

458.401 Process & Product Design

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Synthesis of the PFD from the Generic BFD

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PFD from GBFD

Creation of a Full PFD from GBFD

🔧 Synthesis of a full PFD:

- A starting point for designing machines, structures, and electrical/electronic components
- Involves all subareas of chemical engineering: reaction engineering, thermodynamics, process control, unit operations and transport, and material and energy balances
- These principles of the subareas are applied to six general sections of GBFD - reactor feed preparation, reactor, separator feed preparation, separator, recycle, and environmental control
- Broader context of the project (e.g., ROI) + details such as the number of stages in a column
- Consider as many alternatives as possible in the early stages

“It is a common human trait to resist change more strongly as more effort is expended on a project.”

1. Information Needs and Sources

- Physical property and kinetics information are prerequisite
- Market values of products of different purities
- Marketing engineers and process design engineers should communicate
- Lab scale vs. Plant scale
 - small-lot, high-purity laboratory reagents (L)
 - isothermal operation of reactor (L)
 - high-pressures/volume is economical (P)
 - small batch (L)
 - scheduling, ramp rates, cycle sequencing, choice of operating mode (P)

1.A Reaction Kinetics Data

- For the PFD structure or topology (# and position of recycle streams; types, #, and locations of separators; batch or continuous operating modes; sterilization operation needed for aseptic operation)
 - A knowledge of the kinetics of unwanted side reactions as well as the main reaction is crucial
 - ▶ $dC/dt = f(T, p, x)$
 - Knowledge of detailed reaction pathways, elementary reactions, and unstable reaction intermediates is not required

1.B Physical Property Data

- Required to determine material and energy balances and size equipment items
- Easier to obtain than kinetics data
- Pure components: heat capacity and density (simulator)
- Enthalpies of mixtures
 - Equation of state for gases and nonionic liquids (simulator)
 - Electrolyte system: care should be taken
- Thermal conductivity and viscosity: design of heat exchanger
 - Usually available or can be estimated by GCM
- Phase equilibrium data
 - Most crucial and least available
 - E.g.) For VLE, a single EOS for both phases or a combination of vapor-phase EOS, pure-component vapor pressure, and liquid-state activity coefficient model is required
 - Choice of thermodynamic package (Section 13.4)
 - Binary interaction parameters (BIPs) - experimentally determined mixture parameters for either EOS or activity-coefficient models

2. Reactor Section

- Determine the configuration: PFR, CSTR, batch, semibatch, adiabatic, isothermal (chemical reaction engineering)
- Given T, P, feed composition and specifications (e.g., conversion), calculate the outlet composition, pressure, and temperature
- For later optimization, general effects of varying the feed conditions should be investigated.
- Utility needs: heating or cooling
- Different catalysts, parallel vs. series, conversion vs. selectivity
- Duties of reactor feed preparation and separator feed preparation units

2. Reactor: Important Questions

- In what phase does the reaction take place?
- What are the required temperature and pressure ranges for the reactor?
 - Fired heater for the feed temp. > _____ °C
- Is the reaction kinetically or equilibrium controlled?
 - affects both the maximum single pass conversion and the reactor configuration
 - The majority of gas and liquid-phase reactions in the CPI are kinetically controlled. Exceptions are the formation of methanol from synthesis gas, synthesis of ammonia from nitrogen and hydrogen, and the production of hydrogen via the water-gas shift reaction

2. Reactor: Important Questions

- Does the reaction require a solid catalyst, or is it homogeneous?
 - e.g., immobilization of enzymes → fluidized bed reactor or packed-bed reactor
- Is the main reaction exothermic or endothermic, and is a large amount of heat exchange required?
- What side reactions occur, and what is the selectivity of the desired reaction?
- Single-pass conversion
 - determined from detailed parametric optimizations
- For gas-phase oxidations, should the reactor feed be outside the explosive limits?
 - Often, _____ is added both as a diluent and to provide thermal ballast for highly exothermic reaction.

3. Separator

- What **types** of units should be used?
- How should the units be **sequenced**? (N output streams = $N - 1$ units, in general)
- General guidelines: Tables 12.1 and 12.2
- Beware of azeotropes and multiple phases in equilibrium, especially when water and organics are present.
- If a single-stage flash will do the separation, do not use a column with reflux.

3. Separator: Important Questions

- What are the product specifications for all products?
- Are any of the products heat sensitive?
- Are any of the products, by-products, or impurities hazardous?

Phase Equilibrium of Binary Mixture

- Goal of distillation: from the feed to produce a distillate, rich in the light key ($x_D \rightarrow 1.0$), and a bottoms product, rich in the heavy key ($x_B \rightarrow 0.0$)

- Relative volatility, α

$$\alpha_{1,2} = K_1/K_2$$

Raoult's law

$$K_1 = P_1^s/P \quad \text{and} \quad K_2 = P_2^s/P$$

$$\alpha_{1,2} = P_1^s/P_2^s$$

$$\alpha_{1,2} = \frac{y_1/x_1}{y_2/x_2} = \frac{y_1(1-x_1)}{x_1(1-y_1)}$$

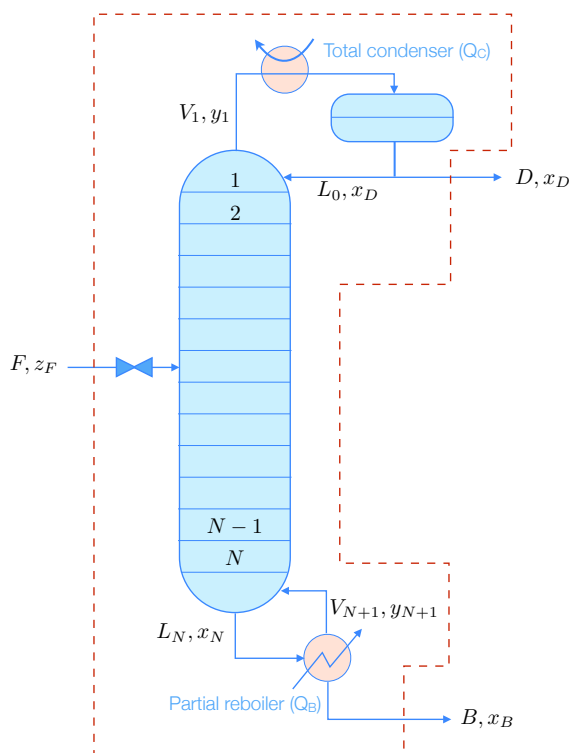
$$y_1 = \frac{\alpha_{1,2}x_1}{1 + x_1(\alpha_{1,2} - 1)}$$

For ideal binary mixtures of components with close boiling points, T changes are small and α is almost constant

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What are operating lines?

Before we look at individual operating lines, let's look at the entire process



Note: mole fractions for light key

Overall mole balance

$$F = D + B$$

Component mole balance (light key)

$$Fz_F = Dx_D + Bx_B$$

Combine the eqns and solve for D

$$Fz_F = Dx_D + (F - D)x_B$$

$$D = F \left(\frac{z_F - x_B}{x_D - x_B} \right)$$

$$0 < \cdot < 1$$

The eqn implies $x_D > z_F > x_B$

- makes sense. remember how composition of light key changes in column

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Sequencing of Columns for “Simple” Distillation

To separate N components, a minimum of $N-1$ separators are needed.

Three components, two columns: two-possibilities

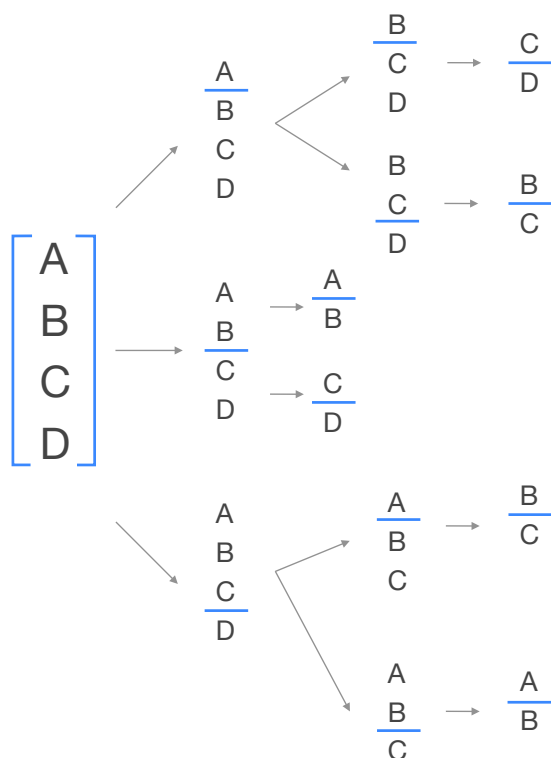
C: water (high ΔH_{vap})

Option (b) is likely to be more economical

C: large amount and corrosive

Option (b) is likely to be more economical

How many unique sequences?



① Direct

$$N_s = \frac{[2(P-1)]!}{P!(P-1)!}$$

②

N_s = # of unique sequences

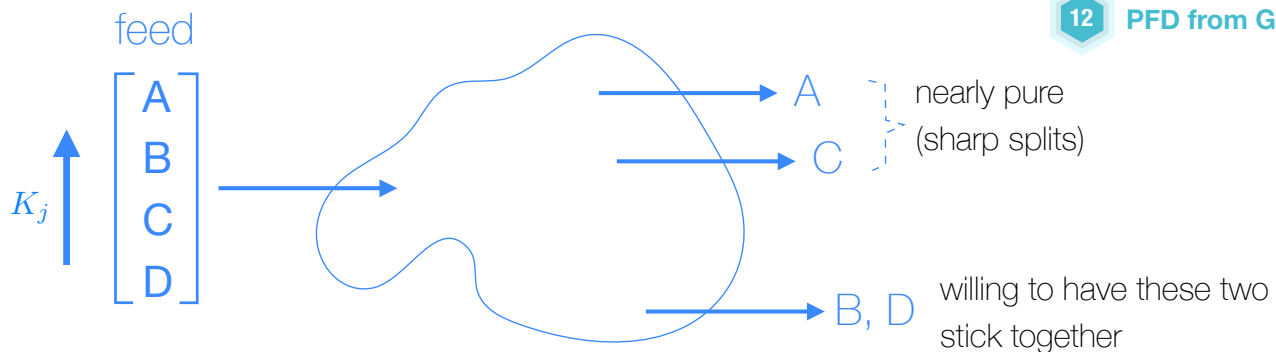
P = # of products

③

④

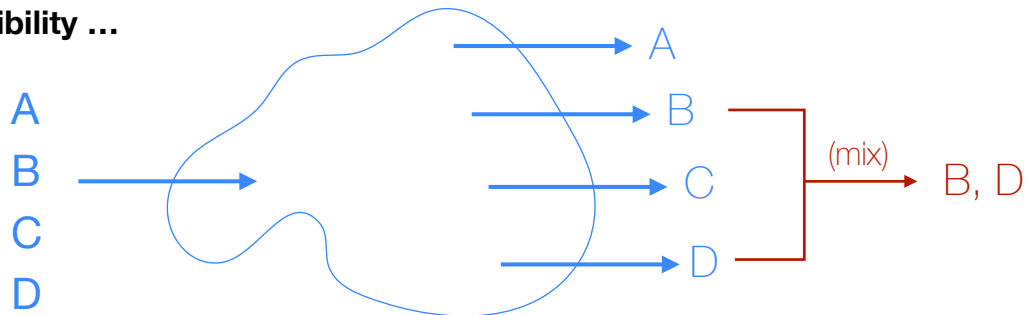
⑤ Indirect

P	# of separators	Ns
2	1	1
4	3	5
8	7	429
10	9	4,862



Consider a four component feed mixture that is to be separated into three desired products... **[A], [C], and [B/D]**

One possibility ...



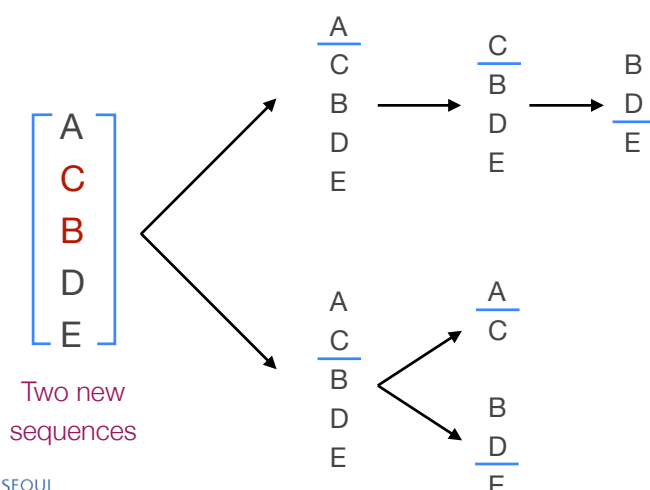
This strategy is thermodynamically inefficient... why would you work to isolate B and D only to then mix them together? The mixing process is always a thermodynamically loss due to entropy.

Introducing Mass Separating Agent

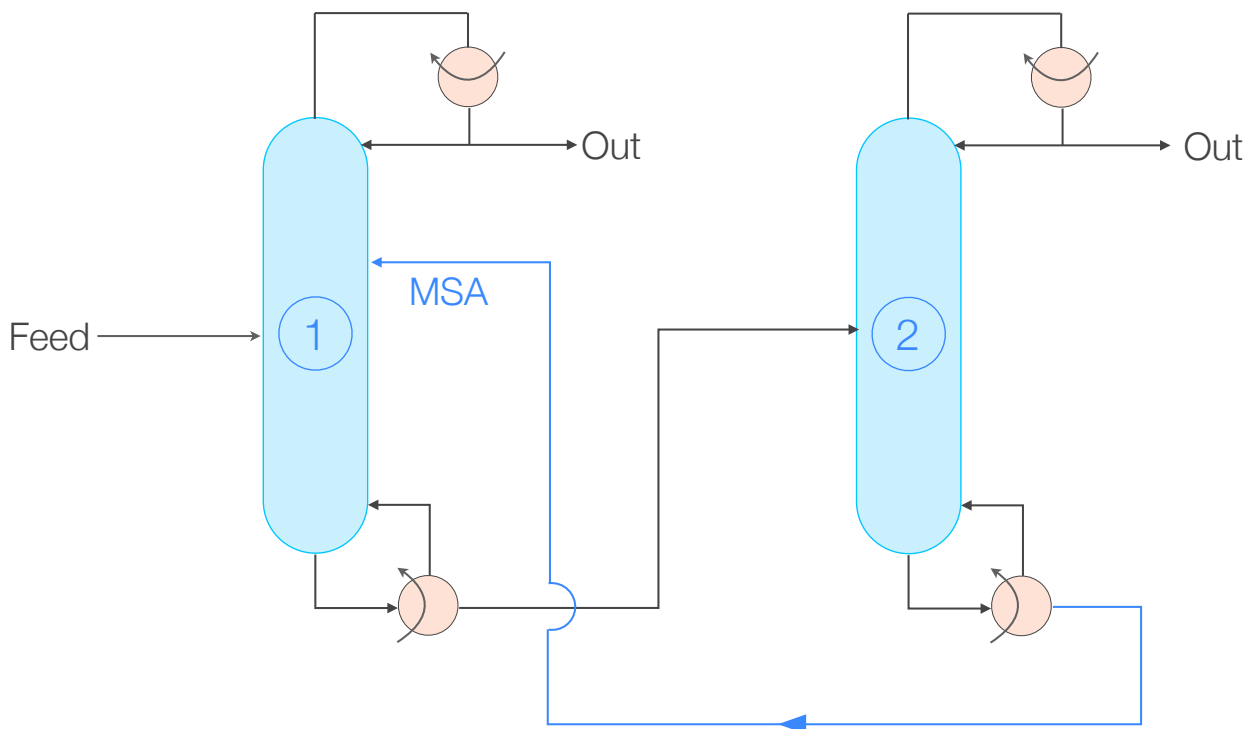
MSA is an additional species whose presence may either

- (1) change the spacing between the volatilities or
- (2) change the order of volatilities (think about the effects of non-ideal behavior)

The addition of an MSA does add another chemical that will need to be separated, but it might still be justified if the separation events become easier enough.



The presence of E leads to a "flip" between B and C. Now we note that [B and D] are adjacent in the order. No need to split [B D].



The second column is designed to recover / recycle the MSA. Look at the overall mass balance - notice that the MSA never exits (or enters) the process. Invest in a quality design for the recover / recycle... and the MSA will not be an operating cost.

Azeotropic Distillation

- Adds an additional level of challenge for problem solving
- An azeotrope is “a mixture of **two or more liquids** in such a ratio that its composition **cannot be changed by simple distillation**.” When an azeotrope is boiled, the resulting vapor phase has the same composition as the original mixture.
- Azeotropes often arise in mixtures of oxygenated organic compounds (alcohols / ketones / ethers / acids) and water. Mixtures such as these are not uncommon in classical chemical engineering processes.
- We will find that **distillation boundaries** confine the compositions of a column to lie within bounded regions - and this can prevent the removal of certain species at high concentrations.

Azeotropic Distillation

- Does not conform to the guidelines
- No McCabe-Thiele construction can be made
- Minimum-boiling (the azeotrope is at a lower temp. than either pure-component boiling point) azeotropes are more common than maximum-boiling azeotropes.

Relative volatility
changes across the
azeotrope

Residue-Curve Maps

A plot of the composition of the liquid residue in a single-stage batch equilibrium still with time at a given pressure

Mass Balance

Expanding

$$x \frac{dN}{dt} + N \frac{dx}{dt} = -Vy$$

Thus,

$$N \frac{dx}{dt} = -x \frac{dN}{dt} - Vy$$



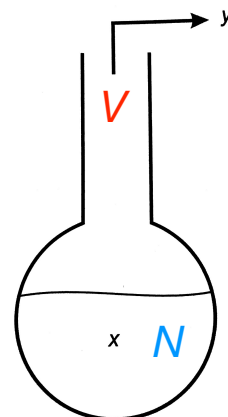
$$y_i = K_i x_i$$

$$\frac{dx_i}{dt} = (y_i - x_i) \frac{1}{N} \frac{dN}{dt}$$

$$\sum_i x_i = 1$$

$$\sum_i y_i = 1$$

Each different feed point will
produce different curve



Residue-Curve Maps

- Residue curves will be present on ternary diagrams.
- Each residue curve is built by tracing the composition of the equilibrium liquid residue of a simple (Rayleigh batch) distillation over time — starting from a selected initial composition.
- Use this idea to monitor how the x-composition (liquid) changes as more and more material is slowly removed from the batch by the exiting vapor (the temperature of the still is slowly increasing). This will draw a residue curve.
- Multiple residue curves are possible — each a function of the initial composition of the original liquid in the still.
- The residue curves approximate the operating lines of a distillation tower operating at total reflux. (same Mass Balance equation)

If we repeat for many feed positions, we can build up the map

- Arrows point in _____
direction of T
- Aspen plus can make these for you
- This curve represents the changes in residue composition with time as the result of a simple, one-stage batch distillation
- But, it is still a good approximation because it is not very different from the “total reflux” case (the other extreme).

Some Possible Azeotropic Situations for Ternary Systems

Simulation 1 - Aspen Plus V10 - aspenONE

RESID-1 (RESIDUE) x Control Panel x RESID-1 (RESIDUE) - Input x RESID-1 Residue Curves x Components x +

Select components

Component ID	Type	Component name	Alias
WATER	Conventional	WATER	H2O
ETHANOL	Conventional	ETHANOL	C2H6O-2
CYCLO-01	Conventional	CYCLOHEXANE	C6H12-1

Find Elec Wizard SFE Assistant User Defined Reorder Review

RESID-1 (RESIDUE) x Control Panel x RESID-1 (RESIDUE) - Input x RESID-1 Residue Curves x Methods x +

Global Flowsheet Sections Referenced Comments

Property methods & options

Method filter: COMMON

Base method: UNIFAC

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☒ Use true components

Method name: UNIFAC

Methods Assistant...

Modify

Vapor EOS: ESRK

Data set: 1

Liquid gamma: GCMFAC

Data set: 1

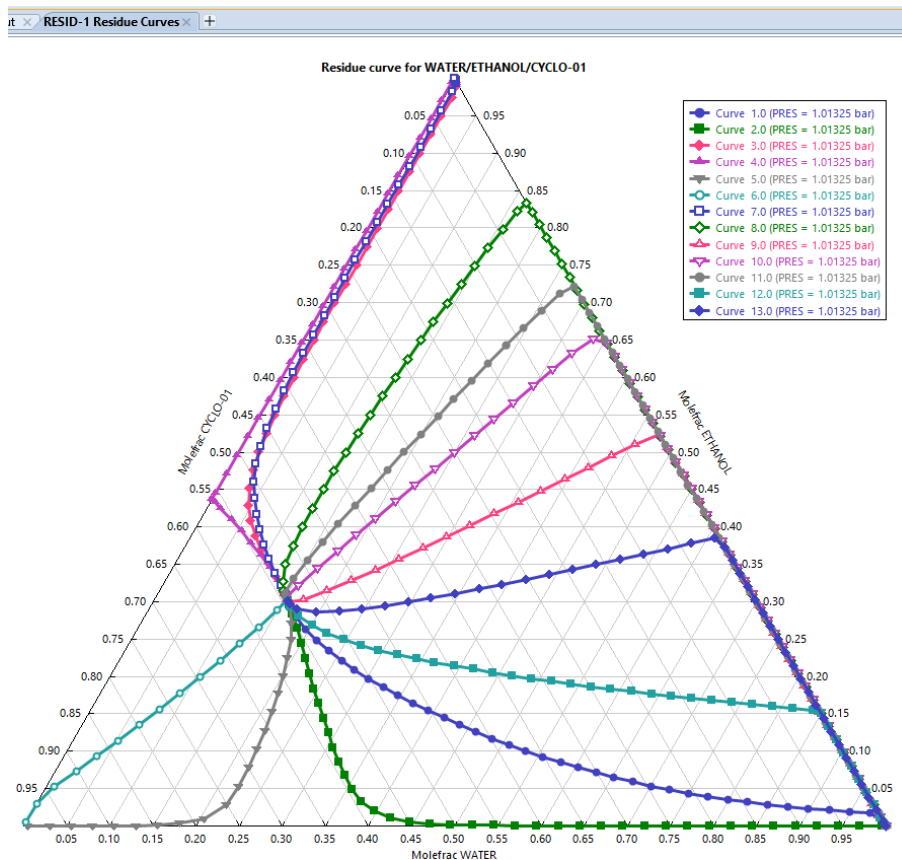
Liquid molar enthalpy: HLMX103

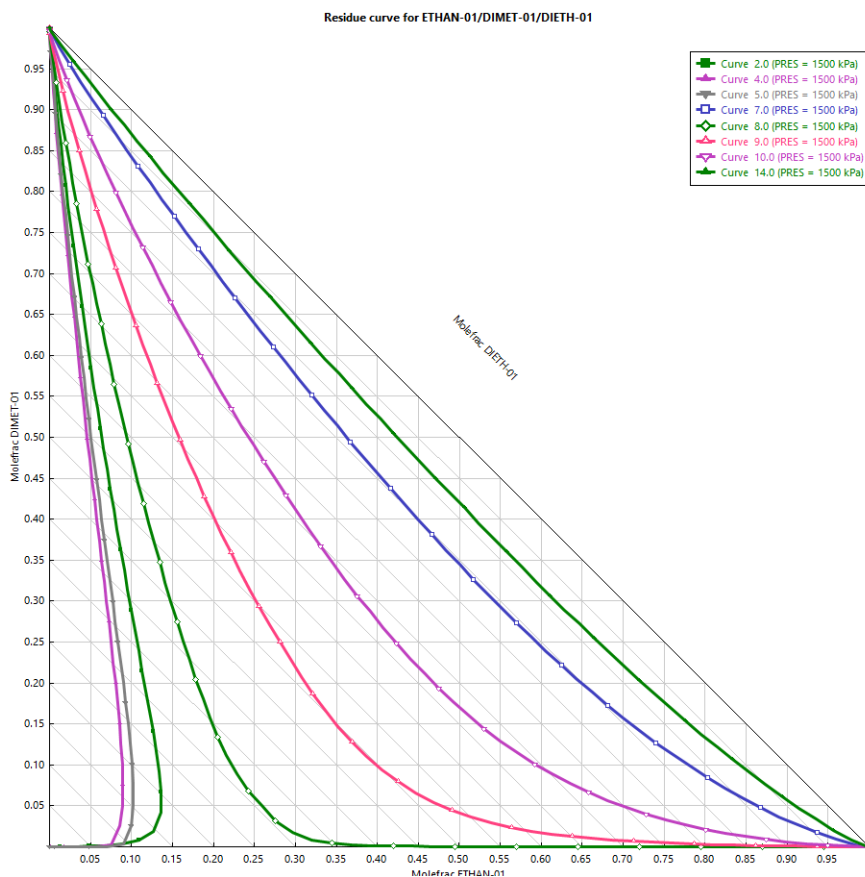
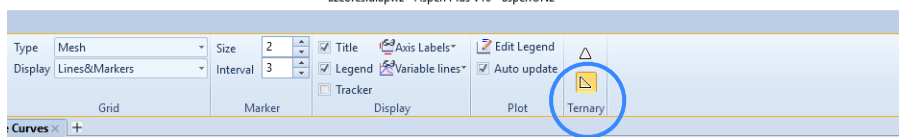
Liquid molar volume: VLMX01

☒ Heat of mixing

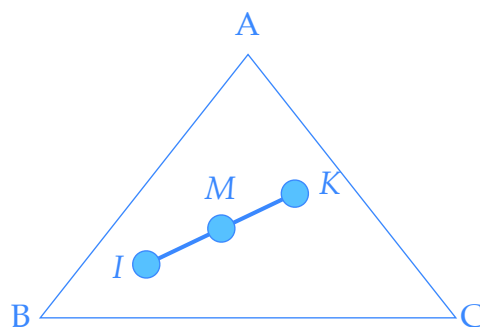
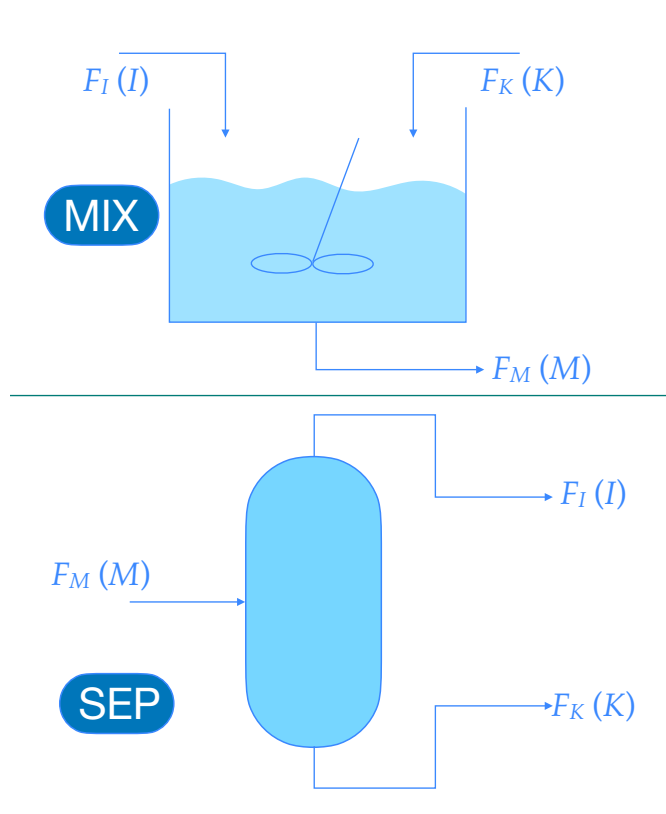
☒ Poynting correction

☐ Use liquid reference state enthalpy





Lever Rule (Mass Balance)



From Overall MB & Component MB

$$\frac{F_I}{F_K} = \frac{\overline{MK}}{\overline{IM}} = \frac{x_M - x_k}{x_I - x_M}$$

Lever Rule

Heterogeneous Azeotropic Distillation

We will look at a process example considering the dehydration of ethanol. We seek to remove water from ethanol. This is a very relevant design challenge in the “ethanol from corn” model ... that process uses an enormous amount of water, and the water must be removed from the bio-reaction product stream so as to create high quality ethanol. The ethanol/water system has an azeotrope (at $P = 14.7$ PSI) of $x_{\text{EtOH}} = y_{\text{EtOH}} = 0.89$

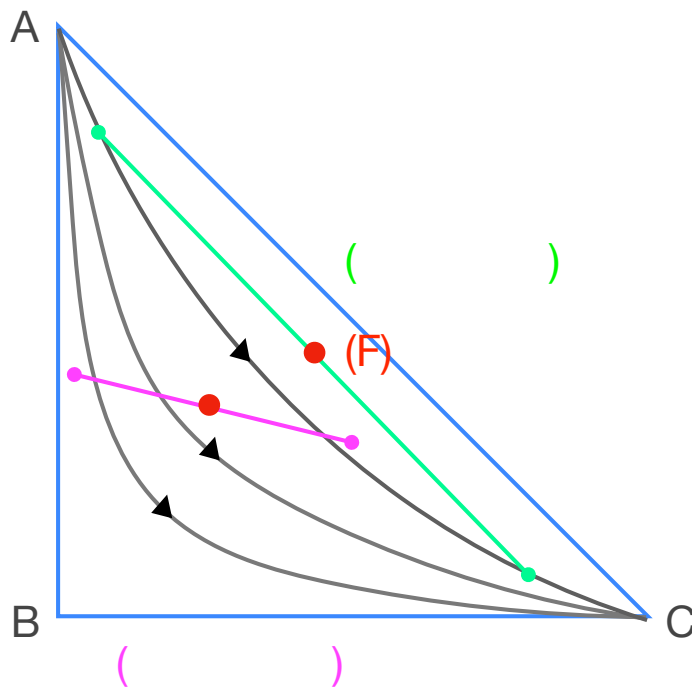
For initial compositions below the azeotrope (and the bio-reaction product stream is typically much less than 89% ethanol) ... it is possible to achieve “water with no ethanol” but it is not possible to achieve “ethanol with no water”.

The strategy will be to create a **heterogeneous azeotropic distillation** process by introducing a third component (toluene – a solvent that is only partially miscible with water) which will result in liquid/liquid equilibrium ideas.

Feasible Product Compositions

- If a straight line is drawn that connects the distillate and bottoms compositions, that line must pass through the feed composition at some intermediate point to satisfy a material balance.
- The distillate and bottoms points (**the end of the line**) must also **cross the same residue curve** _____ to satisfy the column stage equilibriums.

Feasible Product Compositions



Others...

- Reactor feed preparation and separator feed preparation sections
- Recycle section
- Environmental control section
- Major process control loops
- Flow summary table
- Major equipment summary table