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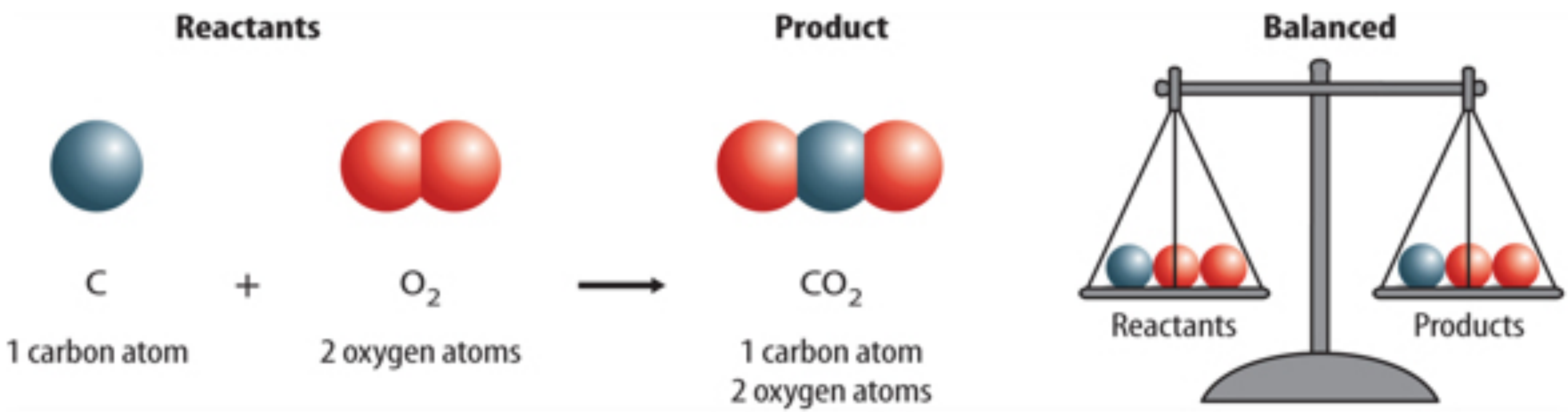
Material Balances 2: Chemical Reactions Involved



Outline

- The Chemical Equation and Stoichiometry
- Excess and Limiting Reactants
- Conversion, Yield, and Selectivity
- Material Balances with Reactions
- Combustion Reactions
- Recycle, Bypass, Purge

Recall: Material Balance Equation

- Conservation Laws
  - Mass (except in nuclear reactions)
    - Moles are NOT conserved when there are reactions!
    - Volume is generally NOT conserved
  - Energy (1st Law of Thermodynamics)
- For any conserved property,

In – Out + Gen = Acc

  - IN: sum of all flow rates into the system
  - OUT: sum of all flow rates going out of the system
  - **GEN: formation or consumption within the system**
  - ACC: net rate of change of the property in the system (zero at steady-state)

Recall: Material Balance Equation

- For steady-state processes involving reactive species:

$$\boxed{\textbf{Input} + \textbf{Generation} = \textbf{Output} + \textbf{Consumption}}$$

- The generation and consumption terms in the molecular balance equation is usually obtained from chemical stoichiometry.
- Atomic balance?

Reaction Stoichiometry

- Refers to calculation of weights of substances involved in chemical reactions

$$aA + bB \longrightarrow cC + dD$$

- a & b, c & d → molecules (moles) of A & B, C & D
- Balanced chemical equation:
  - Number and types of atoms
  - Sum of masses
- Stoichiometric ratios
  - Obtained from numerical coefficients of chemical equations (conversion factors)
- Multiple reactions

$$a_1A + b_1B \longrightarrow cC$$

$$a_2A + b_2B \longrightarrow dD$$

Reaction Stoichiometry

- Example: Balance the reaction of pyrites and oxygen to form ferric oxide and sulfur dioxide.

Pyrites + oxygen $\rightarrow$ ferric oxide + sulfur dioxide

$$FeS_2 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

- Example: How many kg SO_2 and Fe_2O_3 will 100 kg FeS_2 produce? How much O_2 is needed?

Reaction Stoichiometry

- Gravimetric Factor
  - Stoichiometric masses

$$aA + bB \longrightarrow cC + dD$$

  - Mass A = a x MW_A

$$\frac{Mass\ A}{Mass\ C} = \frac{a\left(MW_A\right)}{c\left(MW_C\right)}$$

$$\frac{Mass\ D}{Mass\ B} = \frac{d\left(MW_D\right)}{b\left(MW_B\right)}$$

- Useful to calculate mass balance without writing the balanced chemical equation

- Example: Find the K_2O equivalent of 50 kg KCl.

Reaction Stoichiometry

- Example: We desire to manufacture a fertilizer with a formula 2-12-6 (represented by total nitrogen expressed as %N, available phosphate expressed as $\%P_2O_5$, and soluble potash expressed as $\%K_2O$, respectively.) from ammonium nitrate, calcium phosphate, potassium chloride of 90% purity, and inert fillers. How much of each material should we mix to obtain 1000 kg of the final product?

Excess and Limiting Reactants

- Stoichiometric ratios → theoretical
- Excess and limiting reactants
  - One reactant supplied in excess to hasten or promote the reaction
  - Other reactant is the limiting one (will run out if process goes to completion)

$$\%\ excess = \frac{moles\ in\ excess}{moles\ required\ to\ react} x100\%$$

  - Check: calculate mole ratios in feed, then compare with stoichiometric ratios
- Example: 5 gmol FeS_2 reacts with 10 mol O_2

Excess and Limiting Reactants

$$fractional\ excess = \frac{n_{feed} - n_{stoich}}{n_{stoich}}$$

$$\%\ excess = \frac{n_{feed} - n_{stoich}}{n_{stoich}} x100\%$$

- Check: calculate mole ratios in feed, then compare with stoichiometric ratios

- Example: hydrogenation of acetylene to form ethane:

$$C_2H_2 + 2H_2 \longrightarrow C_2H_6$$

Suppose that 20.0 kmol/h of acetylene and 50.0 kmol/h hydrogen are fed to the reactor, determine the limiting reactant, and calculate for the fractional excess of the other reactant.

Conversion, Yield, Selectivity

- Conversion
  - Fraction of the limiting reactant transformed or converted into products (degree of completion)
  - For multiple products: conversion to a specific product has to be specified

$$\boxed{\textit{fractional conversion} = \frac{\textit{moles reacted}}{\textit{moles fed}}}$$

- Ex: 100 moles fed and 90 moles reacted

- Ex: 20 mol/min of a reactant is fed and the percentage conversion is 80%

Conversion, Yield, Selectivity

$$A + B \longrightarrow C \text{ (desired product)}$$

$$A + B \longrightarrow D \text{ (side product)}$$

- Selectivity

$$selectivity = \frac{moles\ of\ desired\ product\ formed}{moles\ of\ undesired\ product\ formed}$$

- Yield
  - Ratio of the actual amount of desired product formed to the amount of product had the reaction gone to completion
  - Undesired side reactions, incomplete reactions, chemical equilibrium → reduce yield

Conversion, Yield, Selectivity

- Example: Yield and Selectivity

Consider the following pair of reactions

$$A \longrightarrow 2B \text{ (desired)}$$

$$A \longrightarrow C \text{ (undesired)}$$

Suppose 100 mol of A is fed to a batch reactor and the final product contains 10 mol of A, 160 mol of B, and 10 mol of C. Calculate

(a) The fractional conversion of A.

(b) The percentage yield of B.

(c) The selectivity of B relative to C.

Ideal and Industrial Reactions

Comparison of Ideal and Industrial Reactions

Ideal (Theoretical Reaction)	Industrial Reaction
complete	Seldom complete
Stoichiometric amounts are used	Some reactants are in excess
Pure materials are used	Raw materials are impure or mixed with other substances
Assumed to occur at only one condition	Occurs over a wide range of temperature, pressure, and concentration
No competing side reactions are involved	Several reactions may occur simultaneously
Stoichiometric amounts of products are obtained	Products will contain side products and unreacted or excess reactants

Ideal and Industrial Reactions

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

- Condition A:
  - If the reaction is only 95% complete, what are the amounts of compounds present after the reaction?
- Condition B:
  - If the reaction is complete and 20% excess oxygen is used, find the kg of compounds after reaction.
- Condition C:
  - If the reaction is complete and 20% excess air is used, find the kg of compounds after reaction.
- Condition D:
  - If the reaction is complete, pure oxygen is used, and the pyrites contain 10% impurities, find the amounts of products.
- Condition E:
  - If 90% of the pyrites produces SO_2 while 10% produces SO_3, and all the necessary oxygen is provided, find the amounts of the products.

Material Balances with Reactions

Input + Generation = Output + Consumption

- Two approaches:
  - Molecular species balance
    - Applied to each chemical compound involved in the process
    - Generation/Consumption (from stoich)
  - Atomic species balance
    - Applied to each element appearing in the process
    - Conserved (input=output)

Material Balances with Reactions

- Example: The oxidation of ethylene to produce ethylene oxide proceeds according to the equation

$$2C_2H_4 + O_2 \longrightarrow 2C_2H_4O$$

- The feed to a reactor contains 100 kmol C_2H_4 and 100 kmol O_2.

(a) Which reactant is limiting?

(b) What is the percentage excess of the other reactant?

(c) If the process proceeds to completion, how much of the excess reactant will be left? How much C_2H_4O will be formed?

Material Balances with Reactions

- Example: Dehydrogenation Reaction of Ethane

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

100 kmol/min of ethane is fed to the reactor and the molar flow rate of H_2 in the product stream is 40 kmol/min. Compute for the molar composition of the product stream using molecular balance and atomic balance.

- Example: Yield and Selectivity in a Dehydrogenation Reactor

The reactions

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

$$C_2H_6 + H_2 \longrightarrow 2CH_4$$

Take place in a continuous reactor at steady state. The feed contains 85 mole % ethane and the balance inerts (I). The fractional conversion of ethane is 0.501, and the fractional yield of ethylene is 0.471. Calculate the molar composition of the product gas and the selectivity of ethylene to methane production.

Material Balances with Reactions

- Example: Sodium nitrite is manufactured based on the following equation:

$$Na_2CO_{3\,(s)} + 2NO_{(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow 2NaNO_{2\,(s)} + CO_{2\,(g)}$$

- The Na_2CO_3 used is first dissolved in water to form a 40% solution. The NO and O_2 used are 10% in excess of the theoretical amount and the reaction is 90% complete. Per 100 kg of Na_2CO_3, calculate

  (a) the amount of $NaNO_2$ obtained,

  (b) the composition of the resulting solution, and

  (c) the composition of the issuing gas.

  Data: (Molecular Weights)

  - Na_2CO_3 = 106
  - NO = 30
  - O_2 = 32
  - $NaNO_2$ = 69
  - CO_2 = 44

Material Balances with Reactions (Practice!)

- Example: Commercial hydrochloric acid and sodium sulfate are produced by the reaction:

$$2NaCl_{(s)} + H_2O_{(g)} + SO_{3\,(g)} \longrightarrow Na_2SO_{4\,(s)} + 2HCl_{(g)}$$

- The reaction is carried out at 482 °C at which NaCl and Na_2SO_4 exist as solids, and H_2O, SO_3, and HCl are gases. After separation of the Na_2SO_4, water will absorb the HCl. Per 1000 kg of sodium chloride charged, how much Na_2SO_4 and 37% by weight HCl solution are obtained if the reaction goes to 90% completion? If the SO_3 is supplied 20% in excess, and the water 100% in excess, how much 98% H_2SO_4 (by mass) and H_2O should be fed to the reactor?

- Data: (Molecular Weights)
  - NaCl = 58.44
  - H_2O = 18.02
  - SO_3 = 80.06
  - Na_2SO_4 = 142.04
  - HCl = 36.46
  - H_2SO_4 = 98.08

Answers:
1,027.5 kg 98% H2SO4
102.79 kg H2O should be supplied

Combustion Reactions

- Commonly employed for heat generation
- Reaction involving a fuel (gaseous, liquid, solid) and oxygen, usually from air
- Depends on the amount of carbon and available hydrogen in the fuel (Reaction with oxygen produces heat)

(1) $C + O_2 \longrightarrow CO_2 + \text{heat}$

(2) $2C + O_2 \longrightarrow 2CO + \text{heat}$

(3) $2H_2 + O_2 \longrightarrow 2H_2O + \text{heat}$

(4) $CO + 1/2O_2 \longrightarrow CO_2 + \text{heat}$

Combustion Reactions

- Theoretical air - amount required for complete combustion of C, H, (and S)
- Excess air – in excess of that required for complete combustion
- Products of combustion
  - CO_2, CO, O_2, N_2, H_2O
  - Combustion, Flue or Stack gases (wet or dry basis)

$$\% \; excess = \frac{n_{feed} - n_{stoich}}{n_{stoich}} x100\%$$

$$\% \; excess \; air = \frac{n_{excess\,air}}{n_{required\,air}} x100\% = \frac{n_{excess\,O_2}(100/21)}{n_{required\,O_2}(100/21)} x100\% = \% \; excess \; O_2$$

Combustion Reactions

- Example 1

Pure carbon is burned with theoretical amount of air. Calculate the composition of the combustion gases if

(a) The combustion is complete.

(b) 95% of the carbon burns to CO_2 and 5% burns to CO.

- Example 2

100 kg of charcoal per hour is burned with 30% excess air. The charcoal consists of 95% carbon and 5% ash. Calculate the composition of the flue gas if the combustion is complete.

Combustion Reactions

- Example 3

A liquid fuel consists of 90% carbon and 10% hydrogen by mass. It burns in a furnace using air 20% in excess of the theoretical amount necessary for complete combustion. All of the carbon is burned to CO_2 and all the hydrogen to water. The air is substantially dry and contains 21% O_2 and 79% N_2. What is the analysis of the combustion gases on a dry basis?

Combustion Reactions

Example 4

Ethane is burned completely with 30% excess air. Calculate the composition of the combustion gases on a dry basis.

Combustion Reactions

- Example 5

Burning a liquid fuel consisting only of carbon and hydrogen results in a gas analyzing 11.72% CO_2, 1.3% CO, 4.32% O_2, and 82.66% N_2. From this data, calculate the analysis of the liquid fuel. Assume theoretical amount of air is used.

Practice!

Pyrites (FeS_2 ore) is being used as a source of sulfur for the production of sulfuric acid. The ore contains 88% FeS_2 and 12% inert, non-volatile components. Air is 40% in excess of the theoretical amount required for complete reaction according to the chemical equation:

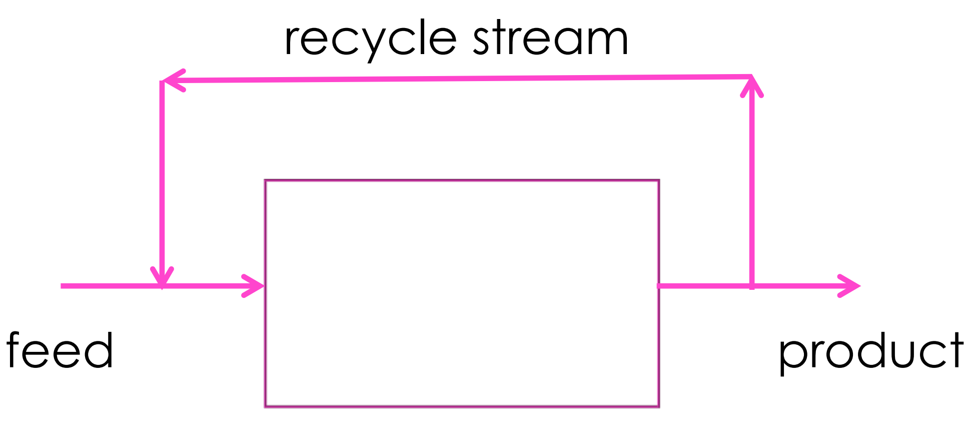
$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

If all the FeS_2 burns out but with only 90% conversion of the sulfur to SO_2 and the remaining 10% is converted to SO_3 ($4FeS_2 + 15O_2 \rightarrow 2Fe_2O_3 + 8SO_3$), what is the analysis of the combustion gases?

Answer:
1.17% SO3, 10.27% SO2, 5.68% O2, 82.88% N2

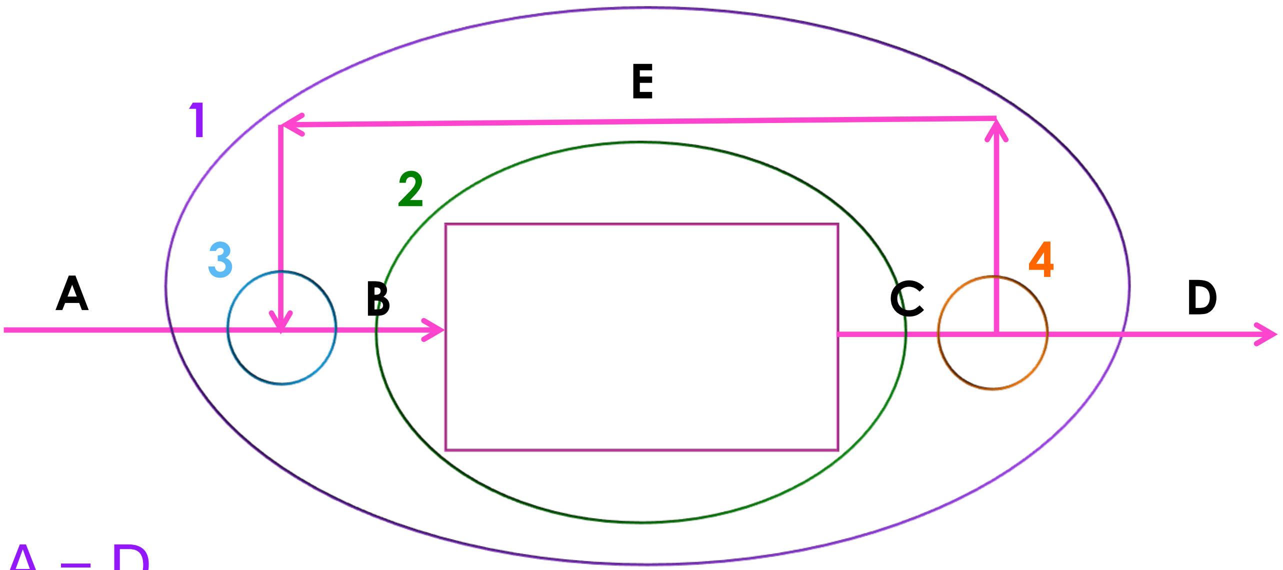
Recycle, Bypass, and Purge

- Recycle
  - Part of the product is returned and mixed with the feed entering a process equipment
    - Enhance yield
    - Product with minimum impurities
    - Energy conservation
    - Better control of product quality



Recycle, Bypass, and Purge

- Mass Balances around a process involving a recycle stream



- A = D
- B = C
- E + A = B
- C = D + E

Recycle, Bypass, and Purge

Recycle Example

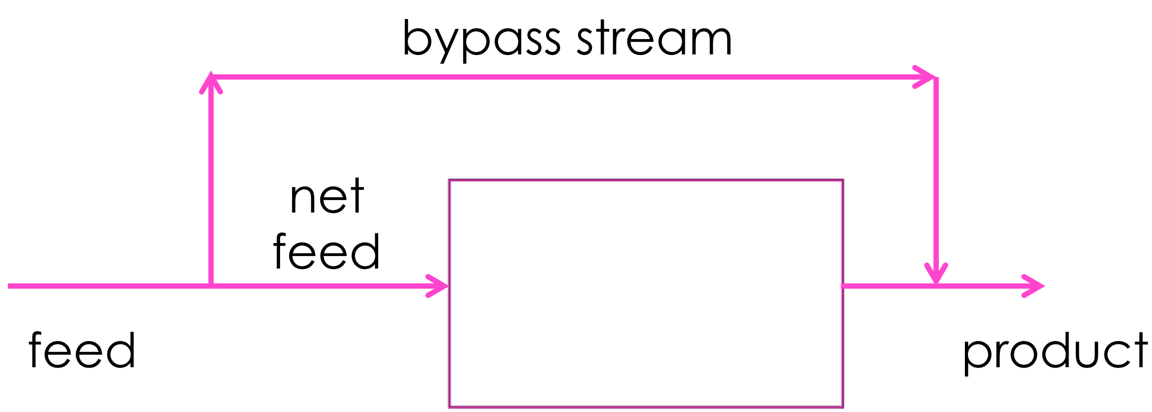
In a pilot process, a sticky material containing 80% water is to be dried. To facilitate the operation, a part of the dried product containing 5% water is recycled and mixed with the feed. If the material entering the drier contains 30% water, calculate

(a) the kg water removed per 2000 kg fresh feed, and

(b) the recycle-to-feed ratio.

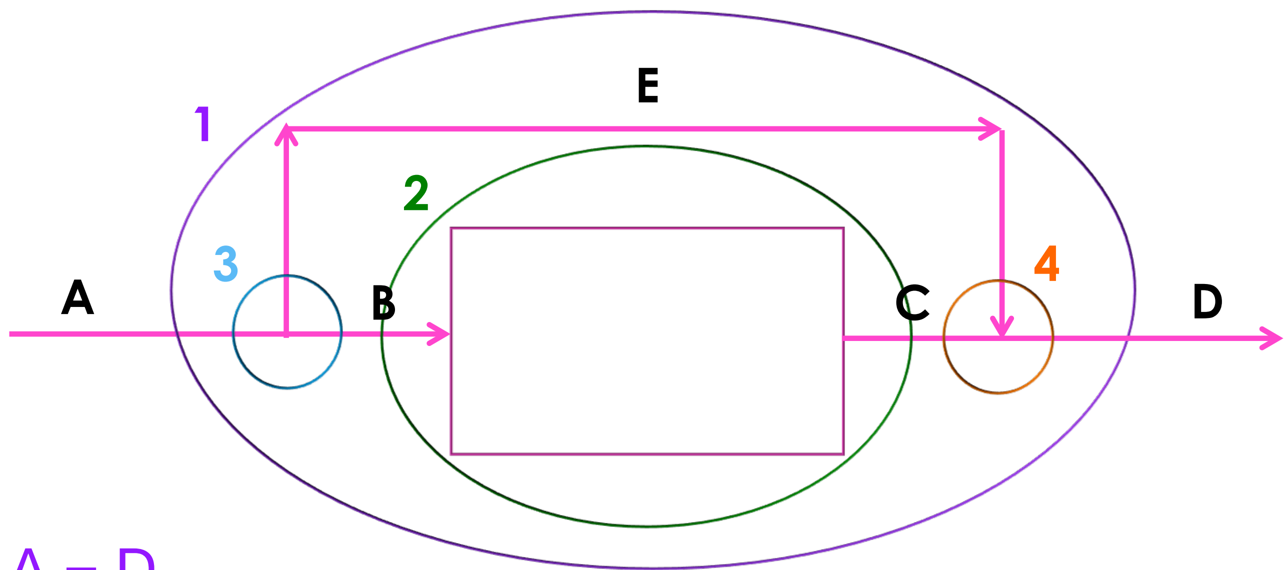
Recycle, Bypass, and Purge

- Bypass
  - A stream skips one or more stages of the process and goes directly to another stage
    - Useful to attain precise control of concentration
    - Energy conservation
    - Smaller-sized equipment is needed compared to that of a recycle stream



Recycle, Bypass, and Purge

- Mass Balances around a process involving a bypass stream

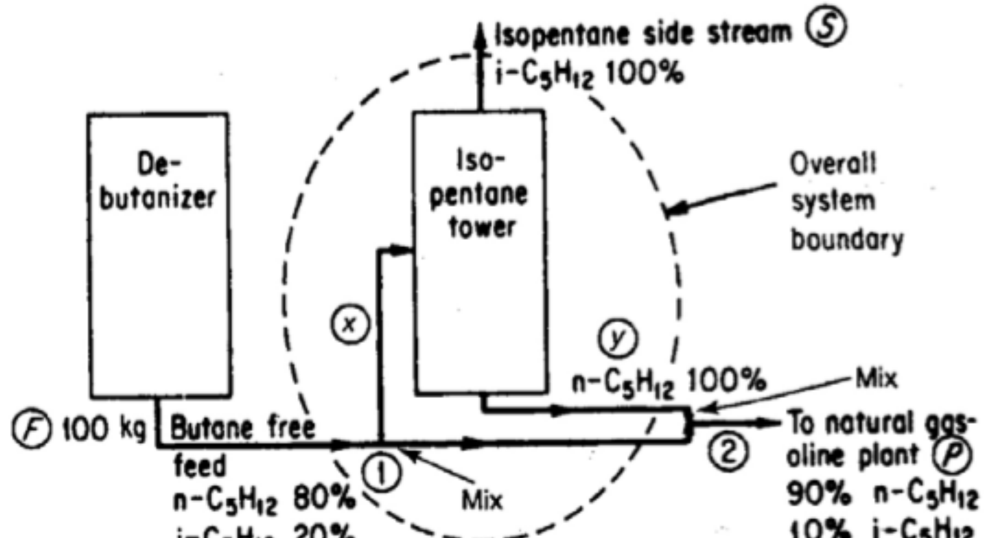


- A = D
- B = C
- A = E + B
- C + E = D

Recycle, Bypass, and Purge

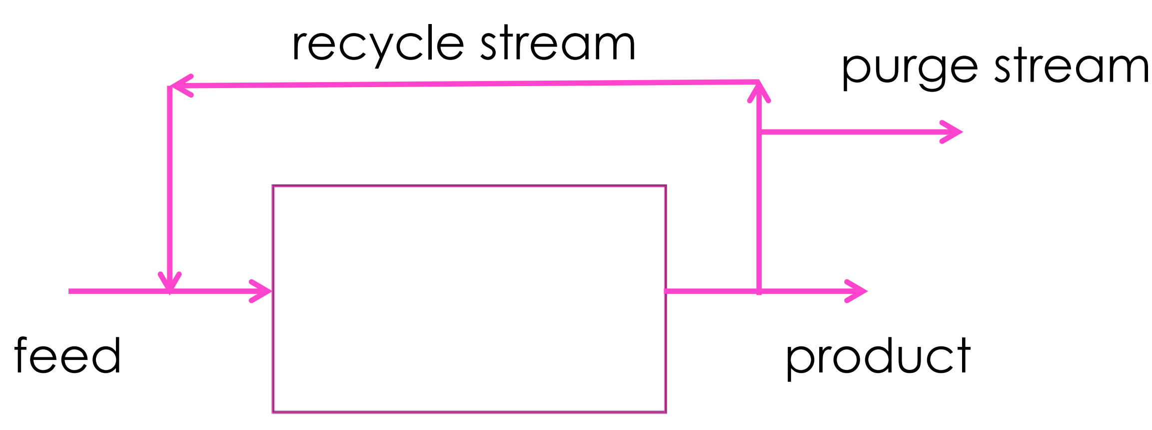
Bypass Example

In the feedstock preparation section of a plant manufacturing gasoline, isopentane is removed from butane-free gasoline. What fraction of the butane-free gasoline is passed through the isopentane tower?



Recycle, Bypass, and Purge

- Purge
  - A stream is bled off to remove an accumulation of inerts or unwanted material that might otherwise build up in the recycle stream



Recycle, Bypass, and Purge

- Purge Example
  - A cooling tower cools water by contacting it with air intimately. Some water evaporates. It gets the latent heat required from the bulk of the liquid water. This provides the cooling effect. This evaporated water is replenished by addition of make-up water. The water used normally contains $CaCO_3$. To avoid scale formation in the process pipes, the $CaCO_3$ should be kept below 130 ppm. This is done by providing a purge stream.
  - In a certain cooling tower, the make-up water contains 30 ppm $CaCO_3$. The evaporation is 1,200 kg/h. What should be the minimum flow of the purge stream in order to prevent deposition of $CaCO_3$? Assume no entrainment of water in the air occurs.

Summary

- By now you should have learned
  - ✓ How to write and balance chemical equations
  - ✓ How to define and determine excess and limiting reactants of a reaction
  - ✓ How to calculate fractional/percentage excess, conversion, yield, and selectivity
  - ✓ How to perform material balances on industrial reactions
  - ✓ How to perform material balances on complete and incomplete combustion reactions
  - ✓ How to draw flow diagrams for problems involving recycle, bypass, and purge streams
  - ✓ How to perform material balances on processes with recycle, bypass, and purge streams

Questions?

Groups - WFW

Cosmetics	Paints and Dyes	Glass	Drugs and Pharma	Food and Beverage	Beer
Lumactod	Almeda	Banag	Betancor	Ng	Abis
Castro	Dizon	Gutierrez	Caramat	Yu	Cua
Reyes	Moya	Ureta	Hadi	Sy, JL	Dy

Rubber	Pulp and Paper	Soaps	Cement	Plastics	
Baladiang	Mirasol	Pabua	Co	Alunan	
Petallo	Sy, S	Roco	Dizon	Tan	
Victor	Joves	Suarez	Lim	Garcia	

Groups - WFX

Cosmetics	Paints and Dyes	Glass	Drugs and Pharma	Food and Beverage	Beer
	Jeresano	Trinidad	Maranon	Santiago	Castillo
	Crisostomo	Conol	Piedad	Canicosa	Carrido
	Perez, G	Barcelona	Vergara	Paet	Catulong
					Sobremonte

Rubber	Pulp and Paper	Soaps	Cement	Plastics	
Go	Dignos	Perez, E	Cudiamat	Baliton	
Reyes	Saban	Quilantang	Dallarte	Caballero	
Ng	Tan	Solis	Li	Rivera	