Chapter 4. Fundamentals of Material Balances (Part 2)

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4.4 Balances on Multiple-Unit Processes

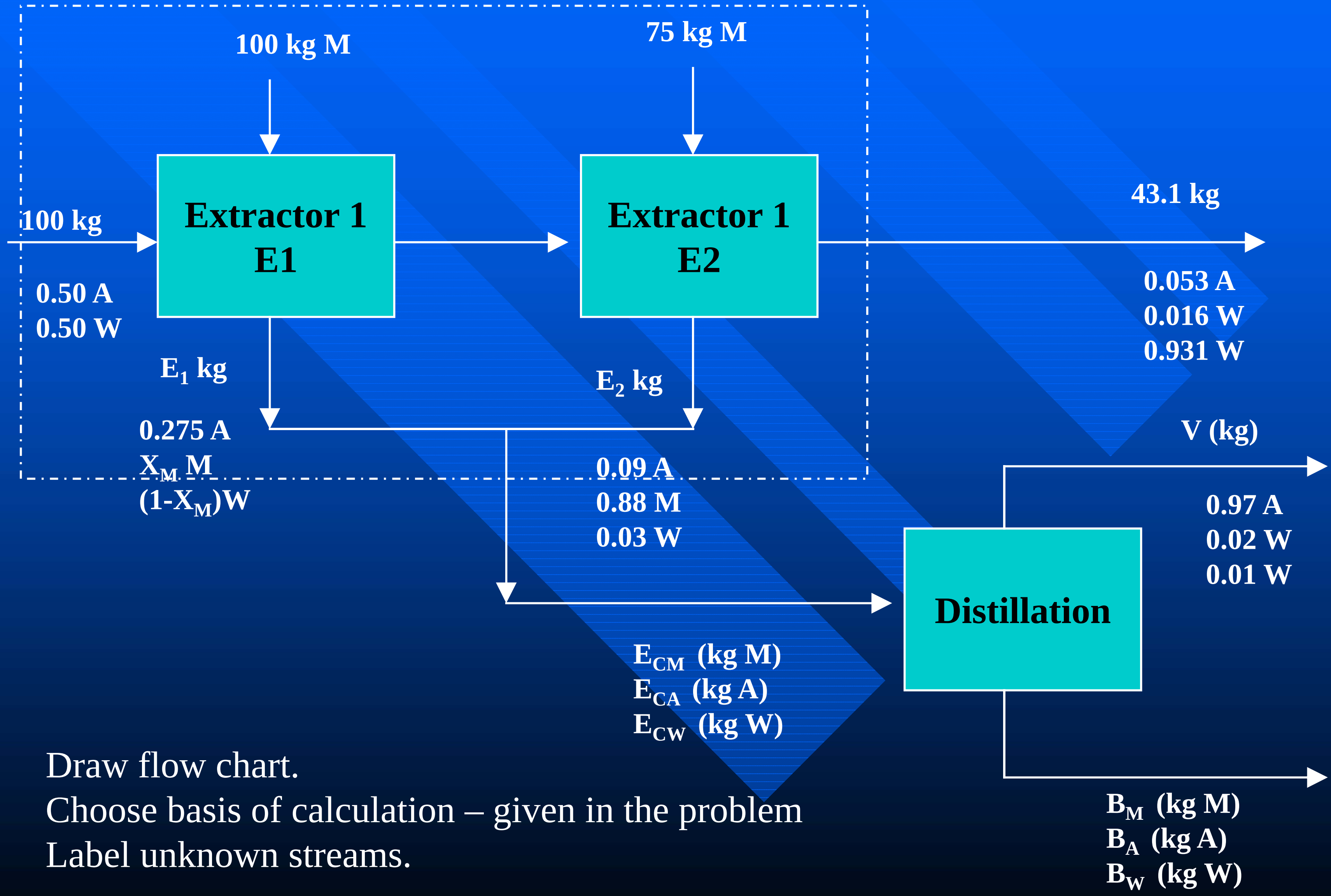
- Industrial processes rarely involve just one unit.
- Keeping track of material flows for overall processes
- Keeping track of material flow of all individual units
- Definition of system : arbitrary choice
- Recommended solving method

  Overall Balances → Balances on Subsystems

Example : An Extraction-Distillation Process

- What is an extraction process ?
  - Use of distribution between immiscible phases
- What is a distillation process ?
  - Use of boiling point differences
- (Acetone + Water) mixture separation
  - Cannot be separated simply by a distillation
    - » Forming azeotrope
  - Use MIKB (methyl isobutyl ketone) to extract acetone

Flow chart



- Draw flow chart.
- Choose basis of calculation – given in the problem
- Label unknown streams.

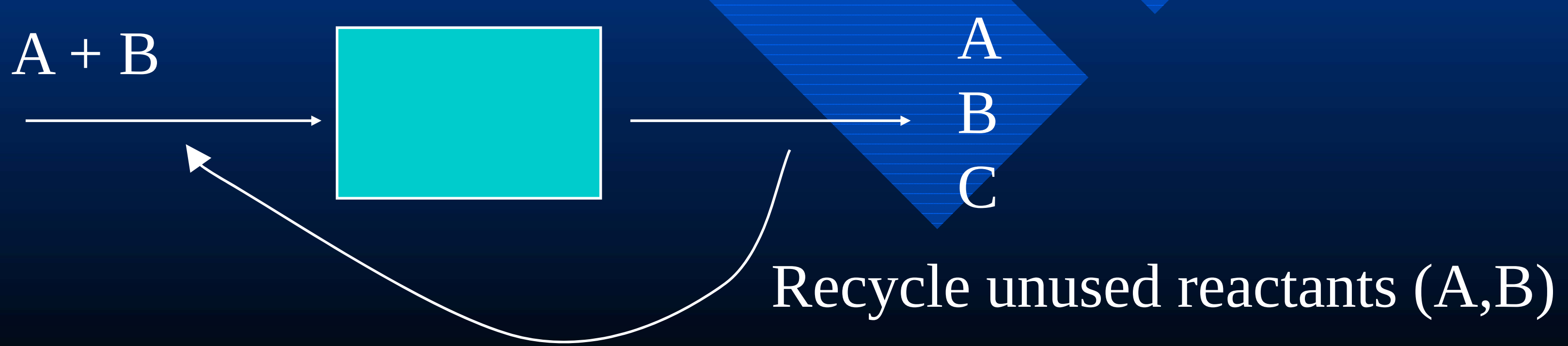
Example 4.4-2) Continues

- Problem bookkeeping
  - Degree of freedom analysis
    - » For overall mass balance
      - Unknown : 4 variables (B_A,B_M,B_W and V)
      - Equations : 3 (= number of components)
      - Cannot be solved
    - » Mass balance for given rectangular box
      - Unknown : 3 variables (E_A,E_M and E_W)
      - Equation : 3 (=number of components)
  - Strategy
    - » Balances around E1 + E2 → E_A, E_M, E_W
    - » Balances around mixing point → E1, E2, X_M
    - » Balances around E1 (or E2) → R_A, R_M, R_W
    - » Distillation column → Cannot be solved.
      - One more specification is required.

4.5 Recycle and Bypass

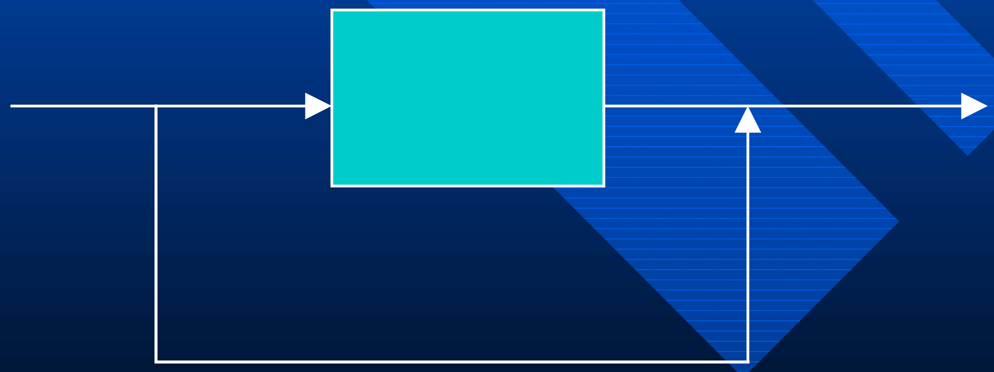
- **Reasons for Recycle**
  - **Recovering and reusing unconsumed reactants**
  - **Recovery of catalyst (catalyst : expensive)**
  - **Dilution of process stream**
  - **Control of process variables**
  - **Circulation of working fluid**

$$A + B \rightarrow C$$



Bypass

- A fraction of the feed is diverted around the process unit and combined with the output stream.
- Controlling properties and compositions of product stream



4.6 Balances on Reactive Systems

- **Stoichiometry (양론식)**
  - **The theory of proportions in which chemical species combine with one another.**
  - **Example) $2SO_2 + O_2 \rightarrow 2\ SO_3$**

Stoichiometric coefficients

- **Stoichiometric Ratio (양론비) :**
  - **Ratio of stoichiometric coefficients**
  - **Example**

$$\frac{2 \text{ mol } SO_3 \text{ produced}}{1 \text{ mol } O_2 \text{ reacted}} \qquad \frac{2 \text{ mol } SO_2 \text{ reacted}}{2 \text{ mol } SO_3 \text{ produced}}$$

Terminology

- **Limiting reactants (한정 반응물)**
  - Exist less than stoichiometric proportion
- **Excess reactants (과잉 반응물)**
  - Exist more than stoichiometric proportion
- **Example**

$$2SO_2 + O_2 \rightarrow 2\ SO_3$$

(30 mol) (10 mol)

Excess Limiting

Terminology

- **Fractional excess** $\frac{n-n_s}{n_s}$
- **Percent excess** $\frac{n-n_s}{n_s}\times 100$
  - n_s : 양론비에 해당하는 몰수
- **Example**
  - $H_2 + Br_2 \rightarrow HBr$
  - H_2 : 25 mol /hr
  - Br_2 : 20 mol /hr
  - Fractional Excess H_2 = (25 – 20) /20 = 0.25

Terminology

- **Fractional conversion**
  - **Chemical reactions are not always completed.**
  - **Factional conversion**
    - » **f = (moles reacted) / (moles fed)**
- **Extent of reaction (반응 진행도)**

$$n_i = n_{i0} + \beta_i \xi$$

where

$\beta_i = \nu_i$ (products)

$\beta_i = \nu_i$ (reactants)

ξ : extent of reaction

Ex)

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$N_2 : 100\ \text{mol}\ , H_2 : 300\ \text{mol}$

$n_{N_2} = 100\ \text{mol} - \xi$

$n_{H_2} = 300\ \text{mol} - 3\xi$

$n_{NH_3} = 2\xi$

Chemical Reaction

- **What is final composition ?**
  - **Chemical equilibrium thermodynamics**

$$K = \prod \hat{f}_i^{\nu_i}$$

$$K = \prod a_i^{\nu_i}$$

$$\frac{d \ln K}{dT} = \frac{\Delta H_r}{RT}$$

- **How long it will take to reach equilibrium ?**
  - **Chemical kinetics**

$$r_i = k(T)\, f(composition)$$

$$= k_o T^m e^{-E/RT} C_A^n C_b^l \ldots$$

Example 4.6-1)

- Acetonitrile is produced by the reaction of propylene, ammonia and oxygen.

$$C_3H_6 + NH_3 + 3/2\ O_2 \rightarrow C_3H_3N + 3H_2O$$

The feed contains 10 mol % propylene, 12 % ammonia and 78 % air. A fractional conversion of 30 % of the limiting reactant is achieved. Determine which reactant is limiting, the percentage by which each of the reactants is in excess, and the molar flow rates of all product gas constituents for a 30 % conversion of the limiting reactants, taking 100 mol of feed as basis.

Solution

- **Basis, 100 mol feed**

100 mol → Reactor →

0.100 mol C3H6 /mol
0.120 mol NH3/mol
0.780 air /mol
- 0.21 mol O2 /mol
- 0.79 mol N2 /mol

n_{C3H6} mol C3H6
n_{NH3} mol NH3
n_{O2} mol O2
n_{N2} mol N2
n_{C3H3N} mol C3H3N
n_{H2O} mol H2O

Composition of the feed

$(C_3H_6)_0 = 100 \times 0.10 = 10.0 mol$

$(NH_3)_0 = 100 \times 0.12 = 12.0 mol$

$(O_2)_0 = 100 \times 0.78 \times 0.21 = 16.4 mol$

Ratios of Reactants

$(NH_3/C_3H_6)_0 = (12.0/10.0) = 1.20$ → NH3 is in excess

$(NH_3/C_3H_6)_{STOI} = (1/1) = 1.0$

$(O_2/C_3H_6)_0 = (16.4/10.0) = 1.64$

$(O_2/C_3H_6)_{STOI} = 1.5/1 = 1.5$ → O2 is in excess

→ C3H6 is limiting

Solution

Percent Exess

$(NH_3)_{STOICH} = 10.0 mol$

$(O_2)_{STOICH} = 15.0 mol$

$\%\text{ Excess } NH_3 = (12-10)/10 \times 100 = 20\%$

$\%\text{ Excess O}_2 = (16.4-15)/15 \times 100 = 9.3\%$

$\text{Fractional concersion} = 30\ \%$

$\xi = 100\text{mol} \times 0.3 = 3\text{mol}$

$n_{C_3H_6} = 10 mol - \xi = 7.0 mol$

$n_{NH_3} = 12 mol - \xi = 9.0 mol$

$n_{O_2} = 16.4 mol - 1.5\xi = 11.9 mol$

$n_{N_2} = (n_{N_2})_0 = 61.6 mol$

$n_{C_3H_3N} = \xi = 3 mol$

Multiple Reaction, Yield, Selectivity

- Multiple reaction : one or more reaction
  - Side Reaction : undesired reaction
  - Example) Production of ethylene

    $C_2H_6 \rightarrow C_2H_4 + H_2$

    (Side Reactions)

    $C_2H_6 + H_2 \rightarrow 2CH_4$

    $C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$
  - Design Objective
    - » Maximize desired products (C_2H_4)
    - » Minimize undesired products (CH_4, C_3H_6)

Multiple Reaction, Yield, Selectivity

- **Yield (수율)**

$$\frac{\text{(moles of desired product formed)}}{\text{(moles of desired products, theoretical)}}$$

- **Selectivity (선택도)**

$$\frac{\text{(moles of desired product formed)}}{\text{(moles of undesired product formed)}}$$

Multiple Reaction, Yield, Selectivity

- **Calculation of molar flow rates for multiple reactions**

$$n_i = n_{i0} + \sum_j \beta_{ij} \xi_j$$

$$\beta_{ij} = \nu_{ij} \text{(if } \mathrm{A_i} \text{ is a product in reaction j)}$$

$$\beta_{ij} = -\nu_{ij} \text{(if } \mathrm{A_i} \text{ is a reactant in reaction j)}$$

$$\beta_{ij} = 0 \text{(if } \mathrm{A_i} \text{ does not appear in reaction j}$$

Balances of Atomic and Molecular Species

- Methods for solving mass balances with reactions
  - Using balances on molecular species
  - Using balances of atoms
  - Using the extent of reaction
- For multiple reactions, sometimes it is more convenient to use atomic balances

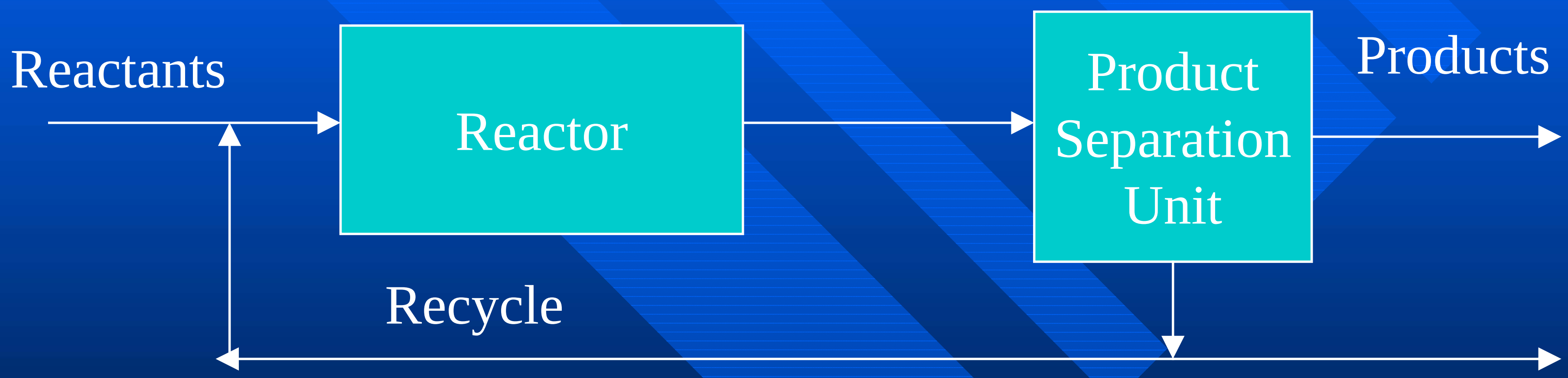
Product separation and recycle

- Normally, reactions are not complete
  - Separation and recycle
  - Improved yield, conversion ,…

- Overall conversion (총괄 전화율)
- Single-pass conversion (단통과 전화율)

Purging

- **Getting rid of undesired materials in recycle stream.**



4.7 Combustion Reaction

- **Combustion**
  - **A rapid reaction of a fuel with oxygen.**
  - **Fuels : coal, fuel oil, gas fuel, solid fuel, …**
- **Complete combustion / incomplete combustion**
- **Wet basis composition / dry basis composition**

Terminology

- Theoretical oxygen : Amount of oxygen needed for complete combustion
- Theoretical air : The quantity of air that contains theoretical oxygen
- Excess air : The amount by which the air fed to reactor exceeds the theoretical air
- Percent excess air

$$\frac{(\text{moles air})_{\text{fed}} - (\text{moles air})_{\text{theroretical}}}{(\text{moles air})_{\text{theoretical}}} \times 100\%$$