Solutions

Topic 0: Conceptual Process Design – General Aspects (14 Points)

0.1 Please explain the main tasks and features of Process Synthesis and Process Analysis. (2 Points)

- Process Synthesis: generate many process alternatives (10^4 to 10^9)
- Process Analysis: evaluate given process alternatives

0.2 Nominate three typical objectives of conceptual process design. (1.5 Points)

a) find the optimal architecture of the flowsheet (efficiency of raw materials and energy, minimal impact on the environment, flexibility in throughput and quality of raw materials).

b) set feasible and optimal tasks for units.

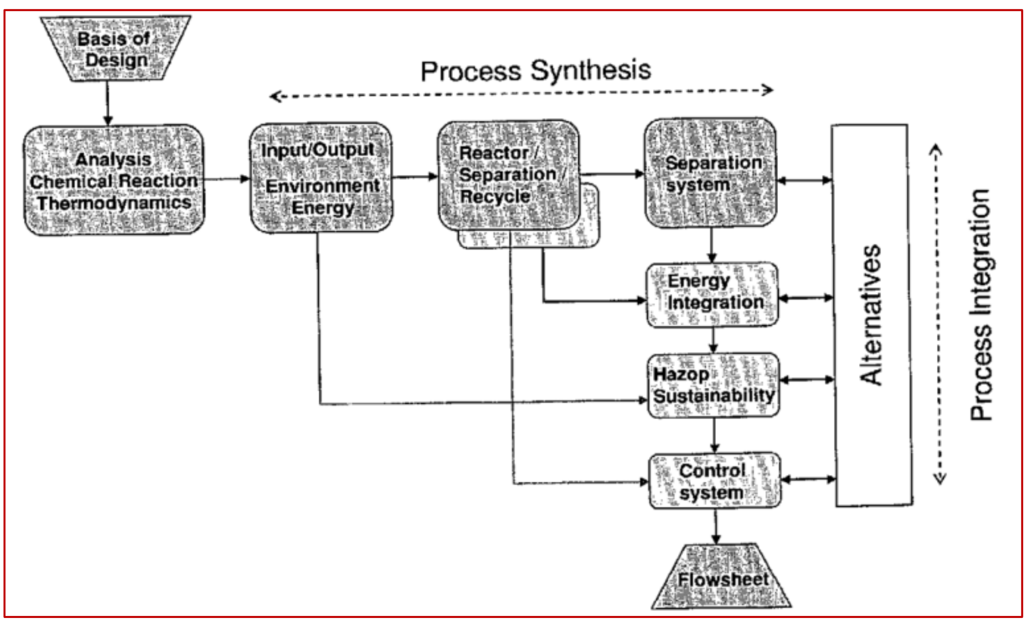
c) evaluate the effect of mass and energy recycles.

d) select and size the main equipment.

0.3 Please explain the main idea of the “superstructure approach” to process design. (1.5 Points)

Idea: embedding all alteratives into a large superstucture, global optimization by MINLP techniques (MINLP: Mixed Integer Nonlinear Programming): not workable by using commercial packages, applicable to smaller subsystems.

0.4 Nominate the 8 levels of the “hierarchical process design” approach of Dimian & Bildea. (4 Points)



0.5 Nominate 4 types of economic data to be gathered as Basis of Design. (2 Points)

a) Product price versus purity specifications, b) Raw materials prices = f(purity), c) Utilities, d) Costs caused by wastes

0.6 Nominate 4 types of plant and site data to be gathered as Basis of Design. (2 Points)

a) Location, b) Storage facilities, c) Climate conditions, d) Utility system, e) Environmental legislation

0.7 Nominate 2 types of safety and health considerations to be gathered as Basis of Design. (1 Point)

a) Explosion risks, b) Fire risks, c) Toxicity

Topic 1: Chemistry and Thermodynamics (21 Points)

Given is a chemical system based on a network of three reversible gas phase reactions:

R1: A + B ⇔ C + D

R2: 2 A ⇔ D + E

R3: 2 B + E ⇔ 2 C + D

A, B: educts; C: target product; D, E: by-products

1.1 Determine the number of independent chemical reactions. (2 Points)

The stoichiometric matrix N and its rank R are given by (due to the fact that 2 x R1 – R2 = R3):

$$\mathbf{N} = \begin{bmatrix} -1 & -2 & 0 \\ -1 & 0 & -2 \\ 1 & 0 & 2 \\ 1 & 1 & 1 \\ 0 & 1 & -1 \end{bmatrix}$$

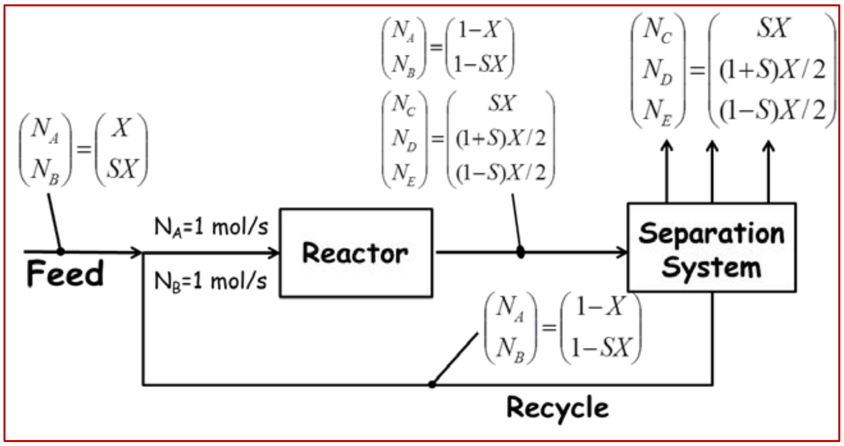
$$R = rank(\mathbf{N}) = 2$$

1.2 Define the conversion X of the educt A, the selectivity S for the formation of product C with respect to educt A, and the yield Y of product C with respect to educt A. (3 Points)

$$X \equiv \frac{N_{A,in} - N_A}{N_{A,in}}; \qquad S \equiv \frac{N_C}{N_{A,in} - N_A}; \qquad Y \equiv \frac{N_C}{N_{A,in}}$$

1.3 Sketch a simple reactor-separator system at input/output level. Calculate the molar flow rates N_i for all components in all streams of the flowsheet, including the feed stream. Express all molar flow rates in terms of the conversion and the selectivity (X, S), as defined in 1.2. (5 Points)

All streams in mol/s !



1.4 Now we assume that only reaction R1 takes place and that the reactor effluent is in chemical equilibrium. Calculate the maximum achievable conversion X_{max}, and the effluent composition, if the reactor is fed with 1 mol/s of A and 1 mol/s of B and if all components behave as ideal gases. The equilibrium constant at reactor temperature is K = 4. (2 Points)

$$K = \frac{x_C x_D}{x_A x_B} = \frac{X_{\max}{}^2}{(1-X_{\max})^2} = 4 \Rightarrow X_{\max} = \frac{2}{3}$$

$$\Rightarrow x_A = 1/6, x_B = 1/6, x_C = 1/3, x_D = 1/3$$

1.5 R1 is an exothermic reaction. For achieving a high conversion, how should the reactor temperature be chosen and why? How should the pressure be chosen and why? (4 Points)

Le Chatelier's principle => low temperature for exothermic reactions to achieve high equilibrium conversion, because K(T) is decreasing with increasing T; pressure has no influence in this case because the total number of moles in R1 does not change.

1.6 We want to check how the ternary mixture A, B, C can be separated by distillation. For this purpose, write down the complete set of governing equations for the calculations of residue curve maps. (Assumption: ideal behavior in the liquid phase as well as in the gas phase!). Draw a qualitatively correct residue curve map for the boiling point sequence: $T_{b,C} < T_{b,A} < T_{b,B}$. (5 Points)

$$y_i \cdot p = x_i \cdot p_i^{sat}(T)$$ **VLE**

$$K_i \equiv \frac{y_i}{x_i} = \frac{p_i^{sat}(T)}{p}$$ **Equilibrium Ratio**

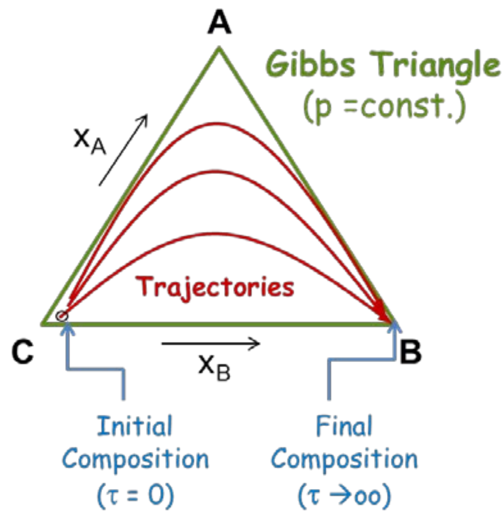
Mass Balances

$$\left.\begin{aligned} \frac{dn_i}{dt} &= -V y_i \\ \frac{dn_t}{dt} &= -V \end{aligned}\right\} \xRightarrow{x_i = n_i/n_t} \begin{aligned} \frac{dx_i}{d\tau} &= (x_i - y_i) \\ d\tau &\equiv V/n_t \cdot dt \end{aligned}$$

$$y_i = K_i x_i; \quad i = 1,\dots,(N-1)$$

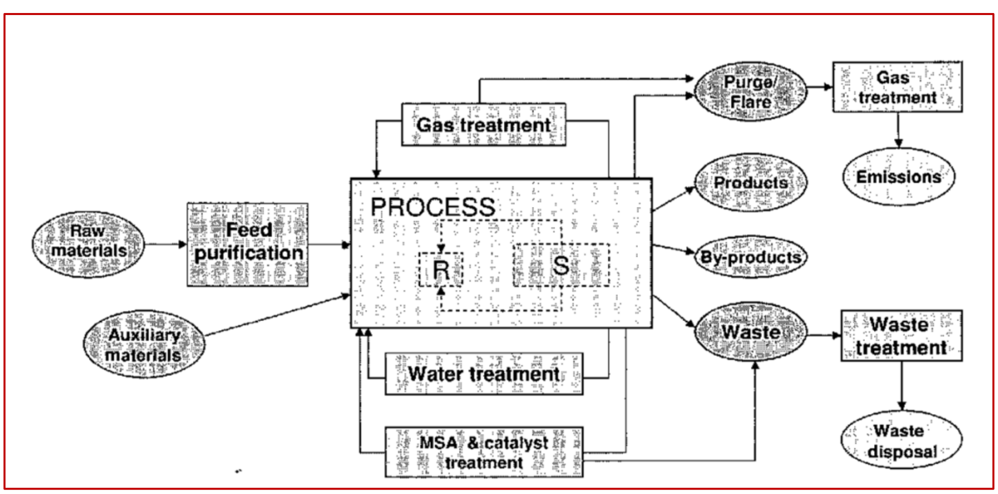
$$\sum_{i=1}^{N} x_i = 1; \ \sum_{i=1}^{N} y_i = 1 \Rightarrow \sum_{i=1}^{N} p_i^{sat}(T) \cdot x_i = p$$

Boiling Point Equation
(gives T at given p,x)



Topic 2: Input/Output Analysis (13 Points)

2.1 Draw a complete general process flowsheet at the input/output (I/O) level. (5 Points)



2.2 Define the economic potential $(EP)_0$ at I/O level and explain all contributions. (2.5 Points)

$$\boxed{\begin{aligned}&EP_{I/O} = \{\text{Product value}\} + \{\text{Byproduct value}\} - \{\text{Raw material costs}\}\\ &- \{\text{Auxiliary materials costs}\} - \{\text{Ecological costs}\}\end{aligned}}$$

2.3 How is the economic potential calculated on later levels of process design, $(EP)_n$? (2.5 Points)

$$\boxed{\begin{aligned}&EP_n = EP_{I/O} - \{\text{Processing costs}\}_n\\ &\{\text{Processing costs}\} = +\{\text{Equipment costs/Payback time}\} + \{\text{Cost of utilities}\}\\ &+ \{\text{Additional environmental costs}\}\end{aligned}}$$

2.4 Nominate the three main design decisions to be taken at the I/O level. (3 Points)

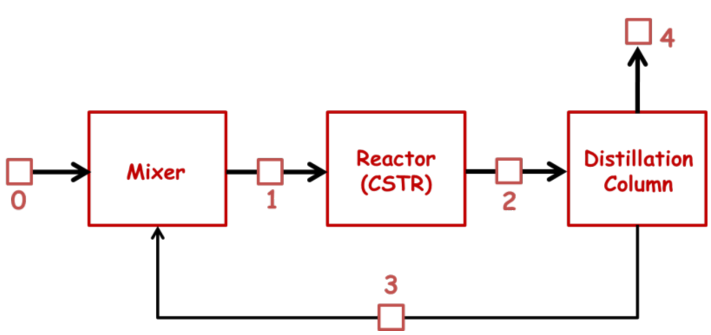
1) Feed purification
2) Recycling of reactants and auxiliary materials
3) Purge and bleed streams

Topic 3: Reactor-Separation-Recycle Structure (25 Points)

Given:

- Reversible isomerization reaction A ⇔ B. No other substances are involved.
- Reaction rate: $r = k\,(x_A - x_B/K)$, in units of $mol/(m^3 s)$; x_i: mole fraction, k: rate constant, K: equilibrium constant
- A continuously stirred tank reactor (CSTR) with volume V_R is applied.
- The A-B mixture is zeotropic, where A is the high boiler.

3.1 Propose a suitable reactor-separator-recycle (RSR) flow scheme. (2 Points)



3.2 Derive a complete set of mass balance equations at steady state in terms of molar variables, thereby including the reaction kinetic expression. (6 Points)

$$0 = F_0 x_0 + F_3 x_3 - F_1 x_1;\ \ 0 = F_0 + F_3 - F_1$$
$$0 = F_1 x_1 - F_2 x_2 - V_R k\left(x_2 - (1 - x_2)/K\right);\ \ 0 = F_1 - F_2$$
$$0 = F_2 x_2 - F_3 x_3 - F_4 x_4\ \ ; 0 = F_2 - F_3 - F_4$$

3.3 Propose a suitable process control structure relying on self-regulation. (4 Points)

Self-regulation: Fixation of external feed stream F0 and x0.

Additional controllers: LC for VR, TC for k and K, TC for x3, TC for x4.

3.4 Determine the Degrees of Freedom (DoF) based on the control scheme proposed in 3.3. (1 Point)

Variables: F0, F1, F2, F3, F4, x0, x1, x2, x3, x4, VR, k, K

DoF = Number of Variables – Number of Equations = 13 – 6 = 7

Control scheme yields: DoF = 0 !

3.5 Derive a feasibility condition for the reactor volume, which guarantees non-negative mass fluxes in the process flow scheme. Thereby, introduce the Damköhler number $Da = k\,V_R/F_0$; F_0: external feed flow rate. (6 Points)

$$f_k \equiv F_k / F_0; Da \equiv kV_R / F_0; \alpha \equiv 1 + 1/K; \beta \equiv 1/K$$

$$\text{Global mass balance yields}: f_4 = f_0 = 1$$

$$\left.\begin{array}{l} 0 = x_0 + f_3 x_3 - f_1 x_1 \\ 0 = 1 + f_3 - f_1 \end{array}\right\} \Rightarrow f_1 x_1 = x_0 + f_3 x_3$$

$$0 = f_1 x_1 - f_2 x_2 - Da\left(x_2 - (1 - x_2)/K\right) \Rightarrow Da(x_2 \alpha - \beta) = f_1 x_1 - f_2 x_2 = x_0 - x_4 \Rightarrow x_2 = \frac{1}{\alpha}\left(\frac{x_0 - x_4}{Da} + \beta\right)$$

$$0 = f_1 - f_2 \Rightarrow f_1 = f_2 = f_3 + 1 = \frac{x_3 - x_4}{x_3 - x_2}$$

$$\left.\begin{array}{l} 0 = f_2 x_2 - f_3 x_3 - f_4 x_4 \\ 0 = f_2 - f_3 - f_4 \end{array}\right\} \Rightarrow f_3 = \frac{x_2 - x_4}{x_3 - x_2}$$

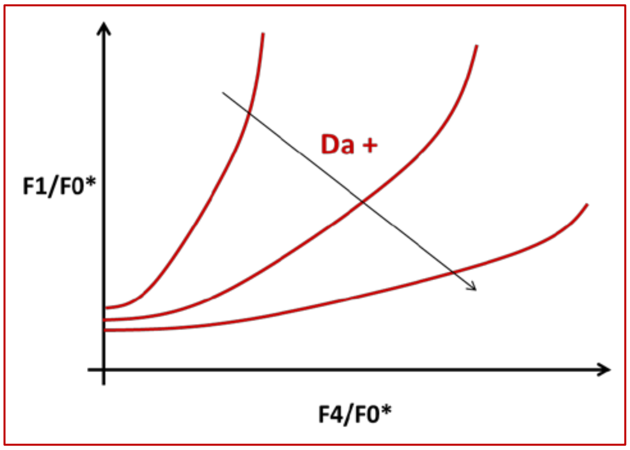
Conditions for Da :

$$x_3 > x_2 \text{ if } Da > \frac{x_0 - x_4}{\alpha x_3 - \beta} \text{ (reactant A cannot leave process)}$$

$$x_4 < x_2 \text{ if } Da < \frac{x_0 - x_4}{\alpha x_4 - \beta} \text{ (for meaningful separation)}$$

3.6 Explain and illustrate the “snowball effect” which is typically observed for a control structure which is based on self-regulation. (4 Points)

Snowball effect: Small deviations from the nominal production point, i.e. nominal external fluxes F4 or F0, lead to large changes of the internal mass fluxes due to high sensitivity of the system.



3.7 Specify two possible remedies to avoid “snowball effects” in a RSR process. (2 Points)

a) apply large enough reactor volume

b) apply control scheme which fixes the reactor inlet stream

Topic 4: Reactor Design (8 Points)

Given: two coupled irreversible, strongly exothermic reactions

R1: A + B → P, rate expression: $r_1 = k_{10} e^{-E_{a,1}/(RT)} c_A c_B$

R2: A + P → R, reaction rate: $r_2 = k_{20} e^{-E_{a,2}/(RT)} c_A c_P$

K_{i0}: rate constant, $E_{a,i}$: activation energy, R: universal gas constant, T: temperature, c_i: concentration

4.1 Propose and explain a process strategy to achieve the highest possible differential selectivity $S_d = r_1/r_2$. (3 Points)

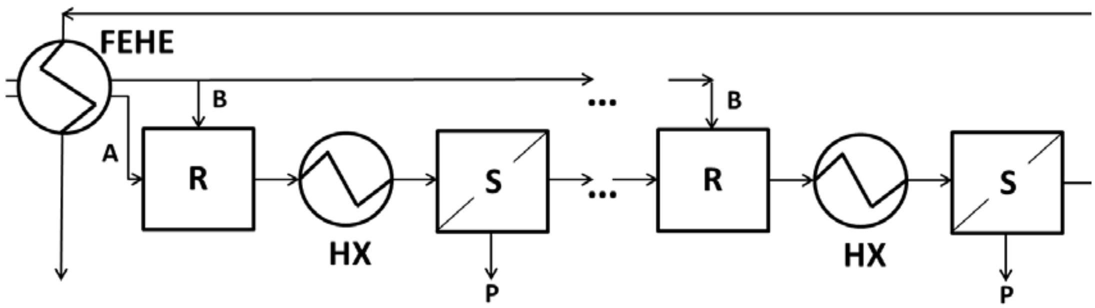
$$S_d = \frac{k_{01}}{k_{02}} \frac{c_B}{c_P} e^{-(E_{a1}-E_{a2})/(RT)}$$

$$E_{a2} > E_{a1} \Rightarrow \text{T as low as possible} \Rightarrow \text{strong cooling}$$

$$E_{a2} > E_{a1} \Rightarrow \text{T as high as possible} \Rightarrow \text{less cooling}$$

$$c_B: \text{high}, \quad c_P: \text{low}$$

4.2 Sketch and explain a reaction-separation flowsheet which maximizes the differential selectivity at any point along the process for the case that $E_{a1} > E_{a2}$. (4 Points)



R: Reactor section, HX: Heat eXchanger, S: Separator

4.3 Add a feed-effluent heat exchanger (FEHE) to the flowsheet proposed in 4.2. (1 Point)

See flowsheet in 4.2.

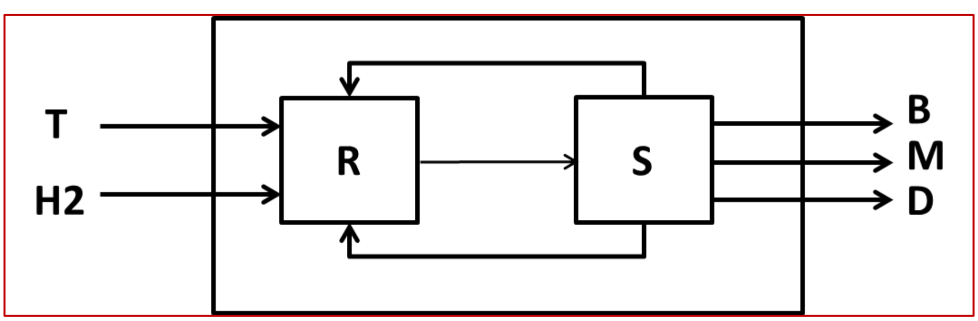
5) Synthesis of Separation System (25 Points)

The hydrodealkylation of toluene (T) to the product benzene (B) obeys the following reaction scheme:

Main reaction:	C_7H_8 (Toluene) + H_2 (Hydrogen)	→	C_6H_6 (Benzene) + CH_4 (Methane)
Side reaction:	2 C_6H_6 (Benzene)	→	$C_{12}H_{10}$ (Diphenyl) + H_2 (Hydrogen)

The ranking of the vapour-liquid equilibrium ratios, $K_i=y_i/x_i$, is: $K_H > K_M >> 1 >> K_B > K_T > K_D$

5.1 Sketch the input/output structure of a suitable process system. (3 Points)



5.2. Consider a single isothermal flash as first separation step. (a) Write down the complete set of governing equations, in terms of molar flows, mole fractions, and relative volatilities. (b) Calculate the mole fractions in the gas and liquid streams leaving the flash unit, at given feed composition x_i^F and feed flow rate F. (5 Points)

$$F = V + L$$

$$Fx_i^F = Vy_i + Lx_i$$

$$\sum_{i=1}^{N} x_i = 1 \; ; \; \sum_{i=1}^{N} y_i = 1$$

$$y_i = K_i x_i \; ; \; x_i = \frac{Fx_i^F}{(K_i - 1)V + F}$$

$$\alpha_{ij} = K_i / K_j$$

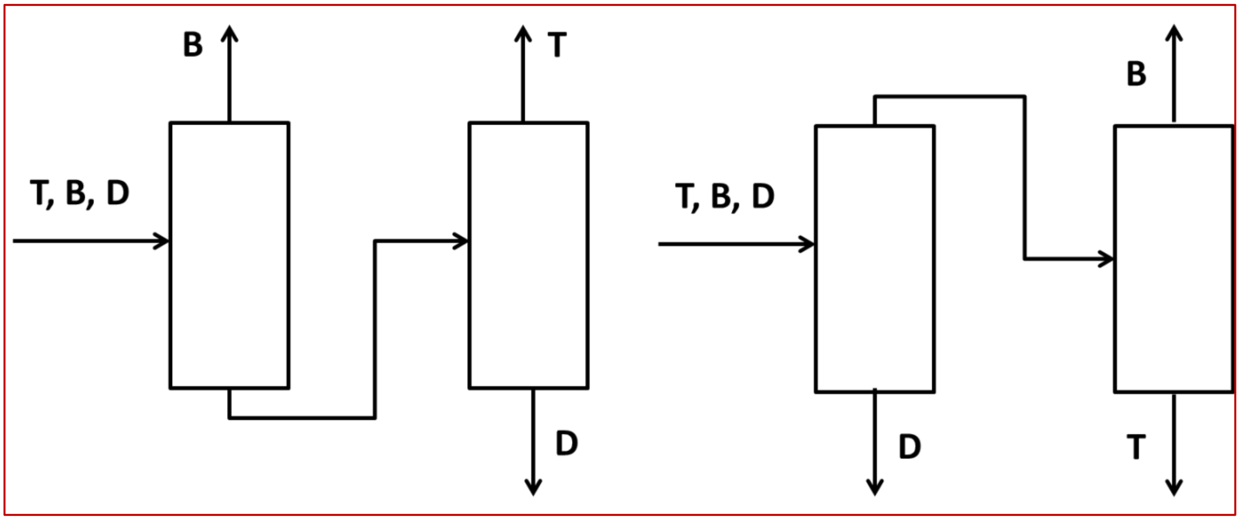
5.3 Consider the gas separation of methane and hydrogen. Propose three suitable physical separation methods (i.e. <u>no</u> chemical separation methods) using the selector "sharp separation". (3 Points)

Sharp separation methods: cryogenic distillation, physical absorption; molecular sieve adsorption, equilibrium-limited adsorption, membranes

5.4. Nominate 5 different separation methods for a general liquid mixture. (5 Points)

Methods: distillation, stripping, LL extraction, melt crystallization, adsorption, membrane permeation

5.5 Consider the system toluene, benzene and diphenyl as zeotropic mixture. Sketch and nominate all possible sequences for separating this mixture by simple distillation columns. (2 Points)

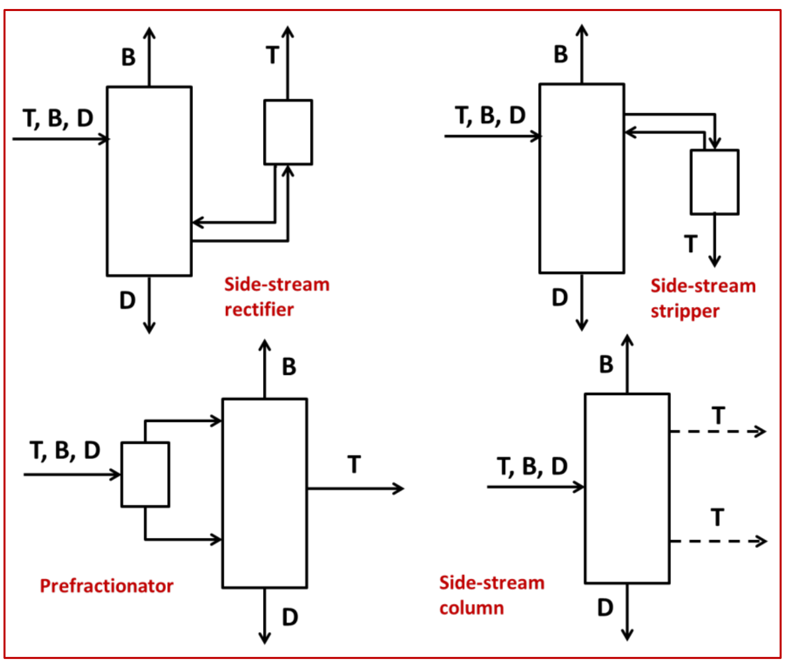


Left: direct sequence
Right: indirect sequence

5.6 Given is the liquid mixture composition: x_T=0.2, x_B=0.6, x_D=0.2. Sketch the best separation sequence for this mixture. The heats of vaporization $\Delta_v h_i$ are: 33 kJ/mol for toluene (T), 31 kJ/mol for benzene (B), 48 kJ/mol for diphenyl (D). (1 Point)

Benzene is most plentiful component in the system. Hence, it should be removed first. This avoids the evaporation of benzene in the second column, thus saves energy. => Direct sequence is beast solution in this case.

5.7 Sketch three possible configurations to separate toluene, benzene and diphenyl via one single complex distillation column. (3 Points)



5.8 Sketch a suitable complete reaction-separation-recycle flow sheet for the considered process. (3 Points)