) and represent 28 % w/w of this stream. Finally, the ratio of streams R and P is 2:1. (a) What is the molar composition of the input stream to the reactor (E)? (b) What is the mass flow rate of the fresh stream A?

**Solution**

**Step I**

**Reading and understanding**

As usual for reactive systems, at least the material balance will be carried out on a molar basis. In addition, it is necessary to determine whether the reaction is balanced and obtain the molecular weights for methanol ($CH_3OH$), oxygen ($O_2$), formaldehyde ($CH_2O$), and water ($H_2O$):

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O.$$

The reaction is balanced because there are two carbon atoms for each side of the equation, eight atoms of hydrogen per side and four atoms of oxygen per side. In addition, the molecular weights of the compounds are as follows:

$MW_{Me} = 32$ [g/mol] or [lb/lb mol]
$MW_{O_2} = 32(g/mol)$
$MW_F = 30$ [g/mol]
$MW_W = 18$ [g/mol]

**Step II**

**Flow diagram, variable definition and codification, and inclusion of all available data**

$F_A$: Mass flow rate of feed stream to system [lb/h]
$X_{A\text{-}Me}$: Mass fraction of methanol in feed stream
$X_{A\text{-}O2}$: Mass fraction of oxygen in feed stream
$X_{A\text{-}F}$: Mass fraction of formaldehyde in feed stream
$F_E$: Mass flow rate of E stream [lb/h]
$X_{E\text{-}Me}$: Mass fraction of methanol in stream E
$X_{E\text{-}O2}$: Mass fraction of oxygen in stream E
$X_{E\text{-}F}$: Mass fraction of formaldehyde in E stream
$F_S$: Mass flow rate of output stream of reactor [lb/h]
$X_{S\text{-}Me}$: Mass fraction of methanol in output stream of reactor
$X_{S\text{-}O2}$: Mass fraction of oxygen in output stream of reactor
$X_{S\text{-}F}$: Mass fraction of formaldehyde in output stream of reactor
$F_F$: Mass flow rate output of system [lb/h]
$X_{F\text{-}Me}$: Mass fraction of methanol in stream F
$X_{F\text{-}F}$: Mass fraction of formaldehyde in stream F
$F_T$: Mass flow rate output of separator [lb/h]
$X_{T\text{-}Me}$: Mass fraction of methanol in output stream of separator
$X_{T\text{-}O2}$: Mass fraction of oxygen in output stream of separator
$X_{T\text{-}F}$: Mass fraction of formaldehyde in output stream of separator
$F_R$: Mass flow rate of recycle stream [lb/h]
~~$X_{R\text{-}Me}$: Mass fraction of methanol in output stream of the separator~~
~~$X_{R\text{-}O2}$: Mass fraction of oxygen in output stream of the separator~~
~~$X_{R\text{-}F}$: Mass fraction of formaldehyde in output stream of the separator~~
$F_P$: Mass flow rate of purge stream [lb/h]
~~$X_{P\text{-}Me}$: Mass fraction of methanol in output stream of the separator~~
~~$X_{P\text{-}O2}$: Mass fraction of oxygen in output stream of the separator~~
~~$X_{P\text{-}F}$: Mass fraction of formaldehyde in output stream of the separator~~
$\chi_R$: Fractional conversion of reaction

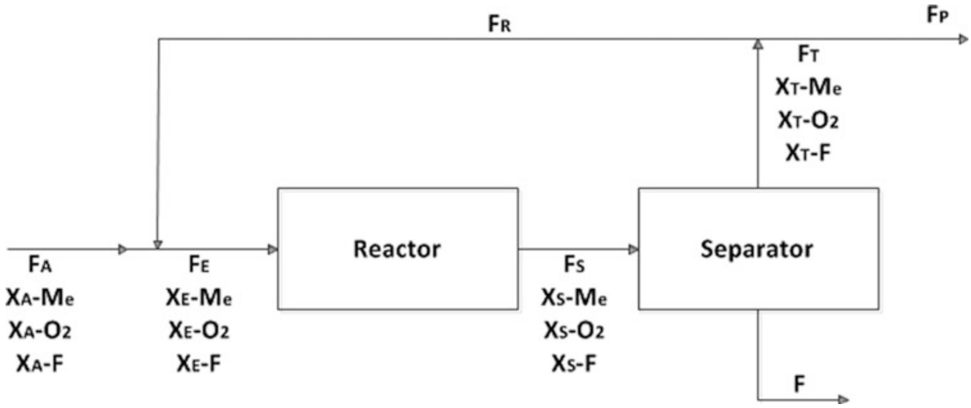


**Fig. 8.10** Process for formaldehyde production including all variables

$X_{\text{R-Me}}$, $X_{\text{P-Me}}$, $X_{\text{R-O2}}$, $X_{\text{P-O2}}$, $X_{\text{R-F}}$, and $X_{\text{P-F}}$ will not be considered variables because they are equal to $X_{\text{T-ME}}$, $X_{\text{T-O2}}$, and $X_{\text{T-F}}$, respectively. Streams R and P derive from a division of stream T, so they have exactly the same composition as stream T.

Thus, the total number of variables is 22 (NV = 22).

**STEP III**

**Analysis of degrees of freedom in process**

As depicted in Fig. 8.10, we can carry out four material balances for the mixture of the fresh stream (A) and the recycle stream (S), four material balances on the reactor, four material balances on the separator, and one material balance in the division of stream T.

$$\text{NMB} = 13.$$

We have six specified variables ($X_{\text{S-Me}}$, $X_{\text{S-O2}}$, $X_{\text{S-F}}$, $X_{\text{F-Me}}$, $X_{\text{F-F}}$, and $\chi_{\text{R}}$). In addition, although indirectly, we have information to calculate that $F_{\text{P}}$ and $X_{\text{T-O2}}$ from *205 [lb/h] of $O_2$ leaving the purge (P) and represent 28 % w/w of this stream*. Therefore,

$$\text{NSV} = 8.$$

Finally, NR = 1 ($F_{\text{R}}$:$F_{\text{P}}$ = 2:1), so the degrees of freedom of the system are

$$\text{DF} = \text{NV} - (\text{NMB} + \text{NSV} + \text{NR}) = 22 - (13 + 8 + 1).\ \textit{Thus},\ \text{DF} = 0.$$

The problem can now be quantitatively formulated and solved.

**STEPS IV and V**

**Mathematical formulation, including all available data and solution, results, analysis, and discussion**

First, we calculate that $F_{\text{P}}$ (purge) from *205 [lb/h] of $O_2$ are leaving the purge (P) and represent 28 % w/w of this stream*. Thus, we can formulate the following equations:

$$X_{\text{P-O2}} \times F_{\text{P}} = 205,\ \text{and because}\ X_{\text{P-O2}} = 0.28,$$
$$F_{\text{P}} = 7.32 \times 10^2\ [\text{lb/h}].$$

Global mass balance in division

$$F_{\text{T}} - F_{\text{P}} - F_{\text{R}} = 0\ \text{and}\ F_{\text{R}}:F_{\text{P}} = 2:1$$

**Table 8.10** Calculation of the flow rate (lb mol/h) per each compound at the output of the reactor (stream S)

| Compound | % w/w | Mass per 100 [lb] | lb mol per compound (100 [lb]) | Molar fraction [%] | lb mol/h per compound at the output stream S |
|---|---|---|---|---|---|
| $CH_3OH$ | 25 | 25 | 25/32 = 0.78 | 19.1 | 34.3 |
| $O_2$ | 14 | 14 | 14/32 = 0.44 | 10.7 | 19.2 |
| $CH_2O$ | 23 | 23 | 23/30 = 0.77 | 18.7 | 33.6 |
| H2O | 38 | 38 | 38/18 = 2.1 | 51.5 | 92.4 |

**Table 8.11** Simulation of the reaction of methanol ($CH_3OH$) and $O_2$

| Compound | Input [lb mol/h] (stream E) | Reaction [lb mol/h] | Output [lb mol/h] (stream S) |
|---|---|---|---|
| Methanol | $2x$ | $0.4(2x)$ | 34.3 |
| Oxygen | $x + y$ | $0.4x$ | 19.2 |
| Formaldehyde | $z$ | – | $z + 0.4(2x) = 33.6$ |
| Water | $u$ | – | $u + 0.4(2x) = 92.4$ |

**Table 8.12** Completion of Table 8.11 adding the output mass per compound

| Compound | Input [lb mol/h and lb/h] (stream E) | Reaction [lb mol/h] | Output [lb mol/h and lb/h] (stream S) |
|---|---|---|---|
| Methanol | 57.2 (1,830.4) | 22.9 | 34.3 (1,097.6) |
| Oxygen | 30.64 (980.48) | 11.45 | 19.2 (614.1) |
| Formaldehyde | 10.72 (321.6) | – | 33.62 (1,008.6) |
| Water | 69.5 (1,251) | – | 92.4 (1,663.2) |
| Total | (4,383.5) | | (4,383.5) |

Replacing $F_P$ we obtain $F_T = 2.196 \times 10^3$ [lb/h] and $F_R = 1.464 \times 10^3$ [lb/h].

Then the pound-moles per hour of oxygen in stream T are

$0.28 \times 2.196 \times 10^3$ [lb/h]/32 [lb/lb mol] = 19.2 [lb mol/h], which is the same as the pound-moles per hour of oxygen in stream S because there is no oxygen in stream $F_F$.

With this information and the data given in Table 8.9, we will be able to determine the molar composition at the output of the reactor and from there to calculate the pound-moles per hour of all components because we know the pound-moles per hour of oxygen (Table 8.10).

Material balance for reactor

$$2CH_3OH + O_2 \rightarrow 2CH_2O + 2H_2O$$

The fractional conversion is $\chi_R = 0.4$ (40 %), and oxygen is in excess (methanol is the limiting reagent). Therefore, we can create the following table for the material balance on the reactor:

Thus,

$$x = 28.6 \text{ [lb mol/h]; therefore } y = 2.04 \text{ [lb mol/h] (from } x + y - 0.4x = 19.2);$$
$$z = 10.72 \text{ [lb mol/h]; and } u = 69.5 \text{ [lb mol/h].}$$

Finally, Table 8.11 can be completed, adding the output mass per compound (Table 8.12):

One interesting thing to notice in the table is that the total mass was conserved, as it should be.

(a) What is the molar composition of the input stream to the reactor (E)? (Table 8.13)

**Table 8.13** Molar composition of the input stream to the reactor

| Compound | Input [lb mol/h] (stream E) | Molar composition [%] (stream E) |
|---|---|---|
| Methanol | 57.2 | 34.0 |
| Oxygen | 30.64 | 18.2 |
| Formaldehyde | 10.72 | 6.4 |
| Water | 69.5 | 41.4 |
| Total | 168.06 | 100 |

**Table 8.14** The weight-by-weight composition of the fresh stream A

| Compound | Mass [lb/h] | w/w [%] |
|---|---|---|
| Methanol | 1,165.7 | 39.90 |
| Oxygen | 570.5 | 19.60 |
| Formaldehyde | 5.4 | 0.18 |
| Water | 1,177.6 | 40.32 |
| Total | 2,919.2 | 100 |

(b) What is the mass flow rate of the fresh stream A ($F_A$)?

Global mass balance in separator:

$$F_S - F_T - F_F = 0, \text{ so substituting the available data yields}$$
$$4{,}383.5 - 2{,}196.44 - F_F = 0, \text{ then } F_F = 2{,}187.06 \text{ [lb/h]}$$

Global mass balance for whole system:

$$F_A - F_P - F_F = 0$$
$$F_A - 732.143 - 2{,}187.06 = 0, \text{ so } F_A = 2{,}919.2 \text{ [lb/h].}$$

Furthermore, if you carry additional mass balances, you can check that the w/w composition of the fresh stream A is as follows (Table 8.14):

Analysis

First, with this problem, our experience has been that the procedure developed in Chap. 7 can be directly applied to material balances for reactive systems. Second, as has been continuously stressed, it is very critical to follow the proposed procedure and work patiently and strictly follow the given order, which might get boring sometimes, but in problems with many variables it is worthwhile and rewarding to do just that. In addition, it is also important to identify, define, and correctly codify all the variables.

3. **Continuous steady-state bioreactors [6]**. In warm-up example 7, we discovered that for this specific example, it was a better option to arrange two bioreactors of volume $V/2$ in series instead of one bioreactor of volume $V$. A company interested in your skills wants to design a system of bioreactors with a total volume of 500 [L] and get an output substrate concentration lower than 31 [g/L].

First, you ask for technical data to do some calculations, and finally give your recommendation on how to set up the bioreactors.

Technical data

$$F = 100 \text{ [L/h]};\ S_0 = 50 \text{ [g/L]};\ k = 0.1 \text{ [1/h]};\ V = 500 \text{ [L]}$$

To figure out what to expect, first you start calculating the output concentration of the substrate for one bioreactor with a volume of 500 [L] and obtain

$$S = \frac{FS_0}{F + Vk} = \frac{100 \times 50}{100 + 500 \times 0.1} = 33(\mathrm{g/L}).$$

Now you think that by putting two bioreactors with a volume equal to 250 [L] in series, you will get an output concentration lower than 31 [g/L]. Unfortunately, you get

$S_{\mathrm{II}} = \frac{F^2 S_0}{\left[F + \frac{V}{2}k\right]^2} = \frac{100^2 \times 50}{\left(100 + \frac{500}{2} \times 0.1\right)^2} = 32(\mathrm{g/L})$, which is greater than 31 [g/L].

How many bioreactors with a total volume of 500 [L] should you put in series to get the desired output concentration of 31 [g/L] or less?

**Solution**

**Step I**

**Reading and understanding**

From warm-up exercise 7 and the results presented in the problem 3 statement, we can infer that if we arranged more bioreactors in series (say 3, 4, ...) we would lower the output concentration of the substrate, but the question is by how much? To avoid trial and error, we will try to find a general formula to relate the output concentration of the substrate ($S$) to the number of bioreactors arranged in series ($n$).

**Step II**

**Flow diagram, variable definition and codification, and inclusion of all available data**

From previous calculations we know the following:

1. Bioreactor of volume $V$:

$$S_{\mathrm{I}} = \frac{FS_0}{F + Vk}.$$

2. Bioreactors of volume $V/2$ each (Fig. 8.11):

$$S_{\mathrm{II}} = \frac{F^2 S_0}{\left[F + \frac{V}{2}k\right]^2}.$$

**STEPS IV and V**

**Mathematical formulation, including all available data and solution, results, analysis, and discussion**

Now we will deduce a formula for three bioreactors in series as follows:

First bioreactor:

$$FS_0 - FS_{\mathrm{I}} - \frac{V}{3}kS_{\mathrm{I}} = 0; \text{solving for} S_{\mathrm{I}} \text{we obtain } S_{\mathrm{I}} = \frac{FS_0}{F + \frac{V}{3}k}. \quad (8.31)$$

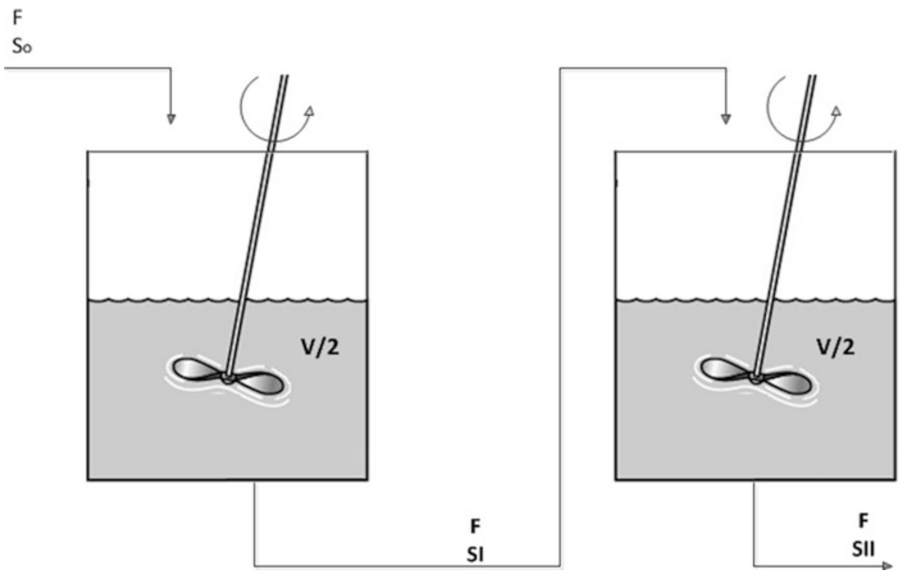


**Fig. 8.11** Two bioreactors in series including all variables

Second bioreactor:

$$FS_{\mathrm{I}} - FS_{\mathrm{II}} - \frac{\mathrm{V}}{3} kS_{\mathrm{II}} = 0. \tag{8.32}$$

Substituting (8.31) in (8.32) and solving for $S_{\mathrm{II}}$, we get

$$S_{\mathrm{II}} = \frac{F^2 S_0}{\left[F + \frac{V}{3} k\right]^2}. \tag{8.33}$$

Third bioreactor:

$$FS_{\mathrm{II}} - FS_{\mathrm{III}} - \frac{\mathrm{V}}{3} kS_{\mathrm{III}} = 0. \tag{8.34}$$

Substituting (8.33) in (8.34) and solving for $S_{\mathrm{III}}$, we get

$$S_{\mathrm{III}} = \frac{F^3 S_0}{\left[F + \frac{V}{3} k\right]^3}. \tag{8.35}$$

Finally, by induction, we can write an equation for $n$ bioreactors of volume $V/n$ each in series:

$$S_n = \frac{F^n S_0}{\left[F + \frac{V}{n} k\right]^n}.$$

According to this formula we get the following output substrate concentration:

| Number of bioreactors | Output substrate concentration (g/L) |
|---|---|
| 1 | 33.3 |
| 2 | 32.0 |
| 3 | 31.5 |
| 4 | 31.2 |
| 5 | 31.04 |
| **6** | **30.93** |
| 7 | 30.85 |
| 8 | 30.78 |

Analysis

Then, to reach a substrate concentration lower than 31 [g/L], we need to arrange six bioreactors of volume 83.34 [L] each in series. Another alternative, possibly better, is to use just one bioreactor, but of a larger volume ($V > 500$ [L]). Please check that using one bioreactor of volume 615 [L], the output concentration of the substrate is lower than 31 [g/L].

## 8.7 Proposed Problems

1. **Carbon composition [2]**. Determine the carbon composition (w/w) in: (a) acetylene, (b) propane, (c) carbon dioxide, (d) carbon monoxide, and (e) ethanol.
   **A**: (a) 92.3 %, (b) 81.8 %, (c) 27.3 %, (d) 42.86 %, and (e) 52.1 %.
2. **Limiting reactant [3]**. A reactor is fed with a stream that contains compounds A, B, and C whose molecular weights are 30, 60, and 20, respectively. The reactor was fed with 30 [kg] of A, 40 [kg] of B, and 15 [kg] of C. The reaction is as follows:

$$A + 0.75B + 1.5C \rightarrow 3D.$$

   (a) What is the limiting reactant? (b) What is the molecular weight of *D*?
   **A**: (a) C. (b) $MW_D = 35$
3. **Stoichiometry [4]**. In a chemistry lab, the technician has the following amount of compounds A, B, and C whose molecular weights are presented in the following table:

| | Amount | Molecular weight |
|---|---|---|
| A | 1.2 [L] ($\rho = 1.4$ [kg/L]) | 25 |
| B | 0.8 [lb] | 40 |
| C | 950 [g] | 18 |

   The reaction is equilibrated according to the following equation:

$$aA + bB + cC \rightarrow dD,$$

   where $a + b + c = 6$, and the feed is stoichiometric.
   (a) How many moles are fed of each compound? (b) What are the numerical values of a, b, and c?
   **A**: (a) 67.2 [mol] of A, 9.08 [mol] of B and 52.8 [mol] of C (b) $a = 3.124$; $b = 0.422$ and $c = 2.454$

4. **Limiting reactant 2 [3]**. To obtain 100 [g] of product C ($MW_C = 28$), 300 [g] of compound A ($MW_A = 30$) and 500 [g] of compound B ($MW_B = 27$) are reacted according to the following reaction:

$$A + 2B \rightarrow 3C.$$

(a) What is the limiting reactant? (b) What is the conversion of the reaction?
**A**: (a) B. (b) 12.86 %.

5. **Methane [3]**. 160 [kg] of $CH_4$ and 180 [kg] of water are fed to a reactor. If the conversion of the reaction is 60 %, calculate how many kilograms of CO and $H_2$ are produced respectively?
**A**: CO: 168 [kg]; $H_2$: 36 [kg].

6. **Limestone [4]**. A limestone is composed of 85.3 % calcium carbonate ($CaCO_3$). How much limestone was used if, when reacting with hydrogen chloride (HCl) in excess, 10 [L] of carbon dioxide ($CO_2$) at 18 °C and 752 mmHg was obtained?
**A**: 48.66 [g] of limestone.

7. **Combustion [5]**. To realize a propane–oxygen combustion, we have 2 [L] of propane at 12 °C and 740 mmHg. The combustion will be carried out at 23 °C and 750 mmHg. (a) How much oxygen is needed (volume)? (b) How much air is needed if the oxygen is in 10 % excess?
**A**: (a) 10.25 [L] of oxygen at 23 °C and 750 mmHg, (b) 2.184 [g mol] of air.

8. **Methane and ethane [7]**. To burn a fuel that has 60 % methane ($CH_4$) and 40 % ethane ($C_2H_6$), air is fed with 50 % molar in excess. If the compounds are totally burned to form $CO_2$ and CO, and, in addition, 10 % of $CH_4$ and 15 % $C_2H_6$ are burned to form CO, then: (a) What is the output w/w composition of the gases? (b) How much $CH_4$ and $C_2H_6$ should be fed to produce 100 [kg/h] of $CO_2$? Consider that air is 20 % $O_2$ and 80 % $N_2$ (molar).
**A**: (a) $O_2$: 7.8 %; $CO_2$: 9.06 %; CO: 0.84 %; $N_2$: 82.3 %. (b) $CH_4$: 27.54 [kg] and $C_2H_6$: 18.36 [kg].

9. **Parallel reactions [8]**. 30 [$cm^3$] of a mixture of ethane and acetylene and 120 [$cm^3$] of oxygen are filled in a graduated test tube. The mixture is burned, and then the water vapor is condensed to go back to the initial conditions. The residue is formed by 81 [$cm^3$] of $CO_2$ and oxygen that was added in excess. Calculate the composition of the ethane–acetylene mixture.

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$
$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

**A**: 24 [$cm^3$] ethane and 6 [$cm^3$] of acetylene

10. **Acetylene [4]**. Acetylene is a gas that is obtained treating calcium carbide ($CaC_2$) with water according to the following reaction:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2.$$

Calculate the number of hours that an acetylene lamp works that consumes 40 [L] of gas per hour at 80 °F and 740 mmHg if we have 1 [kg] of calcium carbide?
**A**: 9.86 h (9 h 51 min 36 s).

11. **Acetylene-2 [4]**. You have 4 [L] of water and 10 [kg] of a product that contains 80 % (w/w) of $CaC_2$. If the conversion of the reaction is 100 %, calculate or determine: (a) What is the limiting reactant? (b) What is the mass of the acetylene that is produced? (c) What is the residual mass of the product?
**A**: (a) Water. (b) 2,888.8 [g] acetylene. (c) 2,888.8 [g] (2 [kg] + 0.888 [kg] of $CaC_2$).

12. **Reactors in series [6]**. A stream containing 30 [kg mol] of A, 100 [kg mol] of B, and 3 [kg mol] of C is fed to the first reactor. Then the output stream is cooled down (113 [kg mol]) and fed to the second reactor, where the output of the second reactor is a total of 103 [kg mol]. In each reactor the following stoichiometric reaction takes place:

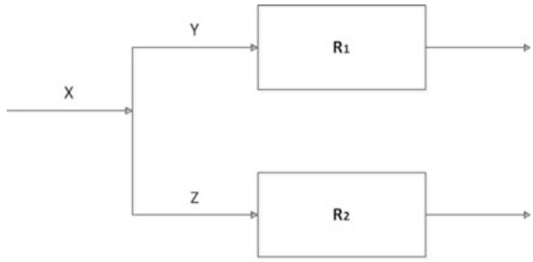


**Fig. 8.12** Two reactors operated in parallel

$$A + 3B \rightarrow 2C$$

Determine: (a) the conversion of the reaction in each reactor and (b) the composition of the output flow in each reactor.
**A**: (a) 33.3 % and 25 %, respectively;
(b)

| | First reactor | | Second reactor | |
|---|---|---|---|---|
| | Output moles | Composition (%) | Output moles | Composition (%) |
| A | 20 | 17.7 | 15 | 14.6 |
| B | 70 | 61.9 | 55 | 53.4 |
| C | 23 | 20.4 | 33 | 32 |
| Total | 113 | 100 | 103 | 100 |

13. **Haber–Bosch synthesis [4]**. The reaction known as the Haber–Bosch synthesis (Chap. 4) is the reaction of nitrogen ($N_2$) and hydrogen ($H_2$) to form ammonia ($NH_3$). A stream of 10 [$m^3$/h] $H_2$ at 2 [atm] and 20 °C will react with a stream of air (79 % $N_2$). The $N_2$ is 30 % in excess and the conversion of the reaction is 16 %. Determine the volumetric composition of the outlet stream.
**A**: $N_2$ 26.36 %, $H_2$ 58.26 %, $NH_3$ 7.40 %, $O_2$ 7.98 %.
14. **Contaminant [7]**. A reactor is charged with 1,000 [ton] of A (solid) and is continuously fed with a liquid stream of 1 [ton/h] of B with 10 % w/w of contaminant D.

$$2A + 5B \rightarrow 40C$$
$$A + D \rightarrow 24E + 2C \text{ (both reactions have 100 \% conversion)}$$

The products of the reactions are gases, and it is desirable to remove 90 % of the contaminating E from this stream, so an adsorption tower will be installed to remove contaminant E. The tower can withdraw 0.05 [kg] E/kg of adsorbent. (a) What is the molecular weight of E? (b) Calculate the load of adsorbent (kg) required if the adsorbent must be regenerated every three reactor loads.

DATA: $MW_A = 150$; $MW_B = 60$; $MW_C = 15$; $MW_D = 24$
**A**: (a) $MW_E = 6$, (b) 21,245.85 [ton].
15. **Reactors in parallel [6]**. Reactors $R_1$ and $R_2$ are operated in parallel, as depicted in Fig. 8.12, and the reaction is as follows:

$$2A + 3B \rightarrow C.$$

The *X* stream has a mass flow rate of 1,000 [kg/h] with 50 % molar A. If stream *X* contains A and B and the total amount of C produced is 675 [kg/h], then: (a) What is the molecular weight of C?

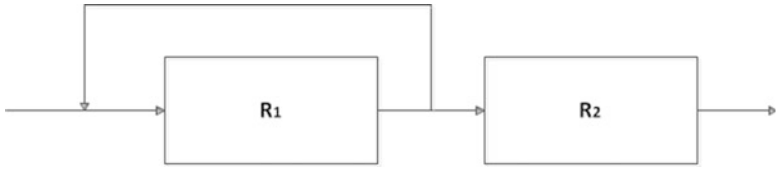


**Fig. 8.13** Two reactors operated in series for a process synthesis

(b) Calculate the mass flow rate of streams $Y$ and $Z$. (c) What is the molar composition at the output of each reactor? (d) What is the limiting reactant?

DATA: $MW_A = 30$; $MW_B = 40$; conversion of reaction in $R_1 = 80$ %; conversion of reaction in $R_2 = 100$ %

**A**: (a) $MW_C = 180$

(b) $Y = 500$ [kg/h] and $Z = 500$ [kg/h]

(c)

| Compound | Reactor $R_1$ | Reactor $R_2$ |
|---|---|---|
| A | 30 % | 66.67 % |
| B | 10 % | – |
| C | 60 % | 33.33 % |

(d) In both reactors, the limiting reactant is $B$.

16. **Fermentation [7]**. A continuous pilot fermenter is fed with a mixture of glucose and xylose as a substrate. The microorganism *S. stipitis* consumes both sugars. Given that the pilot fermenter does not have good instruments to determine how much sugar is being consumed, the operators have been doing some simple measurements. They have determined that in 1 h 50 min, a gas tank of 20 [L] is completely filled with the $CO_2$ released from the reaction (at 32 °C and 1.02 [atm]). Furthermore, literature information indicates that the feed stream has a ratio xylose:glucose of 9:1. Determine how much sugar (weight) is transformed into alcohol and carbon dioxide per hour. Assume a conversion of 100 %.

$$3C_5H_{10}O_5 \rightarrow 5C_2H_6O + 5CO_2,$$
$$C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2.$$

**A**: Xylose 35.31 [g/h], glucose 4.70 [g/h]

17. **Process synthesis [8]**. A synthesis process consists of a system with two reactors in series (Fig. 8.13). The system is fed with 150 [kg/h] (density 1.18 [kg/L]) with compounds A (2 [M]) and B (1.2 [M]). Compounds A and B react to produce compound C, according to the following reaction:

$$A + 2B \rightarrow C \text{ conversion } 35\ \%.$$

The output current of the first reactor is divided into two streams in a 2:1 ratio, where the larger stream is fed to the second reactor. The second stream is recycled to the first reactor. In the second reactor, compound A reacts with compound C, producing compounds D and E, according to the following reaction:

$$A + C \rightarrow D + 2E \text{ conversion } 70\ \%.$$

Determine the mass composition of the outlet stream of the second reactor on a dry basis.

$$MW_A = 64 \text{ [g/mol]},$$
$$MW_B = 88 \text{ [g/mol]},$$

$$MW_D = 22 \text{ [g/mol]}.$$

**A**: **A** 45 %, **B** 29.3 %, **C** 6.1 %, **D** 1.4 % and **E** 17.7 %.

18. **Biogas [7]**. The sulfidric acid ($H_2S$) content must be reduced in a stream of biogas from 4,000 ppm to 10 ppm. For this a filter filler of iron sponge is available that contains 190 [kg] of iron oxide III/m$^3$. The sulfidric acid from the gas reacts with iron oxide III in the sponge, producing iron sulfide III and water. If the flow of biogas to treat is 12 [m$^3$/h], determine the volume of the iron sponge if it is projected to be replaced once a month. Consider that the iron sponge is replaced when 85 % of the iron oxide III is consumed.
    **A**: 0.34 [m$^3$].
19. **Sugars and enzymes [8]**. A student is "playing" with sugars and enzymes in the laboratory. He has a solution of 10 [g/L] sucrose, 5 [g/L] lactose, and 12 [g/L] maltose, and he is experimenting with the enzymes invertase, lactase, and maltase. After some point, he measures the concentrations, getting 0.1 [g/L] lactose, 4 [g/L] fructose, and 11 [g/L] glucose. To finish his fun evening, the student calculates the conversion of each reaction. What are his results?

    **A**:
    Invertase: 76 %
    Lactase: 98 %
    Maltase: 35 %
20. **Reactors in series [10]**. A system composed of two reactors in series is fed with *a* moles of compound A and 3*a* moles of compound B. The object of the process is to get the coveted product D.

    First reactor

    $$A + 2B \rightarrow C \text{ conversion} = x \text{ (decimal form, i.e. } 0 < x < 1).$$

    Thus, the output stream of the first reactor is the feed stream of the second reactor.

    Second reactor

    $$C + B \rightarrow 3D \text{ conversion} = y \text{ (decimal form, i.e., } 0 < y < 1).$$

    (a) What is the molar composition at the output of the first reactor? (b) What is the molar composition at the output of the second reactor? (c) What is the amount of D produced in grams?

    The molecular weight of D is 30 and so (a) and (b) should be expressed as a function of $x$ and $y$.
    **A**: (a) and (b)

| | Molar composition % output of first reactor | Molar composition % output of second reactor |
|---|---|---|
| A | $50(1-x)/(2-x)$ | $100(1-x)/(4-2x+xy)$ |
| B | $50(3-2x)/(2-x)$ | $100(3-2x-xy)/(4-2x+xy)$ |
| C | $50x/(2-x)$ | $100x(1-y)/(4-2x+xy)$ |
| D | – | $300xy/(4-2x+xy)$ |

    (c) *90axy* g of D.
21. **Chain reactions [8]**. The highly desirable product E is obtained through the following chain reactions:

$$A + B \rightarrow 2C \text{ conversion } 80\ \%,$$
$$C + B \rightarrow 3D \text{ conversion } 66.67\ \%,$$

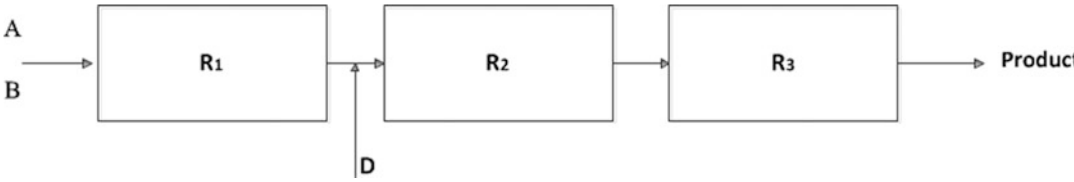


**Fig. 8.14** Three reactors in series

$$D + C \rightarrow 2E \text{ conversion } 50\ \%.$$

The process is continuously operating and producing 4 [kg mol/h] of product E. If the molecular weight of compounds A, B, and E are $MW_A = 30$, $MW_B = 40$, and $MW_E = 20$, then: (a) What is the required mass of A and B to produce 100 [kg] of E? (b) How many hours will it take to produce 100 [kg] of E?

**A**: (a) Mass of compound A = 125 [kg] and mass of compound B = 233.2 [kg]. (b) 1 h 15 min.

22. **Mixture [5]**. 1,508 [g] of a mixture of pure calcium nitrate and barium nitrate are transformed into sulfates in the presence of sulfuric acid. Evaporating the liquid to dryness, the mixture of sulfates weighs 1,314 [g]. Calculate the composition of the mixture of nitrates.

    **A**: 518 [g] of $Ca(NO_3)_2$ and 990 [g] of $Ba(NO_3)_2$.

23. **Conversion [6]**. A reactor is fed with compounds A and B (stoichiometric). The reaction is as follows:

$$A + 2B \rightarrow C.$$

If the feed stream contains 100 [mol] of A and at the output the total moles are 220, then what is the conversion of the reaction?

**A**: 40 %.

24. **Three reactors in series [7]**. The system depicted in Fig. 8.14 shows three reactors in series. The system is fed with 100 [kg/h] of compound A and 180 [kg/h] of compound B. In addition, 675 [kg/h] of compound D are fed to the second reactor. The reactions areas follows:

| | | |
|---|---|---|
| Reactor 1: | $A + B \rightarrow 2C$ | Conversion 80 % |
| Reactor 2: | $3D + C \rightarrow 4E$ | Conversion 85 % |
| Reactor 3: | $E + C \rightarrow F$ | |

If the system generates 27 [kg/h] of product F, then: (a) Determine the molar composition at the output of each reactor. (b) What is the limiting reactant in each reactor, where $MW_A = 20$, $MW_B = 30$, $MW_D = 25$.

**A**: (**a**)

| | Reactor 1 | Reactor 2 | Reactor 3 |
|---|---|---|---|
| A | 9.1 | 2.6 | 2.7 |
| B | 18.2 | 5.3 | 5.3 |
| C | 72.7 | 3.2 | 1.8 |
| D | – | 17.4 | 17.6 |
| E | – | 71.6 | 71.1 |
| F | – | – | 1.4 |

(**b**) Limiting reactant for each reactor is: Reactor 1: A, Reactor 2: C, Reactor 3: C

25. **Ethylene oxide [10⁺]**. The first step in the production process of ethylene oxide ($C_2H_4O$) is depicted in the following flow sheet (Fig. 8.15).

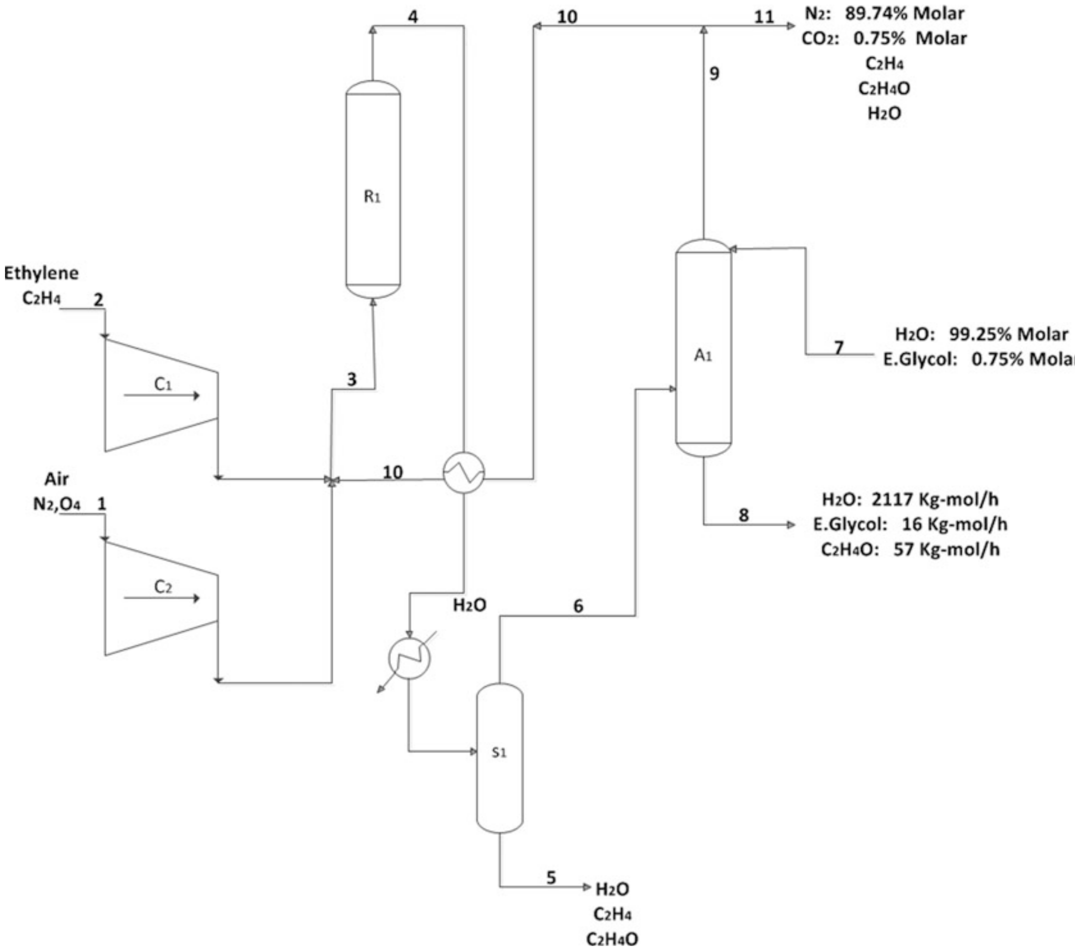


**Fig. 8.15** Process for ethylene oxide production

Ethylene ($C_2H_4$) and air are compressed in compressors C-1 and C-2 and mixed with the recycle stream of the absorber (A-1). The resultant mixture contains 5.02 % ethylene and 12.41 % oxygen (molar basis) and is fed to reactor R-1. The main reactions in R-1 are

$$C_2H_4 + 0.5O_2 \rightarrow C_2H_4O,$$
$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O.$$

The output stream of reactor R-1 is cooled down with the recycle stream from the absorber and then with water. Then the resultant liquid–vapor mixture is separated in the separator drum S-1. The vapor from S-1 feeds the absorber, where 97.85 % of the ethylene oxide is absorbed using an aqueous solution (0.75 % molar) of ethylene glycol ($C_2H_6O_2$).

The gases that are not absorbed leave through the top of the column. 60 % of this stream is recycled to reactor R-1 and the rest is purged.

Separator drum: $C_2H_4O/C_2H_4 = 2$ (molar basis) (this stream also contains $H_2O$).

Fed stream: $O_2/C_2H_4 = 2.033$ (molar basis).

In addition, the output liquid stream from the absorber contains 57 [kg mol] $C_2H_4O$, 16 [kg mol] ethylene glycol, and 2,117 [kg mol] $H_2O$. The purge contains 82.74 % $N_2$ and 8.13 % $CO_2$ and $O_2$, $C_2H_4$, $C_2H_4$, and $H_2O$.

(a) Quantify the output and input streams of the process. (b) What is the degree of conversion of the reactions?

**A**: (a)

| Stream | Molar content (kg mol) |
|---|---|
| 1 (air) | $N_2$: 955.25<br>$O_2$: 254.12 |
| 2 (ethylene) | $C_2H_4$: 125.00 |
| 5 | $H_2O$: 92.77<br>$C_2H_4O$: 0.35<br>$C_2H_4$: 0.175 |
| 7 | $C_2H_6O_2$: 16<br>$H_2O$: 2,117 |
| 11 (purge) | $N_2$: 955.25<br>$O_2$: 84.34<br>$CO_2$: 94.00<br>$C_2H_4O$: 0.5<br>$H_2O$: 1.14<br>$C_2$H4: 19.29 |

(b) First reaction: 37.6 %; second reaction: 31.5 %

## Additional Web References

Balances on Reactive Systems https://www.youtube.com/watch?v=jyso8NSytWw
Single Reaction with Recycle https://www.youtube.com/watch?v=bF19fAoRpVo
Balancing Chemical Equations https://www.youtube.com/watch?v=UGf60kq_ZDI
Balancing Combustion Reactions http://www.youtube.com/watch?v=ed0h11IfEPU
Stoichiometry - Conversions Using Balanced Equations http://www.youtube.com/watch?v=wySZDEbqbnM
Two Continuous Stirred Tank Reactors in Series http://www.youtube.com/watch?v=7RLQ9sHkdkk
Balances on Multiple Units with Reaction https://www.youtube.com/watch?v=tQyrSvll_nc
Extent of Reaction for Material Balances https://www.youtube.com/watch?v=YusSU0jlOUk
Three Methods for Solving Reactive Material Balances https://www.youtube.com/watch?v=MSzTIRAv5io