Laboratory of Computational Systems Biotechnology

EPFL

Introduction to Chemical Engineering

Teaching by:

Vassily Hatzimanikatis (vassily.hatzimanikatis@epfl.ch)

Assistants:

Denis Joly (denis.joly@epfl.ch)
Konrad Lagoda (konrad.lagoda@epfl.ch)
Zi Xuan Ng (zixuan.ng@epfl.ch)

Office hours: Mondays 16h-19h (CH H4 625) or schedule by email

Fridays, 14h15 - 17h00
2024-2025

Course Schedule

Date	Subject
13-Sep	**1. Fundamentals of Material Balances** 1.1. Process definition and classification 1.2. Material balance calculations
20-Sep	1.3. Balances on multiple-unit processes
27-Sep	**Review on Mass Balances (non-reactive)**
04-Oct	1.4. Chemical reaction stoichiometry **1.5.1 Balances on reactive processes (part 1)**
11-Oct	**1.5.2 Balances on reactive processes (part 2)** **1.6. Balances on multiple unit reactive processes** **Review on Mass Balances (non-reactive & reactive)**
18-Oct	**2. Energy and Energy Balances** 2.1. Energy balances on closed systems 2.2. Open systems at steady state
01-Nov	**3. Balances on Non-Reactive Processes** 3.1. Energy balance calculation 3.2. Changes in Pressure, Temperature, Phases 3.3. Mixing and Solution
08-Nov	**4. Balances on Non-Reactive Processes** Problems: Mass and Energy Balances on non-Reactive Systems
15-Nov	**Midterm Exam: Mass & Energy Balances non-Reactive Systems**
22-Nov	**Review Midterm**
29-Nov	**5. Balances on Reactive Processes** 5.1. Heats of reaction/combustion 5.2. Combustion reactions 5.3. Enthalpy of reaction 5.4. Energy balance calculation
06-Dec	**6. Energy balances on mixing processes** **Review**
13-Dec	**Review and Study Session**

Recommended textbook:
Elementary Principles of Chemical Processes
Richard M. Felder & Ronald W. Rousseau

Session IV: Friday 11 October 2024

After studying this session, you will be able to:

1. Perform Mass Balances on Reactive Systems (atom balance)
2. Understand the concepts of Recycle, Bypass and Purge, as well as the advantages of applying them
3. Perform Mass Balances on multiple unit processes with recycle, bypass or purge of streams

1. Mass Balance on Reactive Systems (atom balance)

Mass Balance on Reactive Systems(atom balance)

- Knowing <u>that number of atoms of any given element does not change in any reaction</u>, how the "mother of all equation" changes for atomic balancing??

$$\text{In} + \cancelto{0}{\text{Gen}} - \text{Out} - \cancelto{0}{\text{Cons}} = \cancelto{0}{\text{Acc}}$$

$$\underline{\textbf{In} - \textbf{Out} = \textbf{0}}$$

Assume st.st.

- When analyzing a reacting system, you must choose *either* an atom balance *or* a molecular species balance but **not both**
  - An atom balance often yields simpler algebra (especially for multiple reactions)
  - When doing **atom balances**, <u>the extent of reaction does not count as an unknown</u>, while with a molecular species balance it does
  - When you're doing an atom balance you should only include reactive species, not inerts

Example 1: Balance on reactive process on molecular and/or atomic species

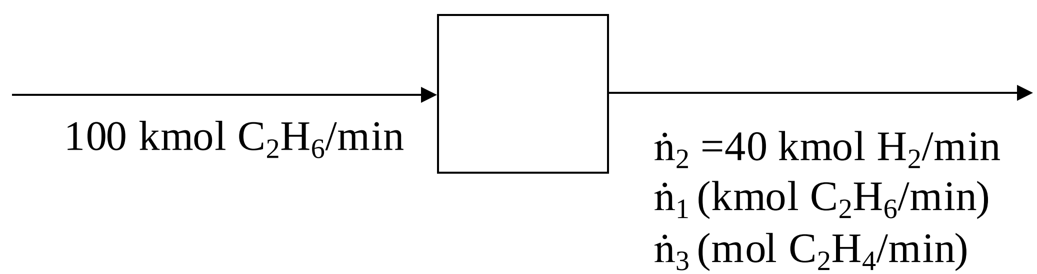
Reaction: Dehydrogenation of ethane is in steady-state continuous reactor

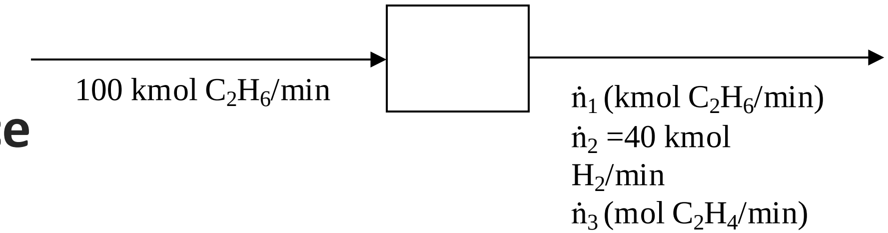
$$C_2H_6 \rightarrow C_2H_4 + H_2$$

100 kmol C_2H_6/min is reacting to produce 40 kmol H_2/min. Balance it !

- For simplification: n_1=ethane, n_2=Hydrogen, n_3= Ethylene

1) Draw the flowchart





a) molecular species balance

2) Mass balance:

Ethane molecular balance : $\dot{n}_{1,in} - \dot{n}_{1,Out} + \dot{n}_{1,Rct} = 0 \rightarrow \dot{n}_{1,in} - \dot{n}_{1,Out} - \xi = 0$

H_2 balance : $\dot{n}_{2,in} - \dot{n}_{2,Out} + \dot{n}_{2,Rct} = 0 \rightarrow \dot{n}_{2,in} - \dot{n}_{2,\ Out} + \xi = 0$

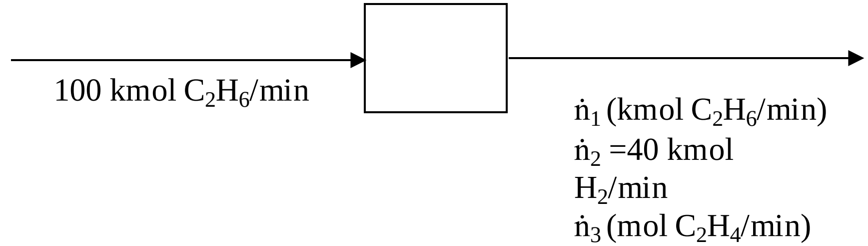
$\rightarrow \xi = 40$

$\rightarrow \dot{n}_{1,Out} = 60$ kmol / min

Ethylene balance: $\dot{n}_{3,in} - \dot{n}_{3,\ Out} + \dot{n}_{3,Rct} = 0 \rightarrow \dot{n}_{3,in} - \dot{n}_{3,\ Out} + \xi = 0$

$\rightarrow \dot{n}_{3,\ Out} = 40$ kmol /min

$n_{tot} = 140$ kmoles $\rightarrow$ 42.9 % C_2H_6, 28.5 % H_2, 28.5 % C_2H_4



b) Balance on atomic species

Carbon balance:

$$\dot{n}_{c,in} - \dot{n}_{c,\,Out} = 0 \quad \rightarrow \quad 2 \times 100 \text{ k mol of } C_2H_6 \,/\, \text{min} = 2 \times \dot{n}_{1,\,Out} + 2 \times \dot{n}_{3,\,Out}$$

$$\rightarrow \quad 100 \text{ kmol of C} \,/\, \text{min} = \dot{n}_{1,\,Out} + \dot{n}_{3,\,Out}$$

Hydrogen balance:

$$\dot{n}_{H,in} - \dot{n}_{H,\,Out} = 0 \rightarrow 6 \times 100 \text{ kmol of } C_2H_6 \,/\, \text{min} = 6 \times \dot{n}_{1,out} + 4 \times \dot{n}_{3,\,Out} + 80 \text{ kmol of H /min}$$

$$\rightarrow \quad 600 \text{ kmol of H} \,/\, \text{min} = 6\,\dot{n}_{1,\,Out} + 4\,\dot{n}_{3,\,Out} + 80 \text{ kmol of H /min}$$

$$\begin{cases} 6\,\dot{n}_{1,\,Out} + 4\,\dot{n}_{3,\,Out} = 520 \text{ kmol of H /min} \\ \dot{n}_{1,\,Out} + \dot{n}_{3,\,Out} = 100 \text{ kmol of C / min} \end{cases}$$

$$\rightarrow \dot{n}_{1,\,Out} = 60 \text{ kmol / min}, \quad \dot{n}_{3,\,Out} = 40 \text{ kmol/min}$$ ☺

Example 2

Methane is burned with air in a continuous steady-state reactor to yield a mixture of carbon monoxide, carbon dioxide, and water. The reactions taking place are:

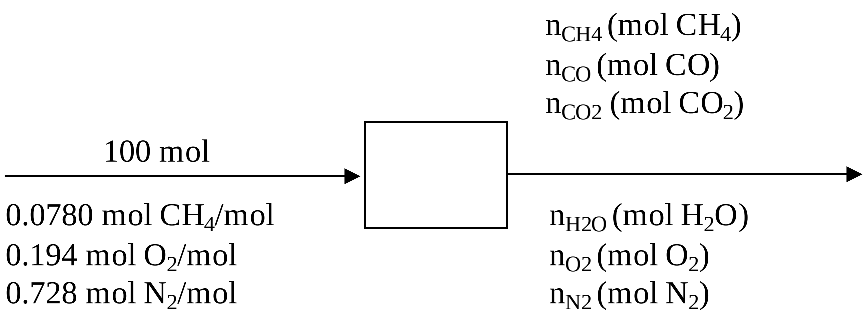
$$CH_4 + 3/2\ O_2 \rightarrow CO + 2\ H_2O \quad (1)$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \quad (2)$$

The feed to the reactor contains 7.80 mol % CH_4, 19.4 mol% O_2 , and 72.8 mol % N_2. The percentage conversion of methane is 90.0%, and the gas leaving the reactor contains 8 mol CO_2/mol CO.

- Carry out a degree-of-freedom analysis on the process. Then calculate the molar composition of the product stream using molecular species balances and atomic balances.

1) Draw a diagram



2) Basis:100 mol feed

$$CH_4 + \mathit{3/2}\ O_2 \rightarrow CO + 2\ H_2O \quad (1)$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \quad (2)$$

a) molecular species balance

3) DOF analysis

Molecular species balance: 5 unknown variables + 2 independent reactions – 5 molecular species balances – relationship between CO and CO_2 – 1 specified methane conversion = 0 degree of freedom

4) Calculations with the Mass balances

Methane balance: $n_{CH4,in} - n_{CH4,out} + (-1\xi_1 - 1\xi_2) = 0$

Oxygen balance: $n_{O2,In} - n_{O2,Out} + (-\mathit{3/2}\ \xi_1 - 2\xi_2) = 0$

Nitrogen balance: $n_{N2,In} - n_{N2,Out} + 0 = 0 \rightarrow n_{N2,In} = n_{N2,Out} \rightarrow n_{N2,Out} = 72.8$ mol

Carbon dioxide balance: $n_{CO2,In} - n_{CO2,Out} + \xi_2 = 0 \rightarrow n_{CO2,Out} = \xi_2$

Carbon monoxide balance: $n_{CO,In} - n_{CO,Out} + \xi_1 = 0 \rightarrow n_{CO,Out} = \xi_1$

Water balance: $n_{H2O,In} - n_{H2O,Out} + (2\xi_1 + 2\xi_2) = 0$

Conversion of methane: $0.9 = (n_{CH4,In} - n_{CH4,Out}) / n_{CH4,In} \rightarrow 0.9 = (7.8 - n_{CH4,Out})/7.8 \rightarrow$

$n_{CH4,Out} = 0.78$ mol

$$CH_4 + \textit{3/2}\ O_2 \rightarrow CO + 2\ H_2O \quad (1)$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \quad (2)$$

- Relationship between CO and CO_2

$n_{CO2,Out} = 8n_{CO,Out} \rightarrow \xi_2 = 8\xi_1$

- By using the methane balance:

7.8 mol – 0.78 mol + $(-1\xi_1 - 8\xi_1) = 0 \rightarrow \xi_1 = 0.78$ mol and $\xi_2 = 6.24$ mol

$n_{CO,Out}$ = 0.78 mol of CO

$n_{CO2,Out}$ = 6.24 mol of CO_2

$n_{O2,Out}$ = 5.75 mol of O_2

$n_{H2O,Out}$ =14.0 mol of H_2O

- Final result:

0.78% CH_4, 0.78% CO, 6.2% CO_2, 14.0% H_2O, 5.7% O_2 & 72.5% N_2

$$CH_4 + 3/2\ O_2 \rightarrow CO + 2\ H_2O \quad (1)$$
$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \quad (2)$$

b) Atomic species balance

3) DOF analysis

DOF: 5 unknowns variables – 3 independent atomic species balance – relationship between CO and CO_2 one specified methane conversion = 0

4) Calculations with the Mass balances

Carbon atomic balance:

$$1n_{CH4,In} - 1n_{CH4Out} - 1n_{CO,Out} - 1n_{CO2,Out} = 0$$

Hydrogene atomic balance:

$$4n_{CH4,In} - 4n_{CH4,Out} - 2n_{H2O,Out} = 0$$

Oxygen atomic balance:

$$2n_{O2,In} - 2n_{O2,Out} - 1n_{CO,Out} - 2n_{CO2,Out} - 1n_{H2O,Out} = 0$$

Relation between CO and CO_2:

$$n_{CO2,Out} = 8n_{CO,Out}$$

$$CH_4 + \mathit{3/2}\ O_2 \rightarrow CO + 2\ H_2O \quad (1)$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \quad (2)$$

Conversion of methane:

$0.9 = (n_{CH4\ ,In} - n_{\ CH4,Out}) / n_{CH4,In} \rightarrow 0.9 = (7.8 - n_{CH4,Out})/7.8 \ \rightarrow n_{CH4,Out} = 0.78$ mole

Carbon atomic balance:

$7.8 – 0.78 – n_{CO,Out} – 8n_{CO,Out} = 0 \rightarrow n_{CO,Out} = 0.78$ mol of CO

$n_{CO2,Out} = 8 \times 0.78 = 6.24$ mol of CO_2

And we found $n_{H2O,Out} = 14.0$ mol of H_2O

$n_{O2,Out} = 5.7$ mol of O_2

2. Concepts of Recycle, Bypass and Purge

Terminology and quantification in reactive mass balances

To understand the chemical processes, first we need to understand the words:

Recycle	To put or pass through a cycle again, as for further treatment
Bypass	An alternative passage created to divert the flow and circumvent an obstructed or congested area
Purge	To free from impurities, purify

3. Mass balance on multiple unit processes

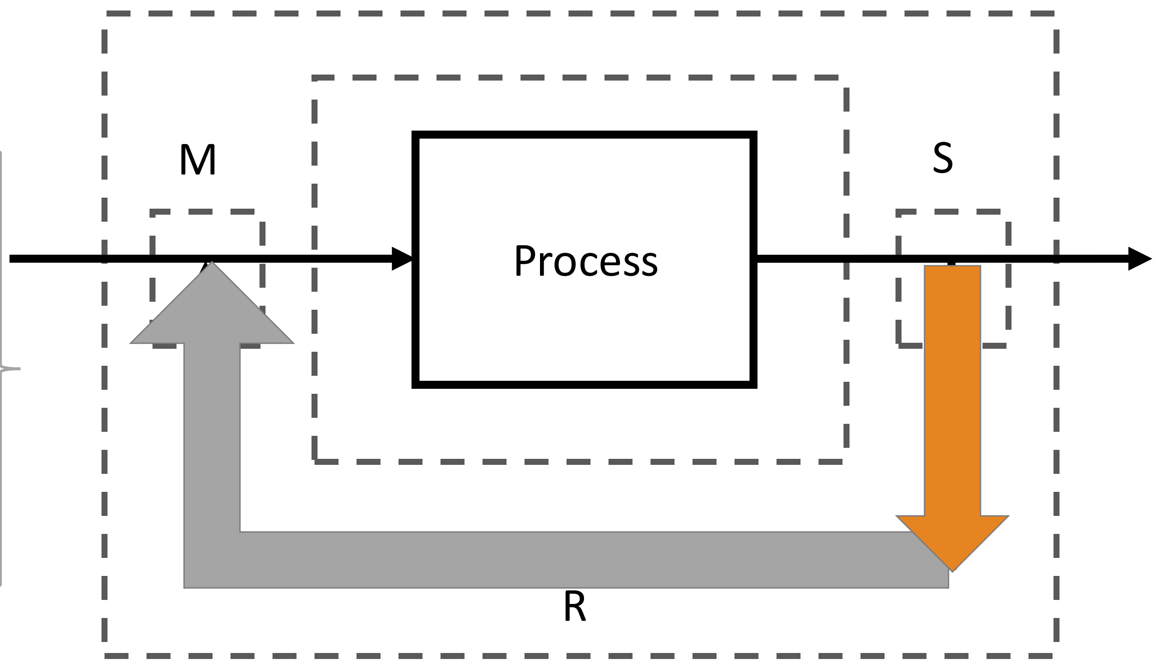
Recycle

A **recycle stream (R)** sends back a part of the outgoing stream of a process unit into a fresh feed stream that enters the same process unit.

Example: we want to recycle a fraction of the product stream from a reactor. How would you draw it?

... and mixing it with the reactants.

The mixture will be fed to the process unit.



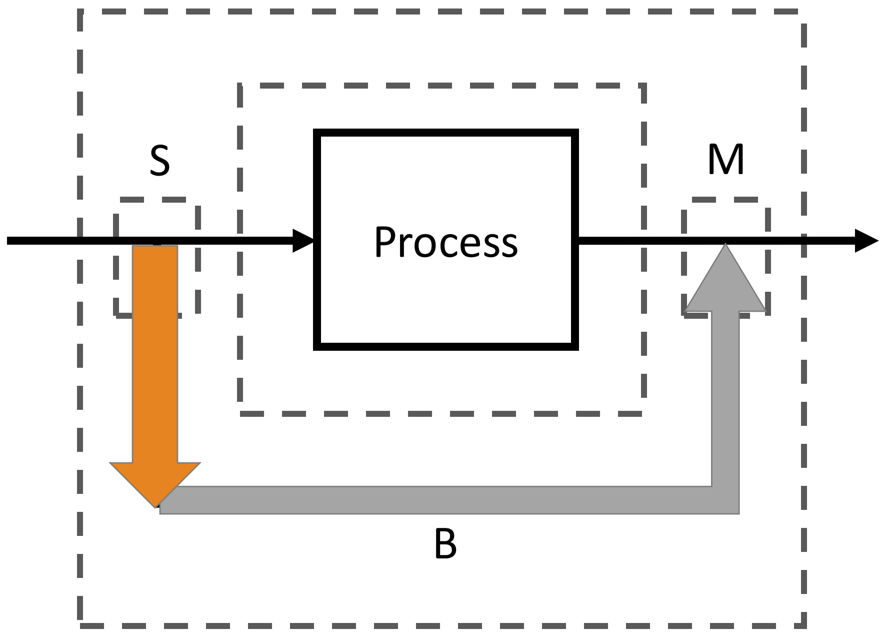
Recycling implies separating part of the product stream ...

Bypass

A **bypass stream (B)** sends forward a portion of the inlet stream in a process unit to the product stream from the process unit. This portion of stream will skip the process unit.

Example: we want to bypass a fraction of the feed stream that would enter a reactor. How would you draw it?

Bypassing implies separating part of the feed stream …



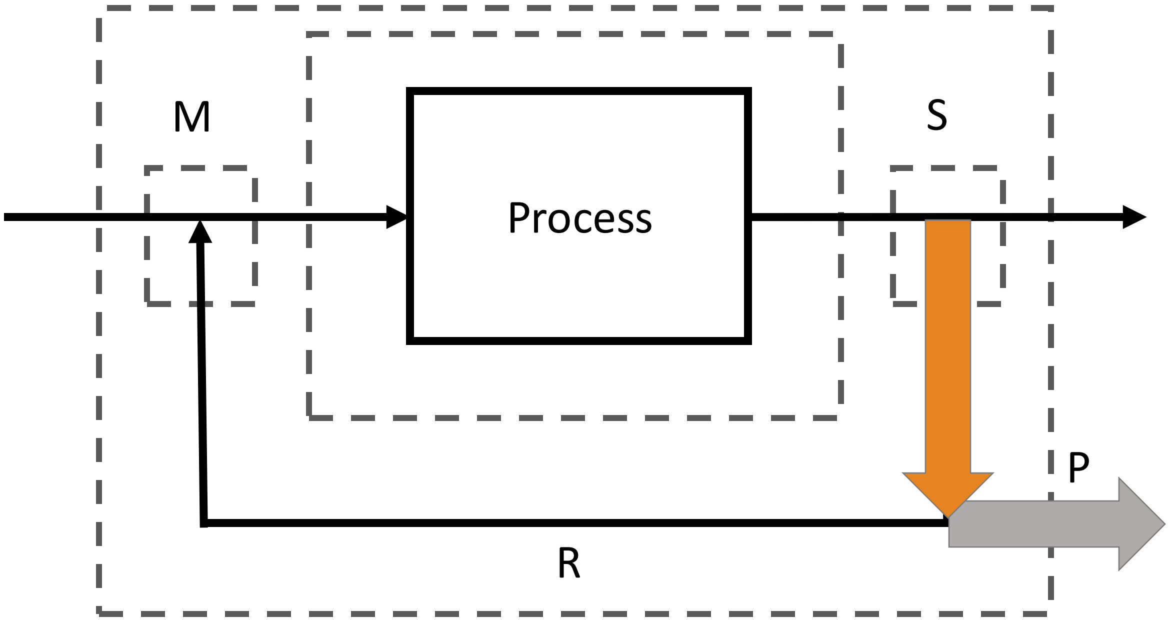
… and mixing it with the product stream.

The mixture will be the final output of the process.

Purge

A **purge stream (P)** sends out of the process a portion of another stream, in order to eliminate undesired components.

Example: we want to purge a fraction of the recycling stream for a reactor. How would you draw it?



Purging implies separating a portion of a stream…

…and sending it out of the process.

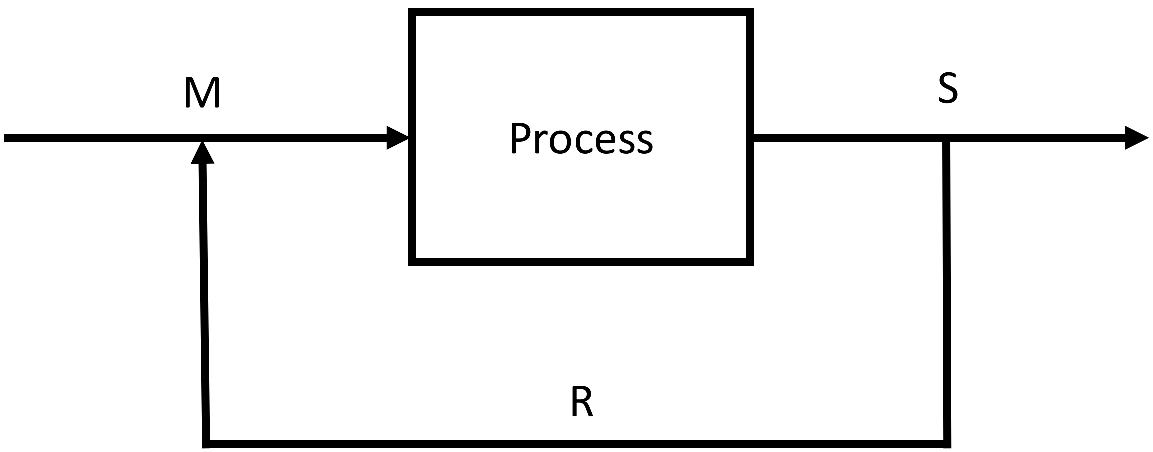
Why purging a recycle stream? to avoid accumulation of undesired materials in a recycled system

Why recycle, bypass or purge?

Process:	**Advantages(examples):**
Recycle	We can separate from the stream the products from reactants that have not reacted. If we recirculate the reactants, we can <u>increment the overall conversion</u> -> ECONOMICALLY AND ENVIRONMENTALLY USEFUL
Bypass	<u>Reach final product specifications</u> (concentration of a component) by mixing streams -> might improve the quality of the final product (see S4E4 orange juice)
Purge	We can <u>eliminate undesired substances</u> and <u>avoid accumulation</u> of them in the system. -> improves the purity of the product and makes waste treatment easier

Recycling: Application and Advantages

Recycling is used in a wide variety of processes



The use of recycle makes a great deal of environmental *and* economic sense

Using recycle lets achieving a wider range of separations

By using recycle, it is possible to recover expensive **catalysts and reagents**

Recycle reduces the amount of waste that a company generates

Recycling: Considerations in the analysis

Remember, when recycling:

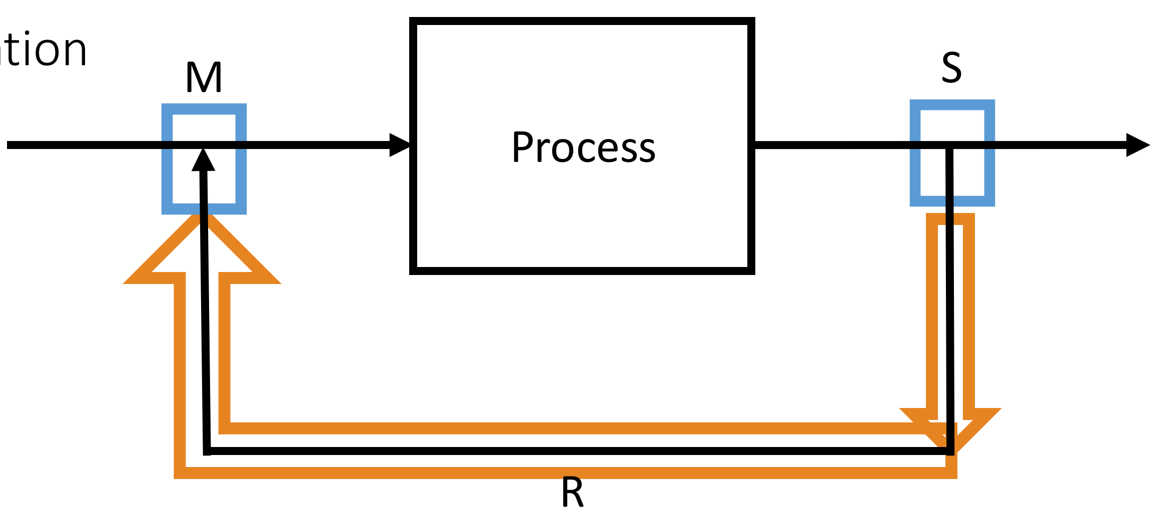
(1) we separate part of the output stream

(2) and we mix it with the feed

Therefore, we generate **two new and important points of study**:

(1) The <u>splitting point OR a separator</u>: separation point in product stream

(2) the <u>recombination point</u>: mixing point in feed stream



Recycling: IMPORTANT Considerations in the analysis

Will the composition of the streams that participate in a recombination point differ?

Yes, unless the feed and the recycle stream have the same composition (which is not normally the case)

Will the composition of the streams that participate in a separator (e.g.: distillation column, evaporator, extractor) **differ?**

Will the composition of the streams that participate in a splitting point differ?

Recycling: Considerations in the analysis

- The **composition of the streams** around the recombination and splitting point (or separator) should be known.

- These **streams are internal** in the process, since they don't cross the boundaries of the system.

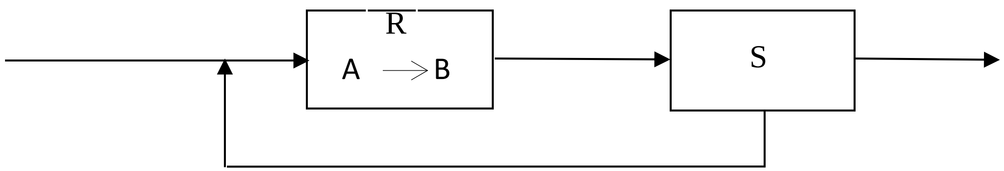
How can we calculate the composition of the new streams?

- The recombinant point and the splitting point or separator will be considered as **new subsystems**

- We have to perform **mass balances** around these points

- The mass balance analysis of these processes follows the same considerations as explained in the **processes with multiple units**

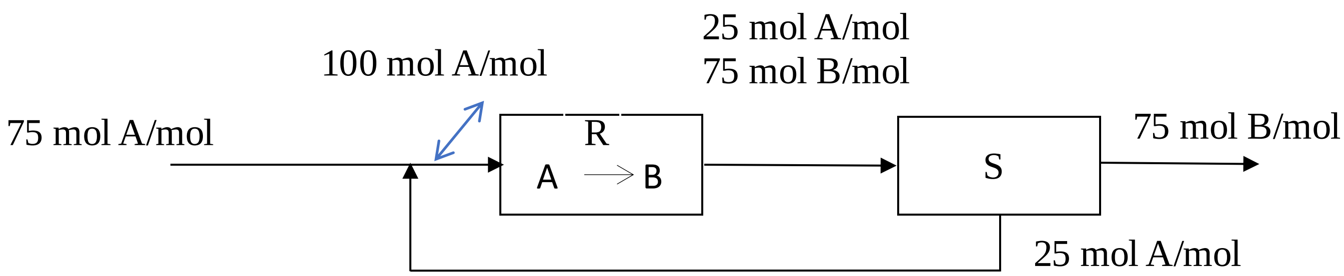
Recycling introduces two types of conversion!



$$\textbf{Single-pass conversion} = 100 * \frac{\text{Reactant input to reactor} - \text{Reactant output to reactor}}{\text{Reactant input to reactor}}$$

$$\textbf{Global/Overall conversion} = 100 * \frac{\text{Reactant input to overall process} - \text{Reactant output to overall process}}{\text{Reactant input to overall process}}$$

Calculate the two types of conversions



Single-pass conversion of A

(100-25)/100 =75%

Global conversion of A

(75-0)/75=100%

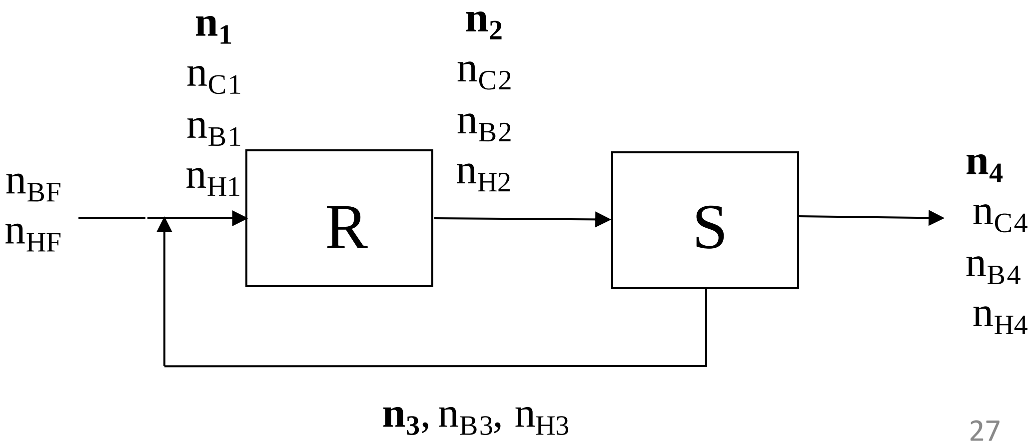
Example 3: Recycling after a reactor

Cyclohexane C_6H_{12} is made from benzene and H_2 according to the following reaction:

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

20% excess H_2 is used in the fresh feed/input and the single pass conversion is 20%, the output goes into a separator and part is recycled. How much should be **the ratio of recycle stream to feed stream** in order to achieve an overall conversion of 95% , if the recycle is 22.74% mol B and 77.26% mol H_2.
For simplification: n total , n_C mol cyclohexane, n_B mol benzene, n_H mol H_2

0) Units: mol, %-mol
1) Flowchart, subsystems
2) Basis: 100 mol B

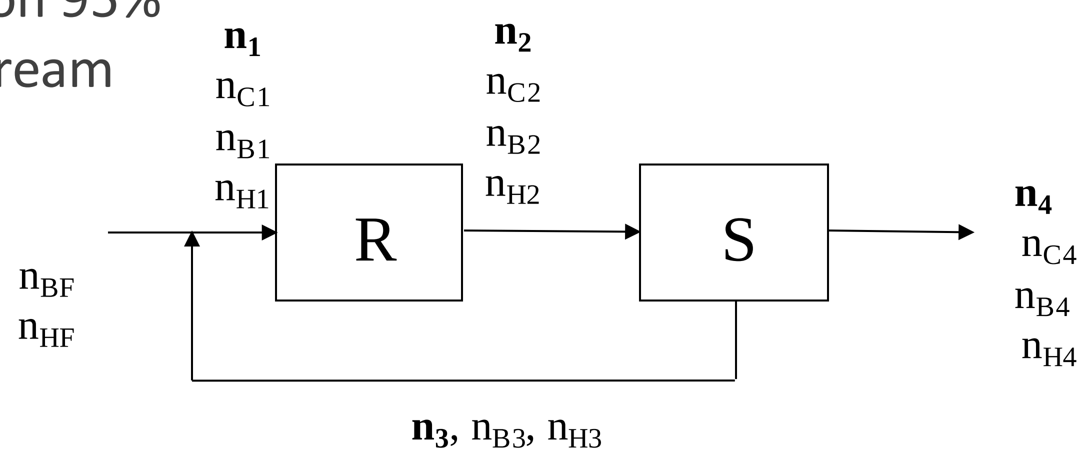


WE NEED TO LOOK FOR :
$n_3 / (n_{BF} + n_{HF})$

Example 3: Recycling after a reactor

KNOWN:

- 20% excess H_2
- Single pass conversion 20%
- We want overall conversion 95%
- Composition of recycle stream



Single pass conversion → conversion only around the reactor

$0.2 = n_{B1} - n_{B2} / n_{B1}$ → $\mathbf{n_{B2}} = 0.8\, n_{B1}$

Overall conversion → conversion on the overall system

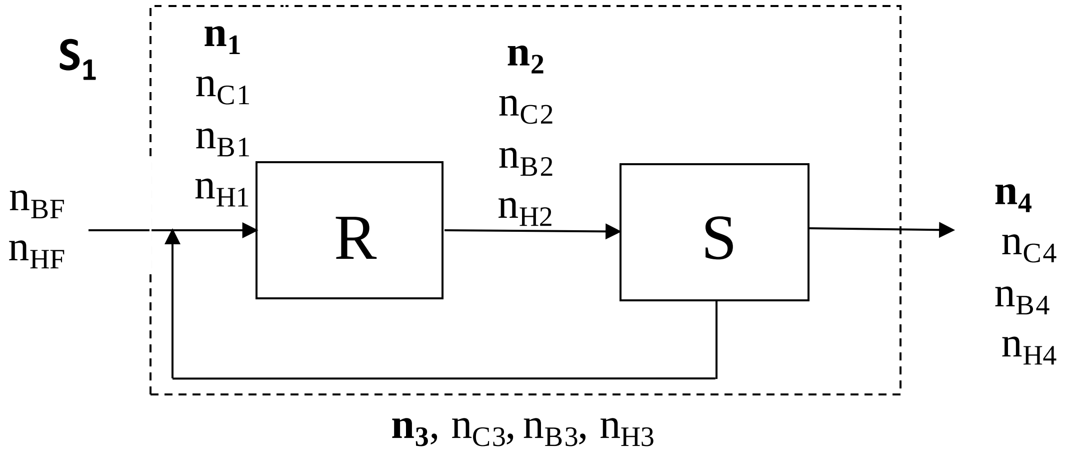
$0.95 = 100 - n_{B4} / 100$ → $\mathbf{n_{B4}} = 5$ mol of B

20% excess H_2: 20% more than if all B had reacted

If all 100 mol B reacted we need 300 mol H_2 → 20% excess H_2 →

$\mathbf{n_{HF}}$ = 360 mol

Example 3: Recycling after a reactor



S_1 (global system) :

- Benzene mass balance:

$100 - 5 - \xi = 0 \rightarrow \boldsymbol{\xi} = 95$ mol

- H_2 mass balance:

$360 - n_{H4} - 3\xi = 0 \rightarrow \mathbf{n_{H4}} = 75$ mol

- Cyclohexane mass balance:

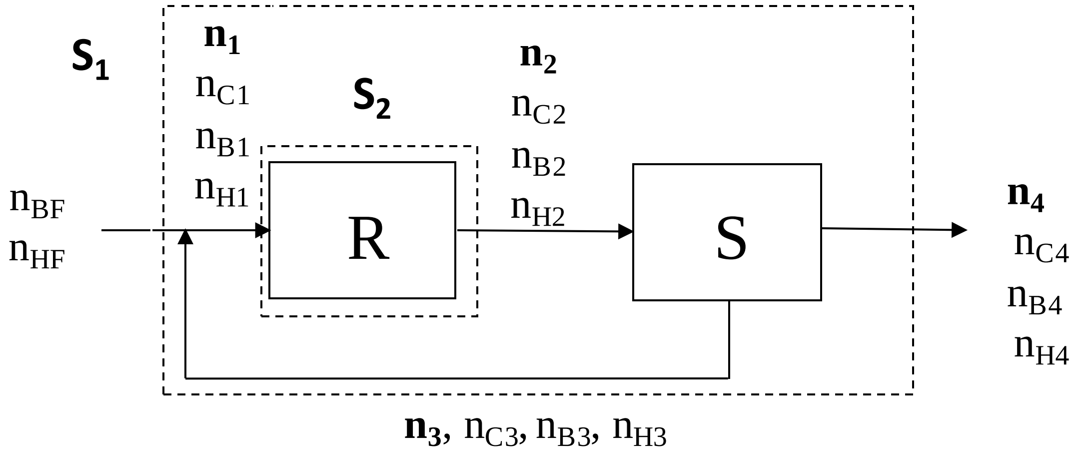
$0 - n_{C4} + \xi = 0 \rightarrow \mathbf{n_{C4}} = 95$ mol

The number of total mol leaving the reactor:

$\mathbf{n_4}$ = 5 mol of benzene + 75 mol of H_2 + 95 mol of cyclohexane = 175 mol

Is ξ in the reactor different from ξ in overall system?

Example 3: Recycling after a reactor



S_2 (reactor) :

- Benzene mass balance:

$n_{B1} - n_{B2} - \xi = 0 \rightarrow n_{B1} - 0.8n_{B1} - 95 \text{ moles} = 0 \rightarrow \mathbf{n_{B1}} = 475 \text{ mol}$

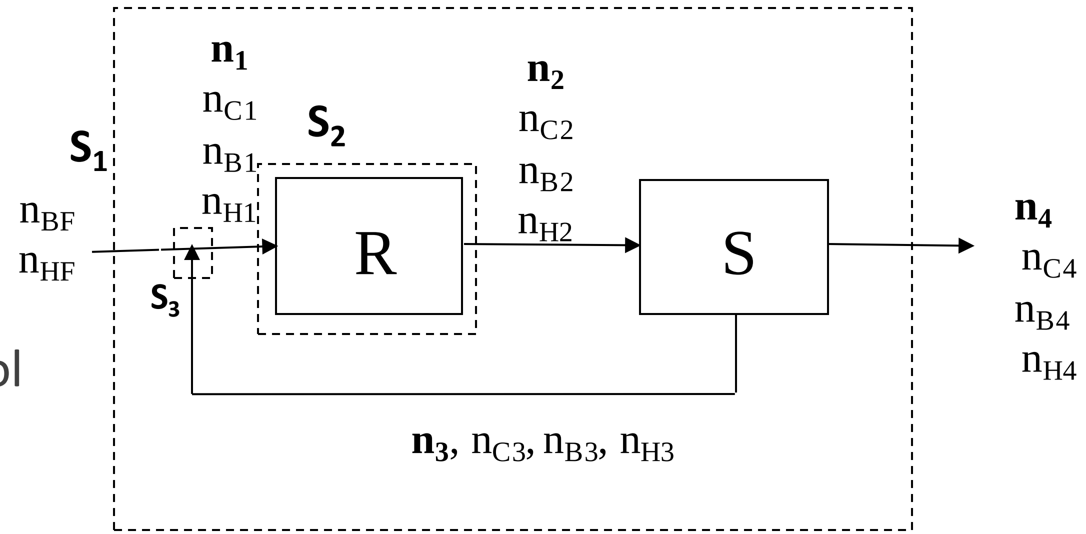
- H_2 mass balance:

$n_{H1} - n_{H2} - 3\xi = 0 \rightarrow \mathbf{n_{H1}} = n_{H2} + 3 \times 95$

- Cyclohexane mass balance:

$n_{C1} - n_{C2} + \xi = 0 \rightarrow \mathbf{n_{C1}} = n_{C2} - \xi$

Example 3: Recycling after a reactor



S_3 (mixing system) :

- B mass balance:

$100 + n_{B3} - 475 = 0 \rightarrow \mathbf{n_{B3}} = 375$ mol

- H_2 mass balance:

$360 + n_{H3} - n_{H1} = 0$

- C mass balance:

$0 + n_{C3} - n_{C1} = 0 \rightarrow \mathbf{n_{C1}} = 0$

(in the recycle stream, there is no cyclohexane, so $n_{C3} = 0$)

From the reactor we find : $\mathbf{n_{C2}} = 95$ mol

$n_{H3}/n_{B3} = 77.26/22.74 \rightarrow n_{H3} = 3.4n_{B3} \rightarrow \mathbf{n_{H3}} = 1275$ mol

$\mathbf{n_{H1}} = 1635$ mol, $\mathbf{n_{H2}} = 1350$ mol, $\mathbf{n_{B2}} = 380$ mol

SOLUTION: recycle stream /feed stream = $(n_{B3} + n_{H3}) / (n_{HF} + n_{BF}) = 1650/460 = 3.6$

-> **most of the stream going into the reactor comes from recycled reactants**