Lecture Fourteen

(MATERIAL BALANCES FOR PROCESSES INVOLVING RECYCLE WITH CHEMICAL REACTION)

In this Lecture we discuss material balances involving **recycle** with chemical reaction. Recycle, is commonly used in the design of chemical processes around the reaction units such as bioreactors as well as catalytic reactors.

14.1 Recycle with Chemical Reaction

14.1.1 Overall fraction conversion

14.1.2 Single - pass fraction conversion

Your Objectives in Studying this Lecture are:

- Draw a flow diagram or sketch for problems involving recycle.
- Apply the 10-step strategy to solve steady-state problems (with and without chemical reaction) involving recycle stream.
- Solve problems involving a modest number of interconnected units by making appropriate balances.
- Use the concepts of extent of reaction, overall conversion, and single-pass (once-through) conversion in solving recycle problems involving reactors.

14.1 Recycle with Chemical Reaction

The most common application of recycle for systems involving chemical reaction is the recycle of reactants, an application that is used to **increase the overall conversion in a reactor**.

If we take a simple example for the reaction

$$A \rightarrow B$$

From the data in **Figure.14.1** you can see that the steady-state material balances for the mixer, reactor, and separator are satisfied.

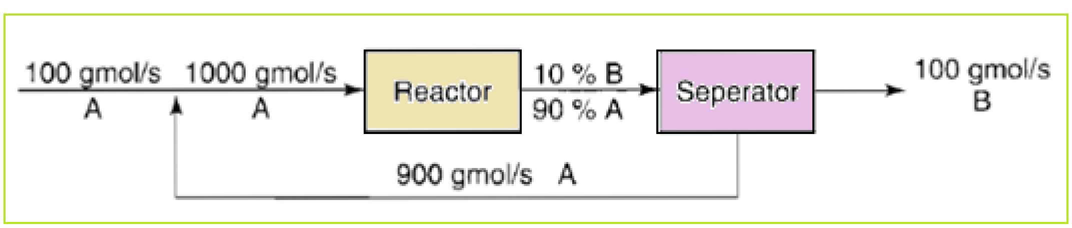


Figure.14.1: A simple recycle system with chemical reaction.

If you calculate the extent of reaction for the overall process in **Figure.14.1**based on **B**

$$\xi_{\text{overall}} = \frac{100 - 0}{1} = 100 \text{ moles reacting}$$

If you use material balances to calculate the output P of the reactor (on the basis of 1 second) you get

A = 900 g mol

B = 100 g mol

and the extent of reaction based on **B** for the reactor by itself as the system is

$$\xi_{\text{reactor}} = \frac{100 - 0}{1} = 100 \text{ moles reacting}$$

In general, **the extent of reaction is the same regardless of whether an overall material balance is used or a material balance for the reactor is used**. This important fact can be used in solving material balances for recycle systems with reactions.

14.1.1 Overall fraction conversion

$$f_{OA} = \frac{n_A^{freshfeed} - n_A^{overallproduct}}{n_A^{freshfeed}} \tag{14-1}$$

14.1.2 Single - pass fraction conversion

$$f_{SP} = \frac{n_A^{reactorfeed} - n_A^{exitingreactor}}{n_A^{reactorfeed}} \tag{14-2}$$

The overall conversion depends only on what enters and leaves the overall process, while the single-pass conversion depends on what enters and leaves the reactor.

The overall conversion is 100%

$$\frac{100 - 0}{100} \times 100 = 100\%$$

and the single-pass conversion is 10%

$$\frac{1000 - 900}{1000} \times 100 = 10\%$$

When the fresh feed consists of more than one reactant, the conversion can be expressed for a single component, usually the limiting reactant, or the most important (expensive) reactant.

The overall conversion and the single-pass conversion can be expressed in terms of the extent of reaction, ξ

$$f_{OA} = \frac{-v_A \xi}{n_A^{\text{fresh feed}}} \tag{14-3}$$

$$f_{SP} = \frac{-v_A \xi}{n_A^{\text{reactor feed}}} \tag{14-4}$$

If you solve Equations (3) and (4) for the extent of reaction, equate the extents, and use a balance at the mixing point $n_{LR}^{\text{reactor feed}} = n_{LR}^{\text{fresh feed}} + n_{LR}^{\text{recycle}}$ you can obtain the following relationship between overall and single-pass conversion:

$$\frac{f_{SP}}{f_{OA}} = \frac{n_A^{\text{fresh feed}}}{n_A^{\text{fresh feed}} + n_A^{\text{recycle}}} \tag{14-5}$$

EXAMPLE -14-1 ***Recycle in a Process in Which a Reaction Occurs***

Cyclohexane (C_6H_{12}) can be made by the reaction of benzene (Bz) (C_6H_6) with hydrogen according to the following reaction:

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

For the process shown in **Figure E14.1**, determine the ratio of the recycle stream to the fresh feed stream if the overall conversion of benzene is **95%**, and the single-pass conversion is **20%**. Assume that **20%** excess hydrogen is used in the fresh feed, and that the composition of the recycle stream is **22.74 mol %** benzene and **78.26 mol %** hydrogen.

Solution:

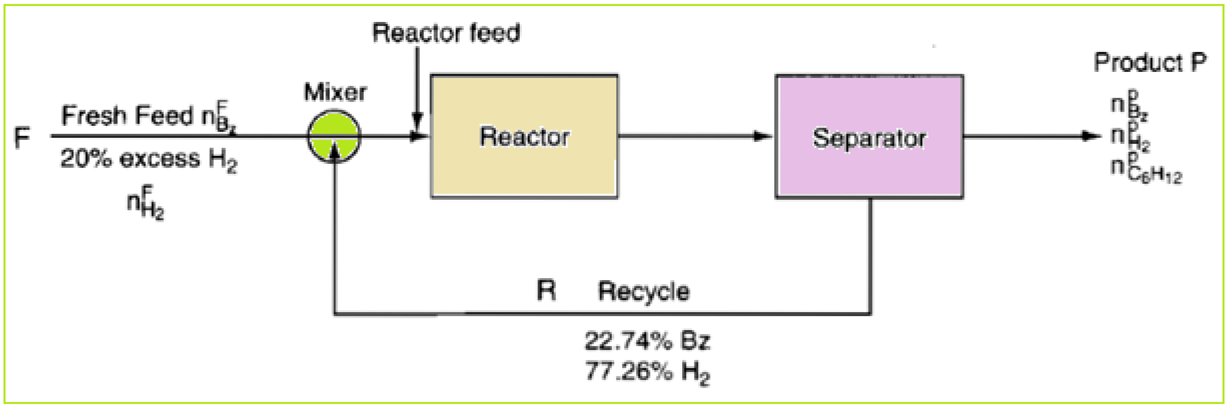


Figure.E14.1: **A Schematic of recycle reactor.**

Solution

The process is open and steady state.

Step 5

A convenient basis to choose would be 100 mol (g mol or lb mol) of fresh benzene feed, although you could select the recycle to be 100 mol.

Steps 1, 2, 3, and 4

Figure E12.2 contains all of the information available about the flowstreams except the amount of H_2, which is in 20% excess (for complete reaction, remember)

$$n^F_{H_2} = 100(3)(1 + 0.20) = 360 \text{ mol}$$

and the total fresh feed is 460 mol.

From Equation (12.1) for benzene ($\nu_{Bz} = -1$)

$$0.95 = \frac{-(-1)\xi}{100}$$

you can calculate that $\xi = 95$ reacting moles.

Steps 6 and 7

The unknowns are R, $n^P_{B_z}$, $n^P_{H_2}$, and $n^P_{C_6H_{12}}$. You can write three species balances for each of the three systems, the mixing point, the reactor, and the separator plus overall balances (not all of which are independent, of course). Which systems should you choose to start with? The overall process, because then you can use the value calculated for the extent of reaction.

Steps 8 and 9

The species overall balances are $n_i^{out} = n_i^{in} + \nu_i \xi_{overall}$

$$\text{Bz:} \quad n_{Bz}^{P} = 100 + (-1)(95) = 5 \text{ mol}$$
$$H_2\text{:} \quad n_{H_2}^{P} = 360 + (-3)(95) = 75 \text{ mol}$$
$$C_6H_{12} \quad n_{C_6H_{12}}^{P} = 0 + (1)(95) = \underline{95 \text{ mol}}$$
$$P = 175 \text{ mol}$$

The next step is to use the final piece of information, the information about the single-pass conversion and Equation (12.2), to get R. The system is now the reactor. The amount of the Bz feed to the reactor is 100+ 0.2274R, and ξ = 95 (the same as calculated from the overall conversion). Thus, for benzene

$$0.20 = \frac{-(-1)95}{100 + 0.2274R}$$

and $$R = 1649 \text{ mol}$$

Finally, the ratio of recycle to fresh feed is

$$\frac{R}{F} = \frac{1649 \text{ mol}}{460 \text{ mol}} = 3.58$$

EXAMPLE -14.2 ***Recycle in a Process with a Reaction Occurring***

Immobilized glucose isomerase is used as a catalyst in producing frutose from glucose in a fixed-bed reactor (water is the solvent). For the system shown in **Figure E14.2 (a)**, what percent conversion of glucose results on one pass through the reactor when the ratio of the exit stream to the recycle stream in mass units is equal to 8.33? The reaction is

$$\underset{\text{Glucose}}{C_{12}H_{22}O_{11}} \rightarrow \underset{\text{Fructose}}{C_{12}H_{22}O_{11}}$$

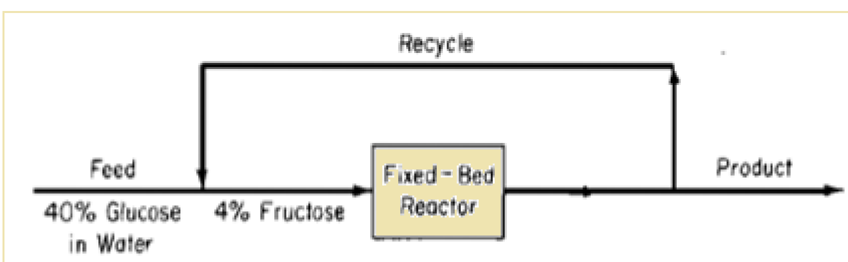


Figure.E14.2 (a): A Schematic of recycle reactor

Solution:

The process is an open, steady-state process with a reaction occurring and a recycle.

Steps 1, 2, 3, and 4

Figure E12.3b includes all the known and unknown values of the variables using appropriate notation (*W* stands for water, *G* for glucose, and *F* for fructose). Note that the recycle stream and product stream have the same composition, and consequently the same mass symbols are used in the diagram for each stream.

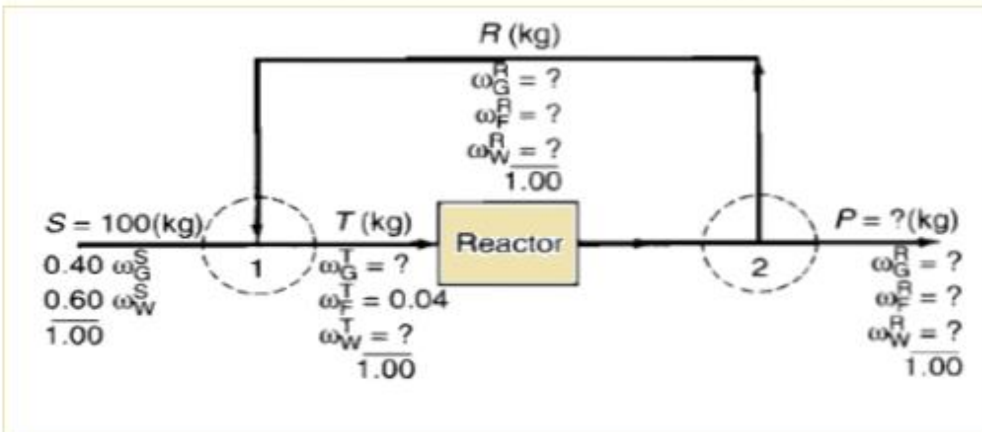


Figure.E14.2 (b)

Step 5

Pick as a basis $S = 100$ kg, given the data shown in Figure E12.3b.

Step 6

We have not provided any notation for the reactor exit stream and composition because we will not be using these values in our balances. Let f be the fraction conversion for one pass through the reactor. The unknowns are R, P, T, ω_G^R, ω_F^R, ω_W^R, ω_G^T, ω_W^T, and f, for a total of 9.

Step 7

The balances are $\Sigma\omega_i^R = 1$, $\Sigma\omega_i^T = 1$, $R = P/8.33$, plus 3 species balances each on the mixing point 1, the separator 2, and the reactor as well as overall balances.

We will assume we can find 9 independent balances among the lot and proceed. We do not have to solve all of the equations simultaneously. The units are mass (kg).

Steps 8 and 9

We will start with overall balances as they are easy to form and are often decoupled for solution.

Overall balances

Total: $P = S = 100$ kg (How simple!)

Consequently, $R = \dfrac{100}{8.33} = 12.0$ kg

Overall no water is generated or consumed, hence

Water: $100(0.60) = P\omega_W^R = 100\omega_W^R$

$$\omega_W^R = 0.60$$

We now have 6 unknowns left for which to solve. We start somewhat arbitrarily with mixing point 1 to calculate some of the unknowns

Mixing point 1

No reaction occurs so that species balances can be used without involving the extent of reaction:

Total: $100 + 12 = T = 112$

Glucose: $100(0.40) + 12\omega_G^R = 112\omega_G^T$

Fructose: $0 + 12\omega_F^R = 112(0.04)$

or

$$\omega_F^R = 0.373$$

Also, because $\omega_F^R + \omega_G^R + \omega_W^R = 1$,

$\omega_G^R = 1 - 0.373 - 0.600 = 0.027$

Next, from the glucose balance

$$\omega_G^T = 0.360$$

Next, rather than make separate balances on the reactor and separator, we will combine the two into one system (and thus avoid having to calculate values associated with the reactor exit stream).

Reactor plus Separator 2

Total: T = 12 + 100 = 112 (a redundant equation)

Glucose: $\omega_G^T T - (R + P)(\omega_G^R) = (f)(\omega_G^T T)$

$$(0.360)(112) - (112)(0.027) = f(0.360)(112)$$
$$40.3 - 3.02 = f(40.32)$$
$$f = 0.93$$

Lecture Fourteen / Tutorials

(MATERIAL BALANCES FOR PROCESSES INVOLVING RECYCLE WITH CHEMICAL REACTION)

Recycle with chemical reaction

P.14.1 If the components in the feed to a process appear in stoichiometric quantities and the subsequent separation process is complete so that all of the unreacted reactants are recycled, what is the ratio for reactants in the recycle stream?

P.14.2 Answer the following questions true or false:

a. The general material balance applies for processes that involve recycle with reaction as it does for other processes.

b. The key extra piece of information in material balances on processes with recycle in which a reaction takes place is the specification of the fraction conversion or extent of reaction.

c. The degrees of freedom for a process with recycle that involves chemical reaction are the same as for a process without recycle.

P.14.3 A catalytic dehydrogenation process shown in **Figure.P14.3**, produces 1, 3 butadiene (C_4H_6) from pure normal butane (C_4H_{10}). The product stream contains 75 mol/hr of H_2 and 13 mol/hr of C_4H_{10} as well as C_4H_6. The recycle stream is 30% (mol) C_4H_{10} and 70% (mol) C_4H_6, and the flow is 24 mol/hr.

d. What is the feed rate, *F*, and the product flow rate of C_4H_6 leaving the proc`ess?

e. What is the single-pass conversion of butane in the process?

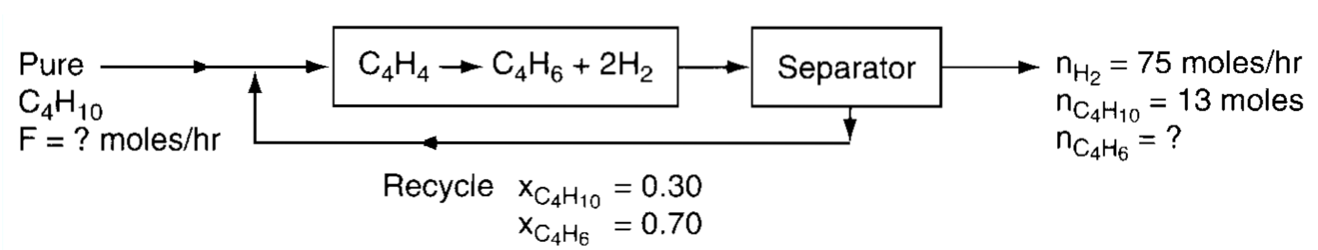


Figure.P14.3 A Schematic of recycle reactor.

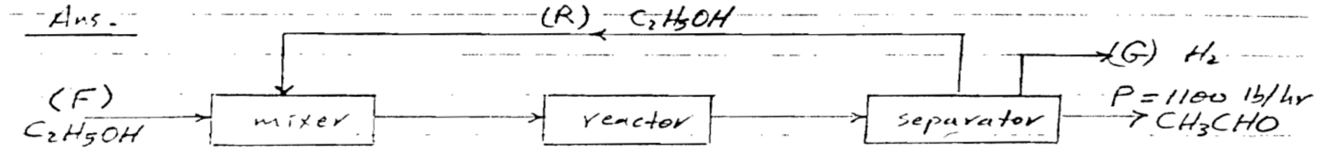
P.14.4

Acetaldehyde (CH_3CHO) is produced at a rate of 1100 lb/hr (P) by catalytic dehydrogenation of ethanol: $C_2H_5OH \rightarrow CH_3CHO + H_2$

M.wt. 46 44 2

It is found that 80% of ethanol input to the reactor are converted, and the rest are completely recycled. Calculate the mass flow rate of fresh ethanol (F), recycle stream (R), and hydrogen evolved (G).

Ans.

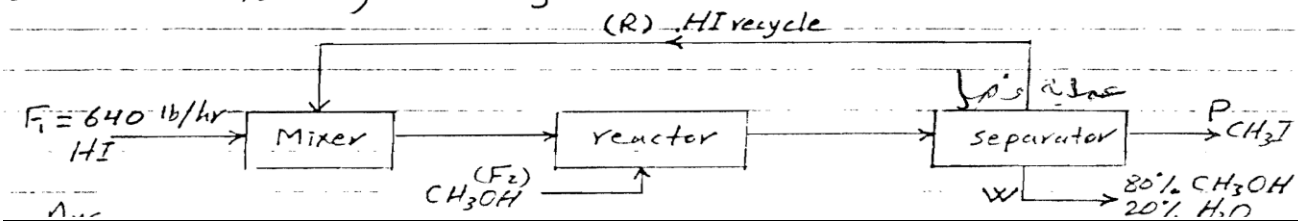


P.14.5

Methyl iodide is produced by adding HI to an excess amount of methanol according to the following reaction: $HI + CH_3OH \rightarrow CH_3I + H_2O$.

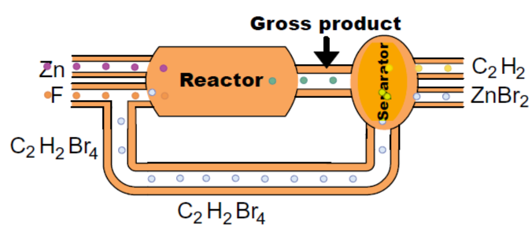
M.wt. 128 32 142 18

Fresh HI are fed to the process at a rate of 640 lb/hr (F_1). The degree of completion of the reaction = 40%. Calculate the flow rates of streams (P), (W), (F_2) and (R) shown in the following block diagram



P.14.6

The reaction of ethyl-tetrabromide with zinc dust proceeds as shown in the diagram below. The reaction is



Based on the $C_2H_2Br_4$, on one pass through the reactor the conversion is 80%, and the unreacted $C_2H_2Br_4$ is recycled. On the basis of 1000 kg of $C_2H_2Br_4$ fed to the reactor per hour, calculate

(1) how much C_2H_2 is produced per hour (in lb);
(2) the rate of recycle in lb/hr;
(3) the amount of Zn that has to be added per hour if Zn is to be 20% in excess;
(4) the mole ratio of $ZnBr_2$ to C_2H_2 in the products.