

## MATERIAL BALANCE

Material balances are the basis of process design. A material balance taken over the complete process will determine the quantities of raw materials required and products produced. Balances over individual process units set the process stream flows and compositions, and provide the basic equations for sizing equipment.

A good understanding of material balance calculations is essential in process design.

Material balances are also useful tools for the study of plant operation and troubleshooting. They can be used to check performance against design, to extend the often limited data available from the plant instrumentation, to check instrument calibrations, and to locate sources of material loss. Material balances are essential to obtaining high-quality data from laboratory or pilot plants.

### THE EQUIVALENCE OF MASS AND ENERGY

Einstein showed that mass and energy are equivalent. Energy can be converted into mass, and mass into energy. They are related by Einstein's equation:

$$E = mc^2 \quad (2.1)$$

where

$E$  = energy, J,

$m$  = mass, kg,

$c$  = the speed of light *in vacuo*,  $3 \times 10^8$  m/s.

The loss of mass associated with the production of energy is significant only in nuclear reactions. Energy and matter are always considered to be separately conserved in chemical reactions.

### CONSERVATION OF MASS

The general conservation equation for any process system can be written as

$$\text{Material out} = \text{Material in} + \text{Generation} - \text{Consumption} - \text{Accumulation}$$

For a steady-state process, the accumulation term is zero. Except in nuclear processes, mass is neither generated nor consumed; but if a chemical reaction takes place, a particular chemical species may be formed or consumed in the process. If there is no chemical reaction, the steady-state balance reduces to

$$\text{Material out} = \text{Material in}$$

A balance equation can be written for each separately identifiable species present, elements, compounds, or radicals; and for the total material. Balances can be written for mass or for number of moles.

### STOICHIOMETRY

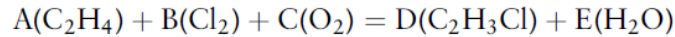
The stoichiometric equation for a chemical reaction states unambiguously the number of molecules of the reactants and products that take part, from which the quantities can be calculated. The equation must balance.

### Example 2.3

Write out and balance the overall equation for the manufacture of vinyl chloride from ethylene, chlorine, and oxygen.

#### Solution

*Method:* Write out the equation using letters for the unknown number of molecules of each reactant and product. Make a balance on each element. Solve the resulting set of equations.



Balance on carbon

$$2A = 2D, \quad A = D$$

on hydrogen

$$4A = 3D + 2E$$

$$\text{substituting } D = A \text{ gives } E = \frac{A}{2}$$

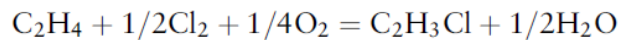
on chlorine

$$2B = D, \quad \text{hence } B = \frac{A}{2}$$

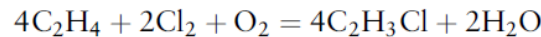
on oxygen

$$2C = E, \quad C = \frac{E}{2} = \frac{A}{4}$$

putting  $A = 1$ , the equation becomes



multiplying through by the largest denominator to remove the fractions



### CHOICE OF SYSTEM BOUNDARY

The conservation law holds for the complete process and any subdivision of the process. The system boundary defines the part of the process being considered. The flows into and out of the system are those crossing the boundary and must balance with material generated or consumed within the boundary.

Any process can be divided up in an arbitrary way to facilitate the material balance calculations. The judicious choice of the system boundaries can often greatly simplify what would otherwise be difficult and tortuous calculations.

No hard and fast rules can be given on the selection of suitable boundaries for all types of material balance problems. Selection of the best subdivision for any particular process

is a matter of judgment, and depends on insight into the structure of the problem, which can only be gained by practice. The following general rules serve as a guide:

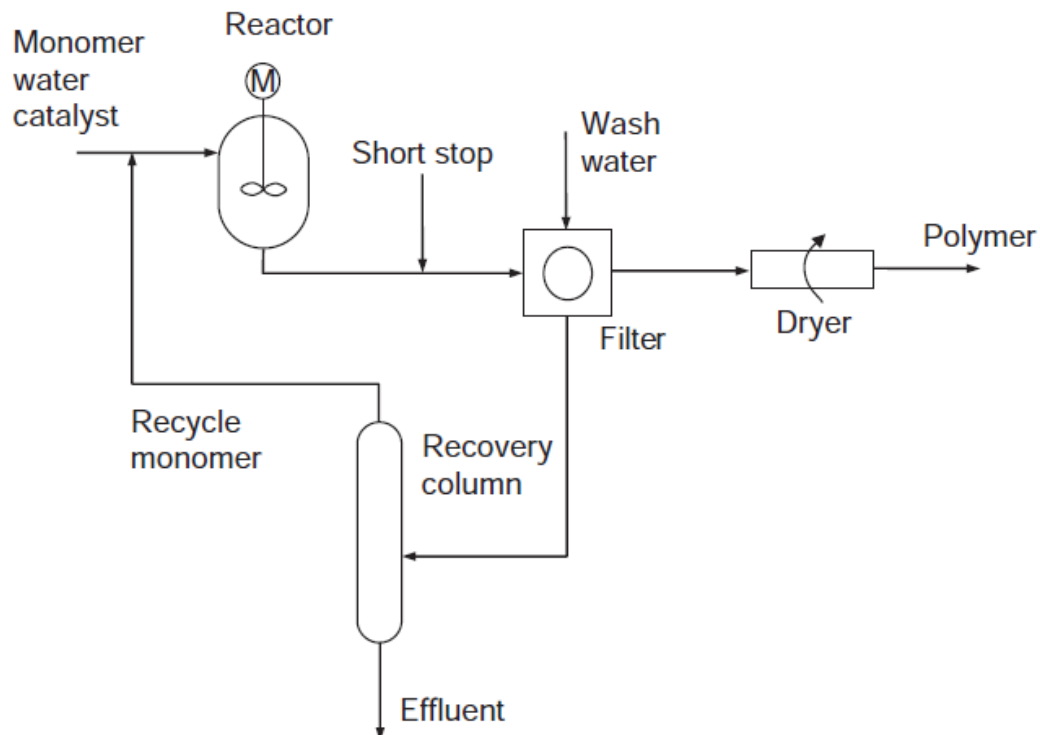
1. With complex processes, first take the boundary around the complete process and if possible calculate the flows in and out. Raw materials in, products and byproducts out.
2. Select the boundaries to subdivide the process into simple stages and make a balance over each stage separately.
3. Select the boundary around any stage so as to reduce the number of unknown streams to as few as possible.
4. As a first step, include any recycle streams within the system boundary (see Example 2.4).

### Example 2.4

The diagram shows the main steps in a process for producing a polymer. From the following data, calculate the stream flows for a production rate of 10,000 kg/h.

Reactor selectivity for polymer	100%
slurry polymerization	20 wt% monomer/water
conversion	90% per pass
catalyst	1 kg/1000 kg monomer
short stopping agent	0.5 kg/1000 kg unreacted monomer

Filter wash water approx. 1 kg/1 kg polymer  
 Recovery column yield 98% (percentage recovered)  
 Dryer feed ~5% water, product specification 0.5% H<sub>2</sub>O  
 Polymer losses in filter and dryer ~1%

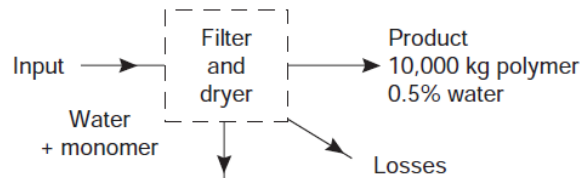


### Solution

Only those flows necessary to illustrate the choice of system boundaries and method of calculation are given in the solution.

Basis: 1 hour

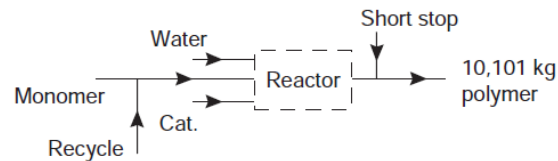
Take the first system boundary around the filter and dryer.



With 1% loss, polymer entering subsystem

$$= \frac{10,000}{0.99} = \underline{\underline{10,101 \text{ kg}}}$$

Take the next boundary around the reactor system; the feeds to the reactor can then be calculated.



$$\text{At 90\% conversion per pass, monomer feed} = \frac{10,101}{0.9} = \underline{\underline{11,223 \text{ kg}}}$$

$$\text{Unreacted monomer} = 11,223 - 10,101 = \underline{\underline{1122 \text{ kg}}}$$

$$\text{Short-stop, at } 0.5 \text{ kg/1000 kg unreacted monomer} = 1122 \times 0.5 \times 10^{-3} = \underline{\underline{0.6 \text{ kg}}}$$

$$\text{Catalyst, at } 1 \text{ kg/1000 kg monomer} = 11,223 \times 1 \times 10^{-3} = \underline{\underline{11 \text{ kg}}}$$

Let water feed to reactor be  $F_1$ , then for 20% monomer

$$0.2 = \frac{11,223}{F_1 + 11,223}$$

$$F_1 = \frac{11,223(1 - 0.2)}{0.2} = \underline{\underline{44,892 \text{ kg}}}$$

Now consider filter-dryer subsystem again.

Water in polymer to dryer, at 5% (neglecting polymer loss)

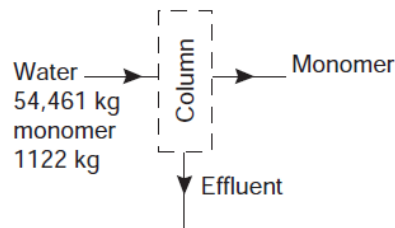
$$= \frac{10,101 \times 0.05}{0.95} = \underline{\underline{532 \text{ kg}}}$$

Balance over reactor-filter-dryer subsystem gives flows to recovery column.

$$\text{water, } 44,892 + 10,101 - 532 = \underline{\underline{54,461 \text{ kg}}}$$

$$\text{monomer, unreacted monomer} = \underline{\underline{1122 \text{ kg}}}$$

Now consider recovery system

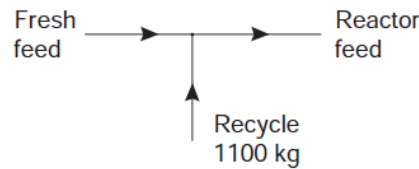


With 98% recovery, recycle to reactor

$$= 0.98 \times 1122 = \underline{\underline{1100 \text{ kg}}}$$

Composition of effluent is 23 kg monomer, 54,461 kg water.

Consider reactor monomer feed



Balance around tee gives fresh monomer required

$$= 11,223 - 1100 = \underline{\underline{10,123 \text{ kg}}}$$

## EXCESS REAGENT

In industrial reactions the components are seldom fed to the reactor in exact stoichiometric proportions. A reagent may be supplied in excess to promote the desired reaction, to maximize the use of an expensive reagent, or to ensure complete reaction of a reagent, as in combustion.

The percentage excess reagent is defined by the following equation:

$$\text{Percent excess} = \frac{\text{quantity supplied} - \text{stoichiometric}}{\text{stoichiometric quantity}} \times 100 \quad (2.7)$$

It is necessary to state clearly to which reagent the excess refers.

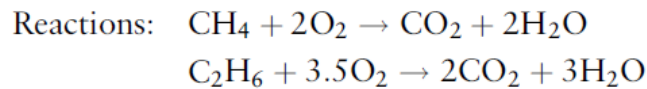
### Example 2.9

To ensure complete combustion, 20% excess air is supplied to a furnace burning natural gas. The gas composition (by volume) is methane 95%, ethane 5%.

Calculate the moles of air required per mole of fuel.

### Solution

Basis: 100 mol gas, as the analysis is volume percentage.



Stoichiometric moles of  $\text{O}_2$  required =  $95 \times 2 + 5 \times 3.5 = 207.5$

With 20% excess, moles of  $\text{O}_2$  required =  $207.5 \times 1.2 = 249$

Moles of air (21%  $\text{O}_2$ ) =  $249 \times 100/21 = 1185.7$

Air per mole of fuel =  $1185.7/100 = \underline{\underline{11.86 \text{ mol}}}$

## CONVERSION, SELECTIVITY, AND YIELD

It is important to distinguish between conversion and yield. Conversion is to do with reactants; yield with products.

### Conversion

Conversion is a measure of the fraction of the reagent that reacts.

To optimize reactor design and minimize byproduct formation, the conversion of a particular reagent is often less than 100%. If more than one reactant is used, the reagent on which the conversion is based must be specified.

Conversion is defined by the following expression:

$$\begin{aligned}\text{Conversion} &= \frac{\text{amount of reagent consumed}}{\text{amount supplied}} \\ &= \frac{(\text{amount in feed stream}) - (\text{amount in product stream})}{(\text{amount in feed stream})} \quad (2.8)\end{aligned}$$

This definition gives the total conversion of the particular reagent to all products.

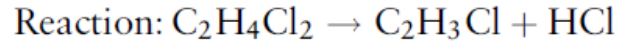
### Example 2.10

In the manufacture of vinyl chloride (VC) by the pyrolysis of dichloroethane (DCE), the reactor conversion is limited to 55% to reduce carbon formation, which fouls the reactor tubes.

Calculate the quantity of DCE fed to the reactor to produce 5000 kg/h of VC.

### **Solution**

Basis: 5000 kg/h VC (the required quantity).



Molar weights: DCE 99, VC 62.5

$$\text{kmol/h VC produced} = \frac{5000}{62.5} = 80$$

From the stoichiometric equation, 1 kmol DCE produces 1 kmol VC. Let  $X$  be DCE feed in kmol/h:

$$\text{Percent conversion} = 55 = \frac{80}{X} \times 100$$

$$X = \frac{80}{0.55} = \underline{\underline{145.5 \text{ kmol/h}}}$$

### **Selectivity**

Selectivity is a measure of the efficiency of the reactor in converting reagent to the desired product. It is the fraction of the reacted material that was converted into the desired product. If no byproducts are formed, then the selectivity is 100%. If side reactions occur and byproducts are formed, then the selectivity decreases. Selectivity is always expressed as the selectivity of feed A for product B and is defined by the following equation:

$$\begin{aligned} \text{Selectivity} &= \frac{\text{moles of B formed}}{\text{moles of B that could have been formed if all A reacted to give B}} \\ &= \frac{\text{moles of B formed}}{\text{moles of A consumed} \times \text{stoichiometric factor}} \end{aligned} \quad (2.9)$$

Stoichiometric factor = moles of B produced per mole of A reacted in the reaction stoichiometric equation

### **Yield**

Yield is a measure of the performance of a reactor or plant. Several different definitions of yield are used, and it is important to state clearly the basis of any yield numbers. This is often not done when yields are quoted in the literature, and judgment must be used to decide what was intended.

The yield of product B from feed A is defined by

$$\text{Yield} = \frac{\text{moles of B formed}}{\text{moles of A supplied} \times \text{stoichiometric factor}} \quad (2.10)$$

For a reactor, the yield is the product of conversion and selectivity:

$$\begin{aligned} \text{Reaction yield} &= \text{Conversion} \times \text{Selectivity} \\ &= \frac{\text{moles A consumed}}{\text{moles A supplied}} \times \frac{\text{moles B formed}}{\text{moles A consumed} \times \text{stoichiometric factor}} \end{aligned} \quad (2.11)$$

With industrial reactors, it is necessary to distinguish between “Reaction yield” (chemical yield), which includes only chemical losses to side products; and the overall “Reactor yield,” which also includes physical losses, such as losses by evaporation into vent gas.

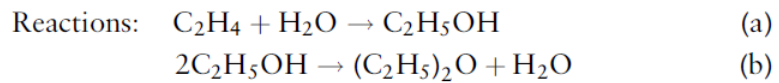
Plant yield (applied to the complete plant or any stage)

$$= \frac{\text{moles of product produced}}{\text{moles of reagent supplied to the process} \times \text{stoichiometric factor}} \quad (2.12)$$

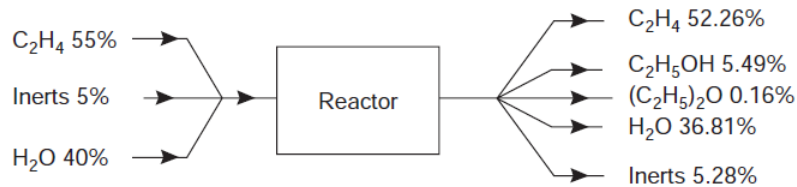
### Example 2.11

In the production of ethanol by the hydrolysis of ethylene, diethyl ether is produced as a byproduct. A typical feed stream composition is 55% ethylene, 5% inerts, 40% water; and product stream: 52.26% ethylene, 5.49% ethanol, 0.16% ether, 36.81% water, 5.28% inerts. Calculate the selectivity of ethylene for ethanol and for ether.

### Solution



Basis: 100 moles feed (easier calculation than using the product stream)



*Note:* The flow of inerts will be constant, as they do not react; and it can thus be used to calculate the other flows from the compositions.



Feed stream	ethylene	55 mol
	inerts	5 mol
	water	40 mol

Product stream

$$\text{ethylene} = \frac{52.26}{5.28} \times 5 = 49.49 \text{ mol}$$

$$\text{ethanol} = \frac{5.49}{5.28} \times 5 = 5.20 \text{ mol}$$

$$\text{ether} = \frac{0.16}{5.28} \times 5 = 0.15 \text{ mol}$$

$$\text{Amount of ethylene reacted} = 55.0 - 49.49 = 5.51 \text{ mol}$$

$$\text{Selectivity of ethylene for ethanol} = \frac{5.20}{5.51 \times 1.0} \times 100 = \underline{\underline{94.4\%}}$$

As 1 mol of ethanol is produced per mol of ethylene, the stoichiometric factor is 1.

$$\text{Selectivity of ethylene for ether} = \frac{0.15}{5.51 \times 0.5} \times 100 = \underline{\underline{5.44\%}}$$

The stoichiometric factor is 0.5, as 2 mol of ethylene produce 1 mol of ether. Note that the conversion of ethylene, to all products, is given by

$$\begin{aligned} \text{Conversion} &= \frac{\text{mols fed} - \text{mols out}}{\text{mols fed}} = \frac{55 - 49.49}{55} \times 100 \\ &= \underline{\underline{10 \text{ percent}}} \end{aligned}$$

The yield of ethanol based on ethylene is

$$\text{Reaction yield} = \frac{5.20}{55 \times 1.0} \times 100 = \underline{\underline{9.45\%}}$$

## RECYCLE PROCESSES

Processes in which a flow stream is returned (recycled) to an earlier stage in the processing sequence are frequently used. If the conversion of a valuable reagent in a reaction process is appreciably less than 100%, the unreacted material is usually separated and recycled. The return of reflux to the top of a distillation column is an example of a recycle process in which there is no reaction.

In mass balance calculations the presence of recycle streams makes the calculations more difficult.

Without recycle, the material balances on a series of processing steps can be carried out sequentially, taking each unit in turn; the calculated flows out of one unit become the feeds to the next. If a recycle stream is present, then at the point where the recycle is returned, the flow will not be known as it will depend on downstream flows not yet calculated. If the recycle flow is not known, the sequence of calculations cannot be continued to the point where the recycle flow can be determined.

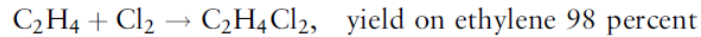
Two approaches to the solution of recycle problems are possible:

- A. The cut-and-try (“tear”) method. The recycle stream flows can be estimated and the calculations continued to the point where the recycle is calculated. The estimated flows are then compared with those calculated, and a better estimate is made. The procedure is continued until the difference between the estimated and the calculated flows is within an acceptable tolerance.
- B. The formal, algebraic method. The presence of recycle implies that some of the mass balance equations must be solved simultaneously. The equations are set up with the recycle flows as unknowns and solved using standard methods for the solution of simultaneous equations.

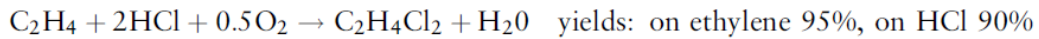
### Example 2.13

The block diagram shows the main steps in the balanced process for the production of vinyl chloride from ethylene. Each block represents a reactor and several other processing units. The main reactions are

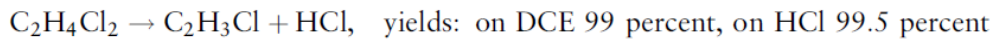
*Block A, chlorination*



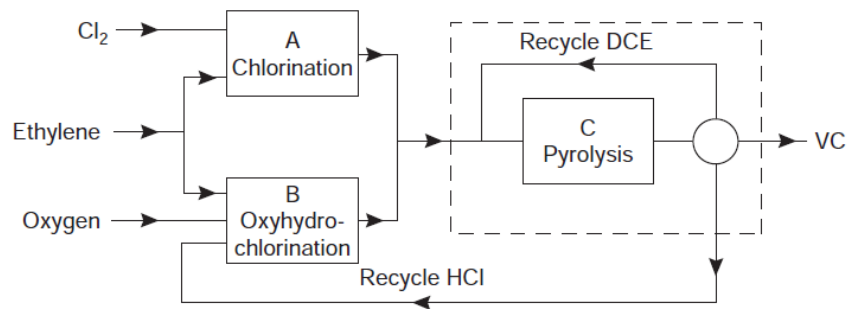
*Block B, oxyhydrochlorination*



*Block C, pyrolysis*



The HCl from the pyrolysis step is recycled to the oxyhydrochlorination step. The flow of ethylene to the chlorination and oxyhydrochlorination reactors is adjusted so that the production of HCl is in balance with the requirement. The conversion in the pyrolysis reactor is limited to 55%, and the unreacted dichloroethane (DCE) is separated and recycled.



Using the yield figures given, and neglecting any other losses, calculate the flow of ethylene to each reactor and the flow of DCE to the pyrolysis reactor, for a production rate of 12,500 kg/h vinyl chloride (VC).

### Solution

Molecular weights: vinyl chloride 62.5, DCE 99.0, HCl 36.5.

$$\text{VC per hour} = \frac{12,500}{62.5} = 200 \text{ kmol/h}$$

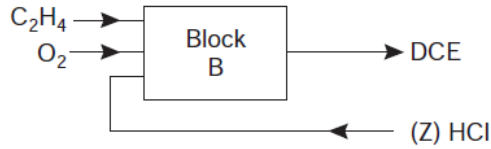
Draw a system boundary around each block, enclosing the DCE recycle within the boundary of step C.

Let the flow of ethylene to block A be  $X$  and to block B be  $Y$ , and the HCl recycle be  $Z$ .

Then the total moles of DCE produced =  $0.98X + 0.95Y$ , allowing for the yields, and the moles of HCl produced in block C

$$= (0.98X + 0.95Y)0.995 = Z \quad (a)$$

Consider the flows to and from block B



The yield of DCE based on HCl is 90%, so the moles of DCE produced

$$= 0.5 \times 0.90Z$$

*Note:* The stoichiometric factor is 0.5 (2 mol HCl per mol DCE).

The yield of DCE based on ethylene is 95%, so

$$0.5 \times 0.9Z = 0.95Y$$

$$Z = 0.95 \times 2Y/0.9$$

Substituting for Z into equation (a) gives

$$Y = (0.98X + 0.95Y)0.995 \times \frac{0.9}{2 \times 0.95} \quad (b)$$

$$Y = 0.837X$$

Turning to block C, total VC produced =  $0.99 \times$  total DCE, so

$$0.99(0.98X + 0.95Y) = 200 \text{ kmol/h}$$

Substituting for Y from equation (b) gives  $X = \underline{\underline{113.8 \text{ kmol/h}}}$

and

$$Y = 0.837 \times 113.8 = \underline{\underline{95.3 \text{ kmol/h}}}$$

HCl recycle from equation (a)

$$Z = (0.98 \times 113.8 + 0.95 \times 95.3)0.995 = \underline{\underline{201.1 \text{ kmol/h}}}$$

*Note:* Overall yield on ethylene =  $\frac{200}{(113.8 + 95.3)} \times 100 = \underline{\underline{96 \text{ percent}}}$

## PURGE

It is usually necessary to bleed off a portion of a recycle stream to prevent the buildup of unwanted material. For example, if a reactor feed contains inert components that are not separated from the recycle stream in the separation units, these inerts would accumulate in the recycle stream until the stream eventually consisted almost entirely of inerts. Some portion of the stream must be purged to keep the inert level within

acceptable limits. A continuous purge would normally be used. Under steady-state conditions:

$$\text{Loss of inert in the purge} = \text{Rate of feed of inerts into the system}$$

The concentration of any component in the purge stream is the same as that in the recycle stream at the point where the purge is taken off. So the required purge rate can be determined from the following relationship:

$$\begin{aligned} & [\text{Feed stream flow rate}] \times [\text{Feed stream inert concentration}] \\ = & [\text{Purge stream flow rate}] \times [\text{Specified(desired) recycle inert concentration}] \end{aligned}$$

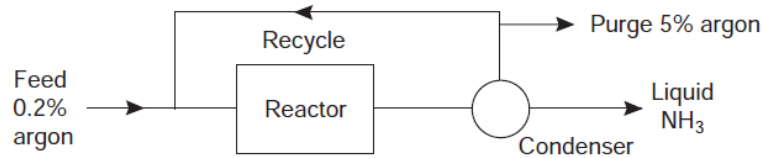
**Example 2.14**

In the production of ammonia from hydrogen and nitrogen, the conversion, based on either raw material, is limited to 15%. The ammonia produced is condensed from the reactor (converter) product stream, and the unreacted material is recycled. If the feed contains 0.2% argon (from the nitrogen separation process), calculate the purge rate required to hold the argon in the recycle stream below 5.0%. Percentages are by volume.

**Solution**

Basis: 100 moles feed (purge rate will be expressed as moles per 100 mol feed, as the production rate is not given).

Process diagram:



Volume percentages are taken as equivalent to mol%.

Argon entering system with feed =  $100 \times 0.2/100 = 0.2$  mol.

Let purge rate per 100 mol feed be  $F$ .

Argon leaving system in purge =  $F \times 5/100 = 0.05 F$ .

At the steady state, argon leaving = argon entering

$$0.05F = 0.2$$

$$F = \frac{0.2}{0.05} = 4$$

Purge required: 4 mol per 100 mol feed.