

# Multicomponent distillation

Maurizio Fermeglia

[Maurizio.fermeglia@units.it](mailto:Maurizio.fermeglia@units.it)

Department of Engineering & Architecture

University of Trieste



# Agenda

- ◆ Multicomponent distillation introduction and terminology
- ◆ Key and non-key components
- ◆ Profiles for multicomponent distillation
- ◆ Degrees of freedom analysis
- ◆ Rigorous models for multicomponent distillation
  - Naphtali Sandholm
  - MESH equations
  - Example of multicomponent distillation with RADFRC
- ◆ Complex distillation methods
  - Energy integration
  - Reflux sub cooling
- ◆ Azeotropic distillation systems
  - Pressure swing distillation
  - Azeotropic distillation by salt addition
  - Extractive distillation
  - Azeotropic distillation

# Multi-Component Distillation (MCD) – The Problem

## ◆ Binary distillation is easy.

- We can graphically solve a binary component distillation system using the McCabe-Thiele method
- It is also possible to do a complete analytical solution using mass and energy balances with the equilibrium relationship.

## ◆ Multi-component systems, $C > 2$ , is not easy

- the number of equations obtained from mass and energy balances with the equilibrium relationship will always be one less than the number of unknowns.

## ◆ Multi-component distillation has no complete analytical solution

- It requires a trial-and-error solution with the additional unknown assumed to be known,
- And special considerations as to enhancing convergence of the solution.

# Degrees of Freedom (DoF)

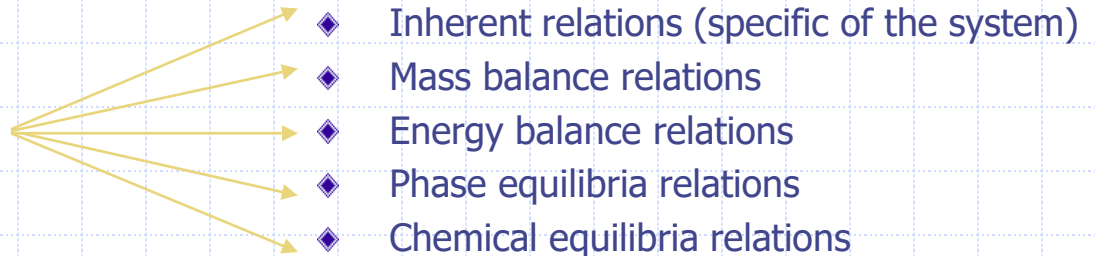
- ◆ Intensive variables:
  - Temperature, Pressure, concentration, ...
- ◆ Extensive variables
  - mass flow, energy flow, ...
- ◆ Iterative variables
  - n° of stages in a distillation column

$$N_i = N_v - N_r$$

$N_i$  = independent variables

$N_v$  = total variables

$N_r$  = independent equations



- ◆  $N_i > 0$ : "problem is underspecified and additional variables must be specified in order to determine the remaining variables"
- ◆  $N_i = 0$ : problem can be solved
- ◆  $N_i < 0$ : problem is overdetermined with redundant and possibly inconsistent relations

# Stream

$$N_v = T, P, \dot{m}, H_{stream}, x_i = 1 + 1 + 1 + 1 + (c - 1) = c + 3$$
$$N_r = 1$$

Enthalpy is a function of composition, T and P

or

$$N_v = T, P, \dot{m}, H_{stream}, x_i = 1 + 1 + 1 + 1 + c = c + 4$$
$$N_r = 1 + 1$$

$$\sum_i^c x_i = 1$$

Enthalpy is a function of composition, T and P

$$N_i = c + 2$$

*e.g.*

c-1: components

1: temperature

1: pressure

1: mass flow

# Separation column: Equilibrium stage

$$N_v = 4 * (c + 2) + 1 = 4c + 9$$

↑  
Number of  
streams

↑  
Heat  
exchanged

$$N_r = c + 1 + c + 2 = 2c + 3$$

↑  
Mass balance

↑  
Energy balance

↑  
Phase equilibria

↑  
T,P equivalence

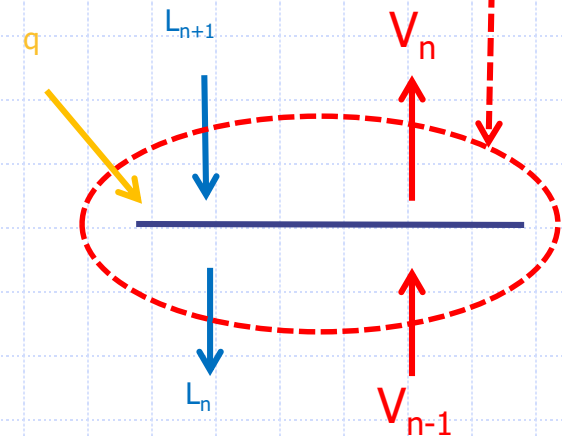
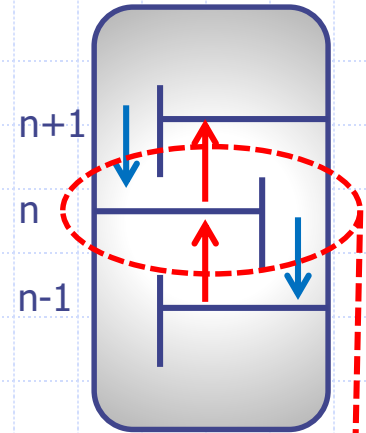
$$N_i = 2c + 6$$

*e.g.*

2(c+2): definition of inlet streams

1: temperature

1: pressure



# Separation column: Feed stage

$$N_v = 5 * (c + 2) + 1 = 5c + 11$$

↑  
Number of  
streams

↑  
Heat  
exchanged

$$N_r = c + 1 + c + 2 = 2c + 3$$

↑  
Mass balance

↑  
Energy balance

↑  
Phase equilibria

↑  
T,P equivalence

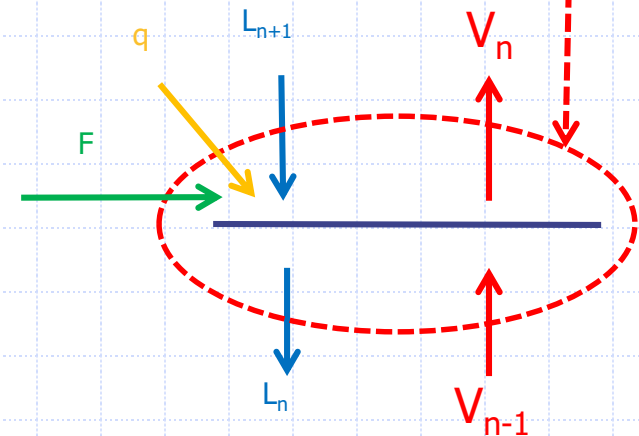
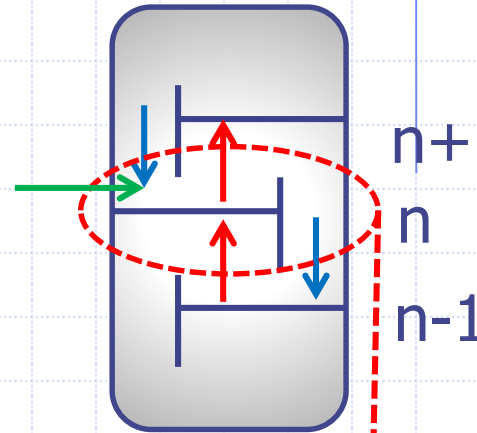
$$N_i = 3c + 8$$

*e.g.*

3(c+2): definition of inlet streams

1: temperature

1: pressure



# Separation column: Side stream stage

$$N_v = 5 * (c + 2) + 1 = 5c + 11$$

↑  
Number of streams

↑  
Heat exchanged

$$N_r = c + 1 + c + 4 + (c - 1) = 3c + 4$$

Mass balance

↑  
Energy balance

↑  
Phase equilibria

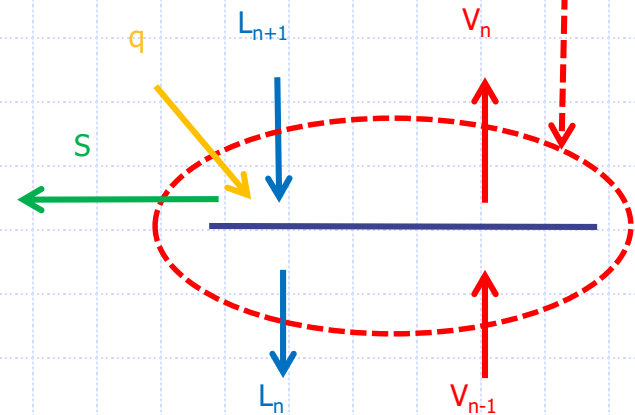
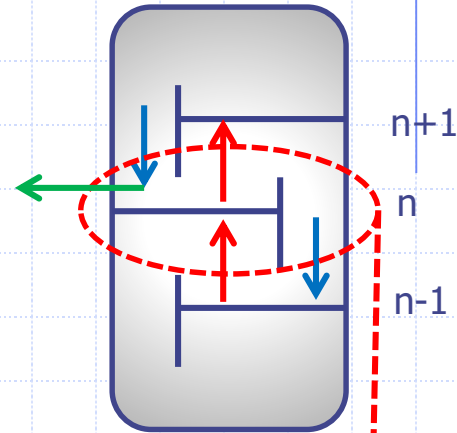
↑  
T,P equivalence for 3 outlet streams

↑  
Composition equivalence with  $V_n$  or  $L_n$

$$N_i = 2c + 7$$

e.g.

- 2(c+2): definition of inlet streams
- 1: heat exchanged
- 1: pressure
- 1: mass flow of stream S





# Absorption column

$$N_v = n * (2c + 6) + 1$$

↑                      ↑                      ↙  
 Number of stages    DoF for each stage    Heat exchanged

$$N_r = 2 * (c + 2) * (n - 1)$$

↗                      ↖                      ↖  
 Streams ∇ stage    DoF for each stream    n-1 independent stages

$$N_i = 2n + 2c + 5$$

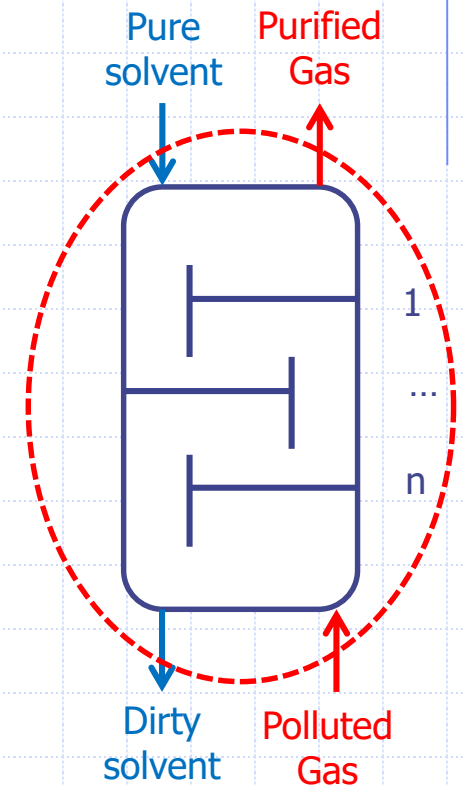
e.g.

2(c+2): definition of inlet streams

n: P ∇ stage

n: Heat loss ∇ stage

1: number of stages



# Distillation column

$$N_v = (c + 4) + (c + 5) + (2c + 2n + 5) + (3c + 8) + (2c + 2m + 5) + (c + 4) = 10c + 2m + 2n + 31$$

↑                      ↑                      ↑                      ↑                      ↑                      ↑  
 Condenser    Splitter                      Rectifying column                      Feed stage                      Stripping column                      Reboiler

Streams      2              3                      4                      5                      4                      3              Total = 21

Streams counted twice = 9

Streams independent = 12

$$N_r = 9 * (c + 2)$$

$$N_i = 2 * (n + m) + c + 13$$

*e.g.*

c+2: definition of feed

n,m: P ∨ stage

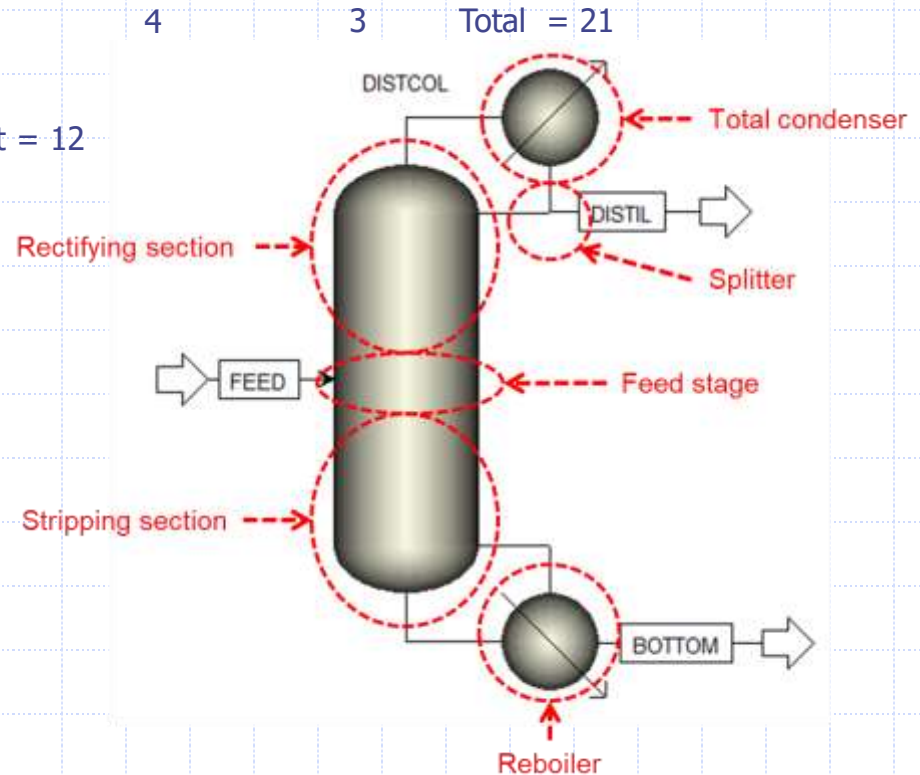
n,m: Heat loss ∨ stage

2: number of stages n,m

1: Reflux ratio

2: LK,HK recovery

6: T,P condenser, reboiler, splitter



# Degrees of freedom for a multicomponent distillation column

$$N_i = 2 * (n + m) + c + 13$$

## ◆ For a conventional column with:

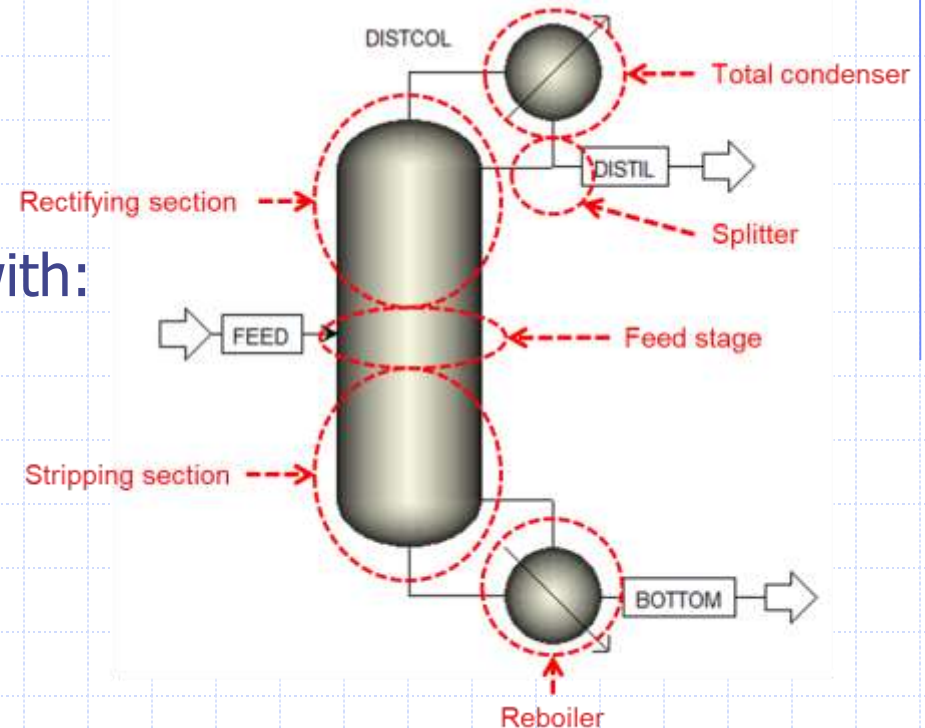
- total condenser
- partial reboiler
- CMO
- constant pressure
- heat leak:

## ◆ In terms of specifications:

- $n+m$ :  $P \forall$  stage
- $n+m$ : Heat loss  $\forall$  stage
- 6:  $T, P$  in condenser, reboiler, splitter
- 1:  $P$  of the feed
- Total :  $2(n+m) + 7$

## ◆ → $n_i = c + 6$ , e.g.:

- $c+1$ : definition of feed
- 2: number of stages  $n, m$
- 1: Reflux ratio
- 2: LK, HK recover



# Degrees of freedom for a multicomponent distillation column

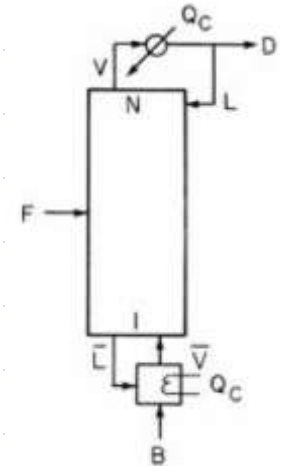
- ◆ Degrees of freedom analysis gives us the number of independent variables to be fixed, but does not indicate which ones. They can be selected among:
  - Total number of stages in both sections
  - Reflux or reflux ratio
  - Reboiler boilup ratio  $\underline{V}/R$ , or vapor flow rate
  - Product composition of a component (max 2 Specifications)
  - Distribution or split of a component (max 2 Specifications)
  - Product ratio  $D/R$
  - Heat duties at reboiler  $Q_R$  and condenser  $Q_C$
- ◆ In column design it is normal that:
  - Feed is at the 'optimal' position to minimize the number of stages (1 Dof)
  - Reflux ratio is at its optimal value to minimize total costs (1 Dof)
  - Two variables remains to be assigned: two product specifications
- ◆ In column rating it is normal that:
  - Total number of stages is known
  - If reflux ratio is fixed, only one DoF is left: on optimal parameter that maximize the separation.

# Degrees of freedom for a multicomponent distillation column

◆ Consider a binary distillation column  $N_i = C+2 = 8$

◆ In a design problem we specify:

- 3:  $F, z, \text{ feed quality } q$
- 1: Optimum feed stage
- 3:  $x_D, \text{ distillate } T \text{ (saturated liquid), } x_B$
- 1: External reflux ratio  $L/D$
- The OL are defined and McCabe-Thiele method can be used.



◆ Consider a 3 components column

- The degrees of freedom is 9. Nine specified variables are listed in Table.
- The extra degree of freedom is used to fully specify the feed composition.
- With 4 C  $\rightarrow$  10 DoF.
- The additional degree of freedom must again be used to fully specify the feed composition.

Number of variables	Variable
1	Feed rate, $F$
2	Feed composition, $z_1, z_2$ ( $z_3 = 1 - z_1 - z_2$ )
1	Feed quality, $q$ (or $h_F$ or $T_F$ )
1	Distillate, $x_{1, \text{dist}}$ (or $x_{3, \text{dist}}$ or $D$ or one fractional recovery)
1	Bottoms, $x_{2, \text{bot}}$ (or $x_{3, \text{bot}}$ or one fractional recovery)
1	$L/D$ or $V/B$ or $Q_R$
1	Saturated liquid reflux or $T_{\text{reflux}}$
1	Optimum feed plate location
-	
9	

Column pressure and  $Q_{\text{col}} = 0$  are already specified.

# Calculation difficulties for MCD: “Off-the-Shelf” Solutions

- ◆ Note that in multicomponent distillation neither the distillate nor the bottoms composition is completely specified because **there are not enough variables** to allow complete specification.
  - This inability to completely specify the distillate and bottoms compositions has major effects on the calculation procedure.
  - Key components are introduced: those that have a specification
- ◆ Fortunately, **numerical design packages**, such as Aspen Plus, have been developed to perform the rigorous solution of multi-component distillation systems.
  - However, as a design engineer, one always needs to know the underlying theory and methods of calculation to enable one to make decisions about the validity of these “off-the-shelf” packages and to verify the results.

# MCD – Some Additional Terminology

- ◆ When dealing with multi-component systems, we introduce some new terminology in addition to the terms used in binary distillation:
  - Fractional recoveries
  - Key components
  - Non-key components
  - Splits – distributing and non-distributing systems
- ◆ Note that binary systems can be handled in the same terms.

# MCD – Fractional Recoveries

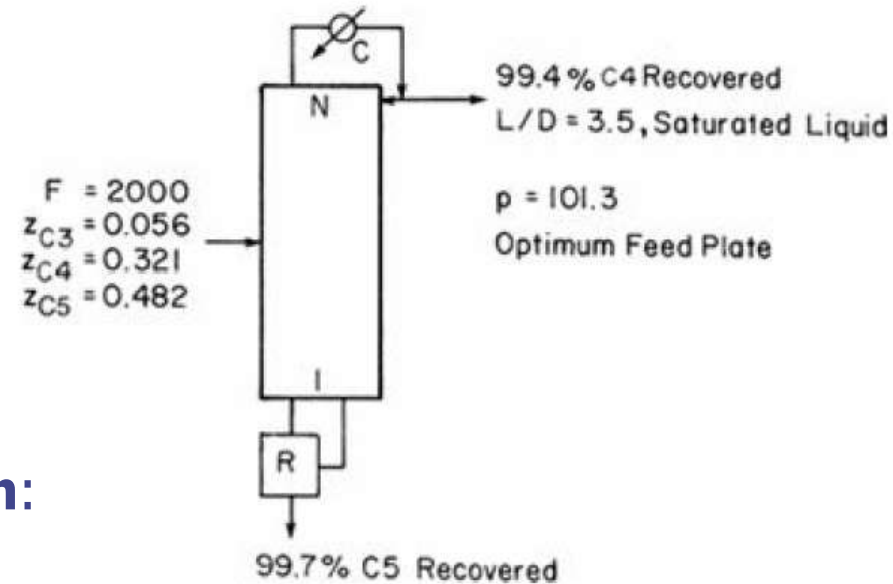
- ◆ Fractional recoveries are often specified in MCD.
- ◆ A fractional recovery,  $FR_i$ , is the amount or **flow rate of component i** in the distillate or bottoms stream **with respect to the amount or flow rate of component i in the feed stream**:

$$(FR_i)_{dist} = \frac{(Dx_i)_{dist}}{Fz_{F,i}} = \frac{Dx_{D,i}}{Fz_{F,i}}$$

$$(FR_i)_{bot} = 1 - (FR_i)_{dist}$$

$$(FR_i)_{bot} = \frac{(Bx_i)_{bot}}{Fz_{F,i}} = \frac{Bx_{B,i}}{Fz_{F,i}}$$

$$(FR_i)_{dist} = 1 - (FR_i)_{bot}$$



- ◆ It is the simple relationships expressed by the right-hand-side equations that make the use of fractional recoveries useful.
- ◆ These are also often specified **simply as % recovery**.



# MCD – Key and non-Key Components

## ◆ Key Components

- The components that have their distillate and bottoms **composition specified are known** as the key components.
- The most volatile of the key components is termed the **light key (LK)**.
- The least volatile of the key components is termed the **heavy key (HK)**.

## ◆ Non-Key Components

- All other components not specified in the distillate or bottoms are termed non-key components (NK's).
- If a non-key component is more volatile than the light key, then it is termed a **light non-key (LNK)**.
- If a non-key component is less volatile than the heavy key, it is a **heavy non-key (HNK)**.
- If a non-key component is neither a heavy non-key nor a light non-key, then it is an **intermediate non-key (INK)** or simply NK (AKA sandwich component).

# MCD – Non-Key Component

## ◆ Non-Key Component Splits

- The split of the non-key components is generally defined as to where the non-key components are obtained **with respect to the distillate or bottoms stream.**
- One can have **two types of situations** concerning the split of the non-key components:
  - ◆ Sharp split – Non-distribution of non-keys
  - ◆ Split – Distribution of non-keys

# MCD – Non-Key Component

## ◆ Non-distribution of NK's

- Non-distribution of non-keys means that essentially all of the non-keys are obtained in either the distillate stream or the bottoms stream. We obtain a sharp split of the NK's.
- Non-distribution of non-keys can be assumed when:
  - ◆ All of the non-keys are either HNK's or LNK's
  - ◆ The fractional recoveries of the LK in the distillate and HK in the bottoms are relatively large.

## ◆ Distribution of NK's

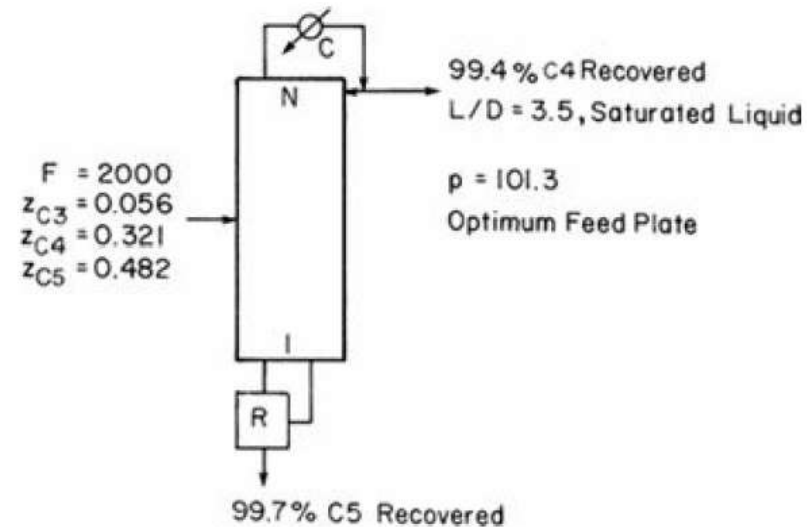
- Distribution of non-keys means that the non-keys are not sharply split between the distillate stream or the bottoms stream. We obtain a split of the NK's.
- Distribution of non-keys occurs when:
  - ◆ Not all of the non-keys are either HNK's or LNK's – we have NK's.
  - ◆ The fractional recoveries of the LK in the distillate and HK in the bottoms are not relatively large.

# How do we determine the keys (LK and HK) and the non-keys (LNK's, HNK's and NK's) in MCD?

- ◆ The classification of components in MCD can be determined **from their relative volatilities**.
  - Relative volatility is defined as the ratio of the K values for two components, which is trivial for a binary system.
- ◆ In order to use relative volatilities in MCD, we choose a **reference component** and define all other component volatilities with respect to the reference component.
  - The relative volatility for the reference component, of course, will be 1.
  - We can then define relative volatilities using equilibrium coefficient K values for each component **from equilibrium data**
  - The choice of the reference component depends upon the problem, but **in general it will be the HK** component since it is less volatile than the LK component.

# Example: Key and Non-Key

- ◆ We wish to distill 2000 kmol/h of a saturated liquid feed.
  - The feed is 0.056 mole fraction propane, 0.321 n-butane, 0.482 n-pentane, and the remainder n-hexane.
  - The column operates at 101.3 kPa.
  - The column has a total condenser and a partial reboiler.
  - Reflux ratio is  $L_0/D = 3.5$ , and reflux is a saturated liquid.
  - The optimum feed stage is to be used.
- ◆ A fractional recovery of 99.4% n-butane is desired in the distillate and 99.7% of the n-pentane in the bottoms.
- ◆ Estimate distillate and bottoms compositions and flow rates.
- ◆ What are the key and non-key designations for this separation?



# Example: Key and Non-Key

- ◆ Component volatilities can be determined from the K values.
  - the order of volatility is: propane > n-butane > n-pentane > n-hexane
- ◆ Since the recoveries of n-butane and n-pentane are specified:
  - We have:

## Volatilities

propane > n-butane > n-pentane > n-hexane

### Component

Propane

n-butane

n-pentane

n-hexane

### Designation

Light Non-Key

Light Key

Heavy Key

Heavy Non-Key

# Key and Non-Key Example

- ◆ If the recoveries of n-butane and n-hexane are specified:

propane > n-butane  $\overset{\text{Volatilities}}{>}$  n-pentane > n-hexane

<u>Component</u>	<u>Designation</u>
Propane	Light Non-Key
n-butane	Light Key
n-pentane	Non-Key
n-hexane	Heavy Key

- ◆ If only the recovery of n-butane is specified:

<u>Component</u>	<u>Designation</u>
Propane	Light Non-Key
n-butane	Key
n-pentane	Non-Key
n-hexane	Non-Key

# Missing Keys

- ◆ In typical MCD problems, one specifies **LK and HK recoveries**.
  - If only the LK or the HK recovery is specified, one typically chooses one of the non-key components to be the HK or LK
  - Usually the non-key component with the greatest feed composition.
- ◆ The fractional recovery of the missing key needs to be determined,
  - But it must be estimated since not enough information is given in the problem to determine it directly.
  - One way to estimate the fractional recovery of the missing key component is to do an **external mass balance** based upon a binary system comprised of the LK and HK.
  - This fractional recovery is then used in the MCD solution.
  - A trial-and-error solution may be required to determine the actual fractional recovery.



# Key and Non-Key Example

- ◆ Consider a distillation column with the following feed components:
  - Methane
  - Ethane
  - Ethylene
  - Propylene
  - Propane
- ◆ It is specified that a distillate concentration,  $x_D$ , for ethylene is required.
- ◆ What are the key and non-key designations for this separation?

# Key and Non-Key Example

- ◆ One source for determining the order of the component volatilities can be determined from the K values from equilibrium data
  - Volatility is: methane > ethylene > ethane > propylene > propane
- ◆ Since  $x_D$  for ethylene is specified it is a key component.

<u>Component</u>	<u>Designation</u>
Methane	Light Non-Key
Ethylene	Light Key
Ethane	Non-Key
Propylene	Non-Key
Propane	Non-Key

- ◆ There is no heavy key specified for this problem.

# Key and Non-Key Example

◆ If an  $x_D$  for ethylene and an  $x_B$  for propylene are specified:

## Component

Methane

Ethylene

Ethane

Propylene

Propane

## Designation

Light Non-Key

Light Key

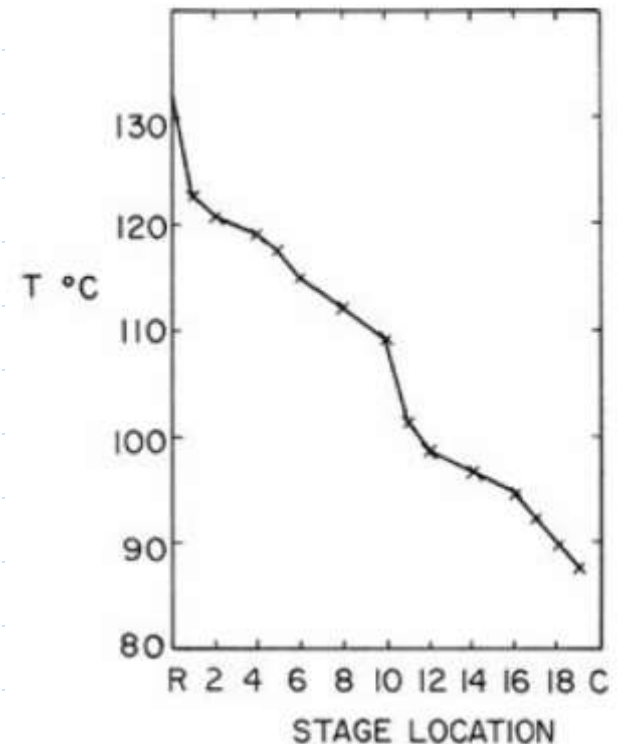
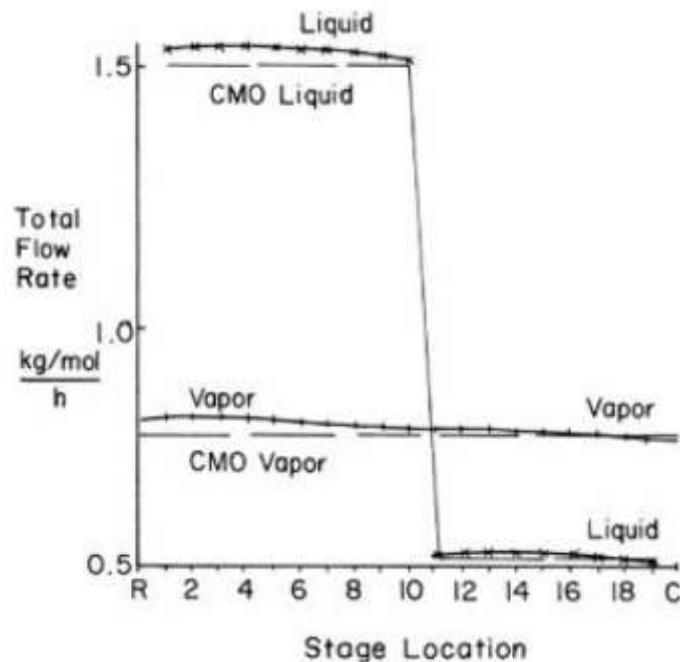
Non-Key

Heavy Key

Heavy Non-Key

# Profiles for multicomponent distillation

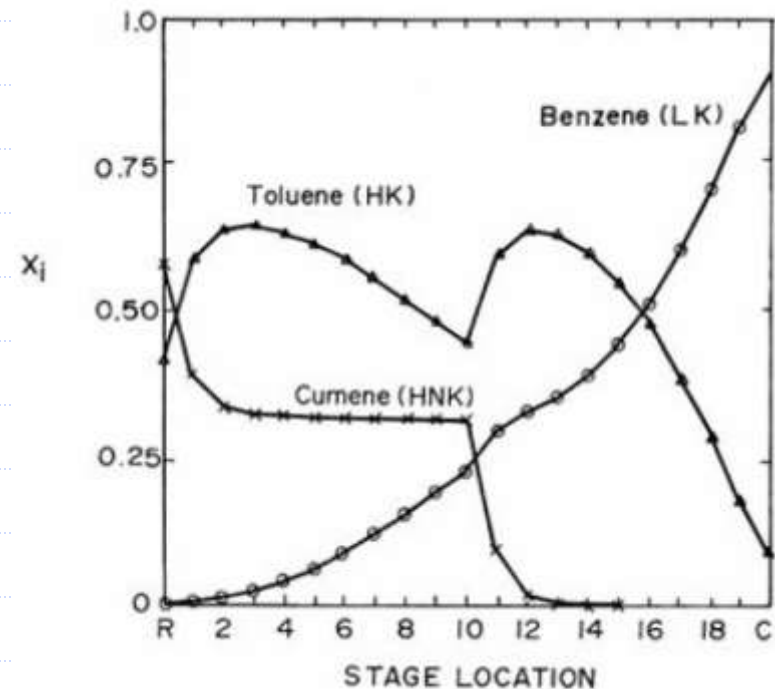
- ◆ Distillation of benzene, toluene, and cumene in a column with 20 stages, 99% recovery of **benzene** in the distillate
  - a) for non constant molal overflow, the total flow rates will vary from section to section but the ratio L/V will be much more constant.
  - b) temperature decreases monotonically from the reboiler to the condenser.



# Profiles for multicomponent distillation

- ◆ Composition profiles: HK, LK and HNK (no LNK)
  - benzene recovery in the distillate was specified as 99%, **benzene is the LK**.
  - typically, the next less volatile component, **toluene, will be the HK**.
  - Thus, **cumene is the HNK**, and there is no LNK.

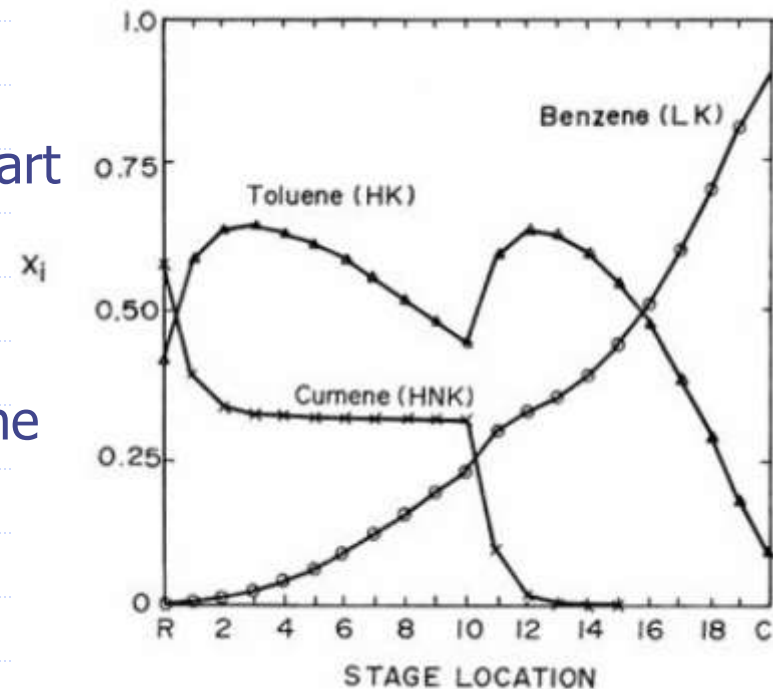
- ◆ Composition profiles: benzene
  - benzene mole fraction is very low in the reboiler and increases monotonically to a high value in the total condenser.



# Profiles for multicomponent distillation

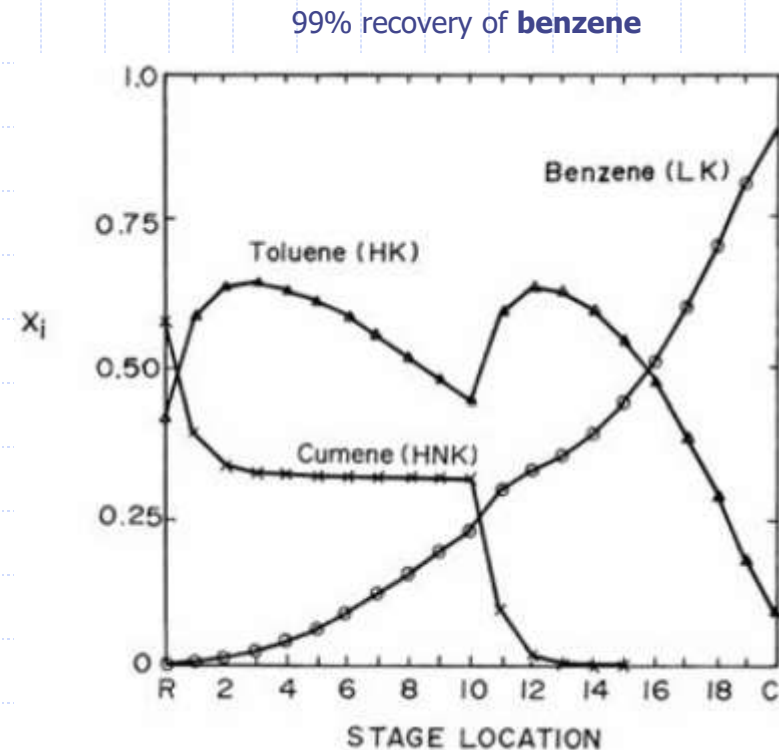
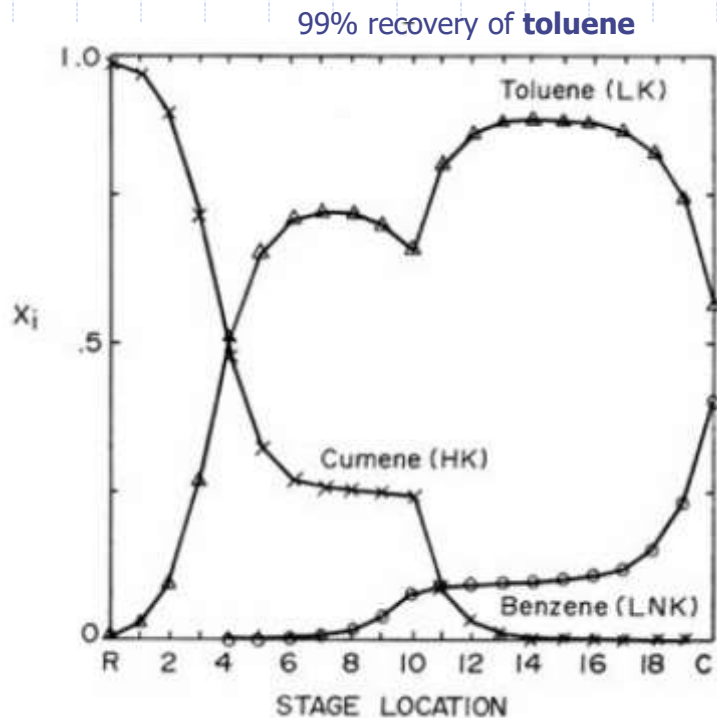
## ◆ Composition profiles: cumene, toluene

- cumene's mole fraction decreases above the reboiler because it is the **least volatile component**, but since there is a large amount of cumene in the feed, there must be a finite concentration at the feed stage. Above the feed stage, cumene concentration decreases rapidly because cumene is the least volatile component.
- toluene: look at **binary pairs of components** are distilling in each part of the column. Primary maximum is due to the raising presence of benzene. Second maximum at stage 12 is due to the decreasing of cumene and the final reduction of toluene is due to the raising of benzene.



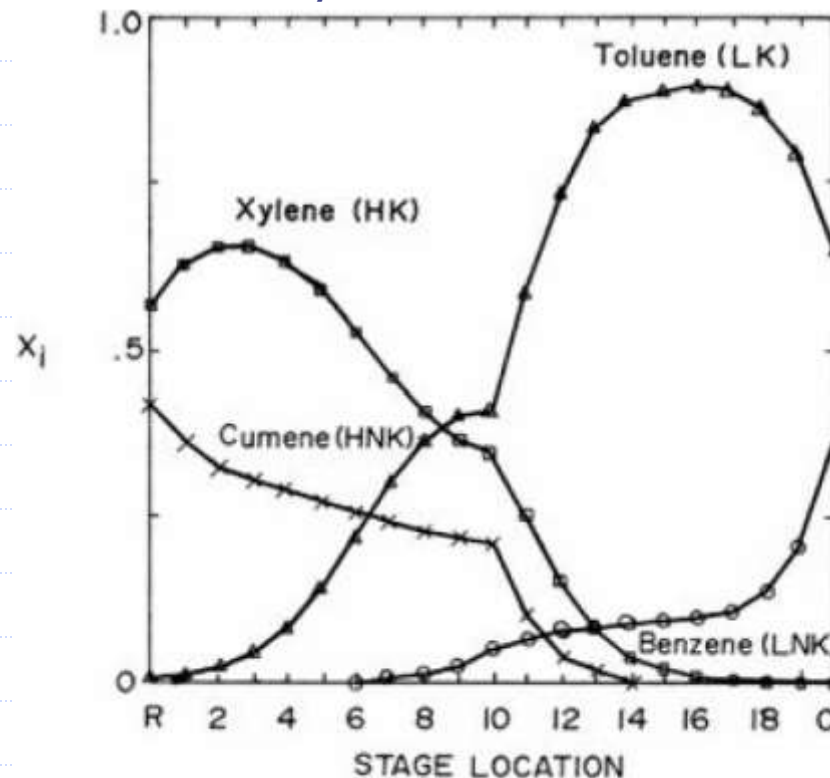
# Profiles for multicomponent distillation

- ◆ Same as before, but with a 99% recovery of **toluene** in the distillate
  - toluene is the LK, cumene is the HK and benzene an LNK. Note that with no HNKs, the HK concentration does not have any maxima.
  - look at binary pairs of components are distilling in each part of the column.



# Profiles for multicomponent distillation

- ◆ 4 components distillation: benzene, toluene, cumene and xylene in a column with 20 equilibrium contacts
  - Recovery of toluene in the distillate 99%.
  - Maxima are present in LK profile and in HK concentration profile.
  - secondary maxima near the feed stage are drastically repressed, but the primary maxima are readily evident.





# Exact calculation for multicomponent distillation

- ◆ Global material balance:

$$Fz_{F,i} = Dx_{D,i} + Bx_{B,i}$$

- ◆ Global energy balance:

$$Fh_F + Q_R = Dh_D + Bh_B + Q_C$$

- ◆ Material balances in enrichment section:

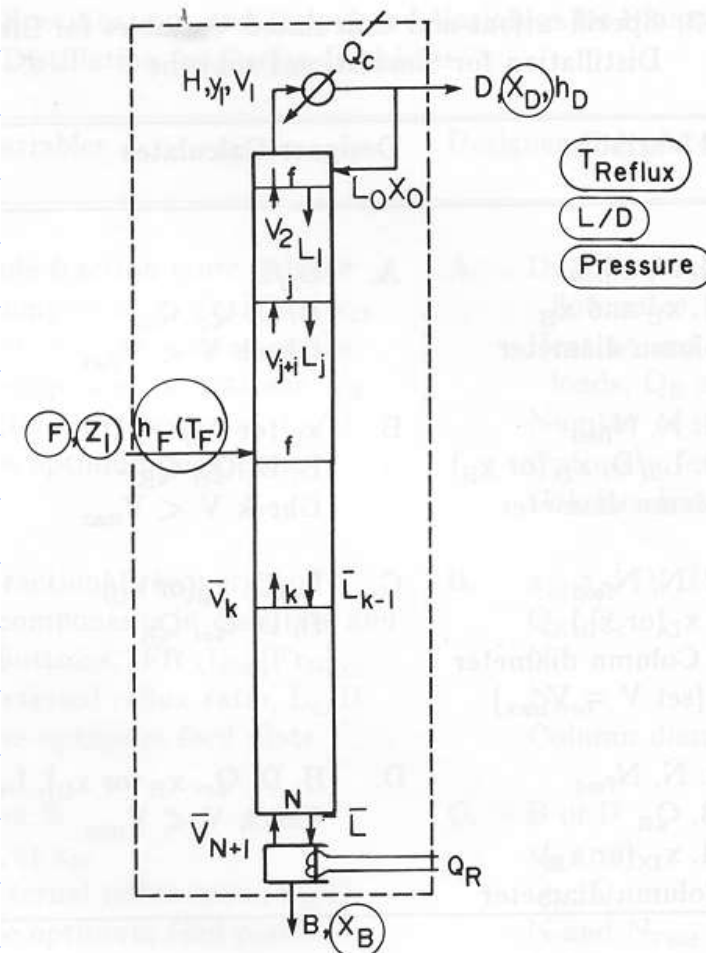
$$Vy_{j+1,i} = Lx_{j,i} + Dx_{D,i}$$

- ◆ Material balances in stripping section:

$$L'x_{j'+1,i} = V'y_{j',i} + Bx_{R,i}$$

- ◆ Equilibrium relationships

$$y_{j,i} = Kx_{j,i}$$



# Exact calculation for multicomponent distillation: Naphtali-Sandholm method

- ◆ Proposed by Naphtali and Sandholm in 1971
- ◆ **Simultaneous solution** of material, energy balances and equilibrium relationships for all column stages.
- ◆ Equations are grouped stage by stage and linearized.
- ◆ A **tridiagonal matrix** is obtained which is solved using a **Newton –Raphson method**.
- ◆ Model equations are written in terms of **departure functions**  $F_{j,k}$  where  $j$  is the stage and  $k$  the particular equation (balance or equilibrium), at the end:

$$F_{j,k} = (\text{inlet} - \text{outlet})_{j,k}$$

$$F_{j,k} = (y - Kx)_{j,k}$$

# Exact calculation for multicomponent distillation: Naphtali-Sandholm method

- ◆ Naphtali-Sandholm **uses molar flow rates** of each single component as variables:

$$l_i = Lx_i \quad v_i = Vy_i$$

$$L = \sum l_i \quad V = \sum v_i$$

- In this way, summation of mole fractions to one are included in the balance and equilibrium equations
- ◆ The nonlinear system of equations is solved by the Newton-Raphson method.
- ◆ This general method of solution is available in most process simulators, including ASPEN+©.

# Exact calculation for multicomponent distillation: MESH equations

- ◆ Alternative approach uses the MESH equations:
  - Mass balances, Equilibrium, Summation, Heat balance
- ◆ For each stage  $(2 C + 3)$  MESH equations can be written:
  - $C$  material balances
  - $C$  equilibrium conditions
  - 1 energy balance
  - 2 mole fractions summation equations
- ◆ With  $N$  stages  $\rightarrow N (2 C + 3)$  equations, and the same number of variables:
  - $2 N C$  molar fractions ( $x_i$  and  $y_i$  for each stage)
  - $2 N$  molar flow rates ( $L$  and  $V$ )
  - $N$  temperatures
- ◆ Comparing with Naphtali-Sandholm
  - Number of equations:  $N (2 C + 1)$  MEH equations
  - Number of unknowns ( $2N C$  flow rates  $l_i$  and  $v_i$  and  $e N$  temperatures)

# Example: multicomponent distillation

## ◆ Multicomponent distillation of benzene-toluene-cumene using RADFRAC. Data:

- Feed is  $x_{\text{BZ}} = 0.233$ ,  $x_{\text{TOL}} = 0.333$ ,  $x_{\text{CUM}} = 0.434$ , saturated liquid,  $F = 1.0$  kmol/h.
- Feed stage is number 10 above the partial reboiler, and there are 19 equilibrium stages plus a partial reboiler. A total condenser is used.
- $L/D = 1.0$
- $P = 101.3$  kPa (1 atm).
- Relative volatilities:  $\alpha_{\text{BZ}} = 2.25$ ,  $\alpha_{\text{TOL}} = 1.0$ ,  $\alpha_{\text{CUM}} = 0.21$ .

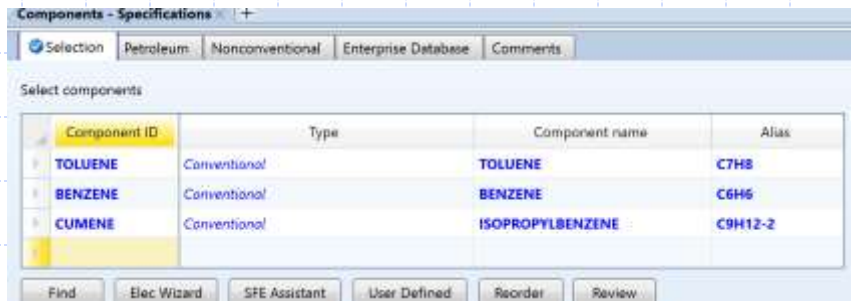
## ◆ Specification: 99% recovery of benzene in the distillate.

## ◆ Find:

- The distillate rate to achieve 99% recovery
- Temperature, flow rate, concentration profiles in the column

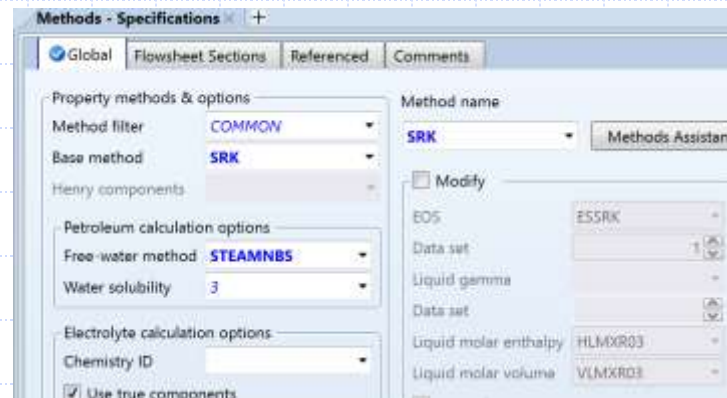
# Example: multicomponent distillation

## ◆ Components



Component ID	Type	Component name	Alias
TOLUENE	Conventional	TOLUENE	C7H8
BENZENE	Conventional	BENZENE	C6H6
CUMENE	Conventional	ISOPROPYLBENZENE	C9H12-2

## ◆ Methods



Property methods & options

Method filter: COMMON

Base method: SRK

Henry components: [empty]

Petroleum calculation options

Free-water method: STEAMNBS

Water solubility: 3

Electrolyte calculation options

Chemistry ID: [empty]

Use true components

Method name: SRK

Modify

EOS: ESSRK

Data set: 1

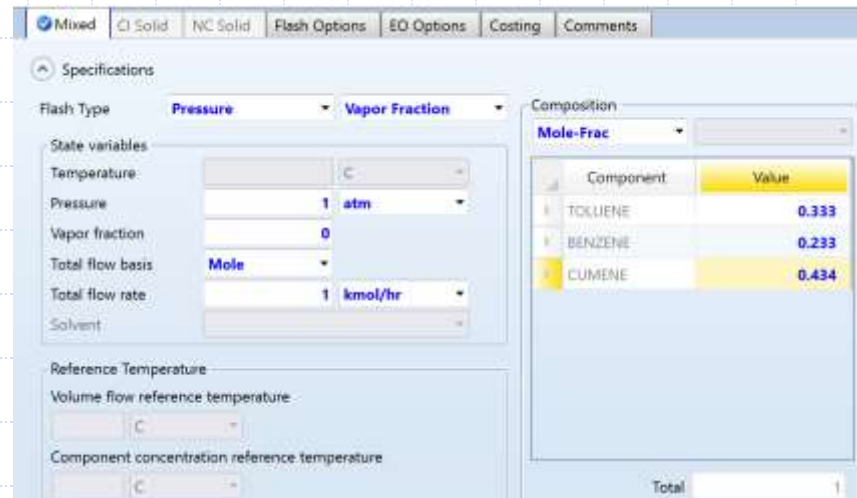
Liquid gamma: [empty]

Data set: [empty]

Liquid molar enthalpy: HLMXR03

Liquid molar volume: VLMXR03

## ◆ Feed



Flash Type: Pressure

State variables

Temperature: [empty] C

Pressure: 1 atm

Vapor fraction: 0

Total flow basis: Mole

Total flow rate: 1 kmol/hr

Solvent: [empty]

Reference Temperature

Volume flow reference temperature: [empty] C

Component concentration reference temperature: [empty] C

Composition: Mole-Frac

Component	Value
TOLUENE	0.333
BENZENE	0.233
CUMENE	0.434

Total: 1

# Example: multicomponent distillation

## ◆ Column specifications

- Initial value of distillate rate from material balance
- Pressure 1 atm
- Feed stage 9

## ◆ Design specification

- Mole recovery of Benzene at 99% mole
- Vary distillate rate (0.1 - 0.5)
- Result:  $D=0.3178$

Configuration | Streams | Pressure | Condenser | Reboiler | 3-Phase | Comm

Setup options

Calculation type: Equilibrium

Number of stages: 19

Condenser: Total

Reboiler: Kettle

Valid phases: Vapor-Liquid

Convergence: Standard

Operating specifications

Distillate rate	Mole	0.2	kmol/hr
Reflux ratio	Mole	1	

Specifications | Components | Feed/Product Stre

Description: Mole recovery, 0.99

Design specification

Type: Mole recovery

Specification

Target: 0.99

Specifications | Components | Results

Description: Distillate rate, 0.1, 0.5

Adjusted variable

Type: Distillate rate

Upper and lower bounds

Lower bound	0.1	kmol/hr
Upper bound	0.5	kmol/hr

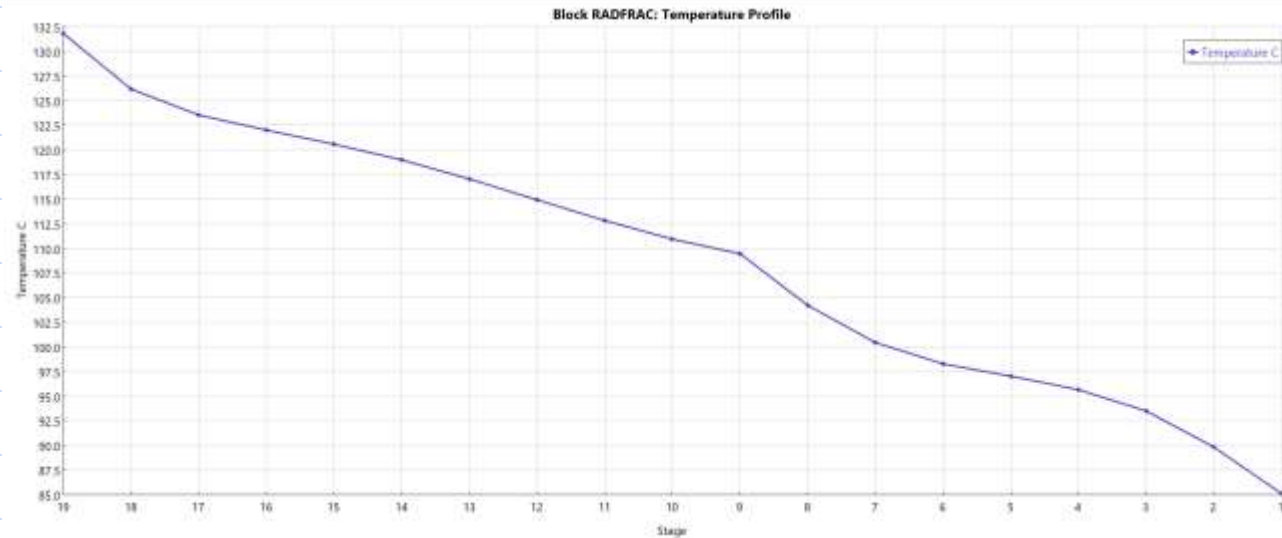
Optional

Maximum step size

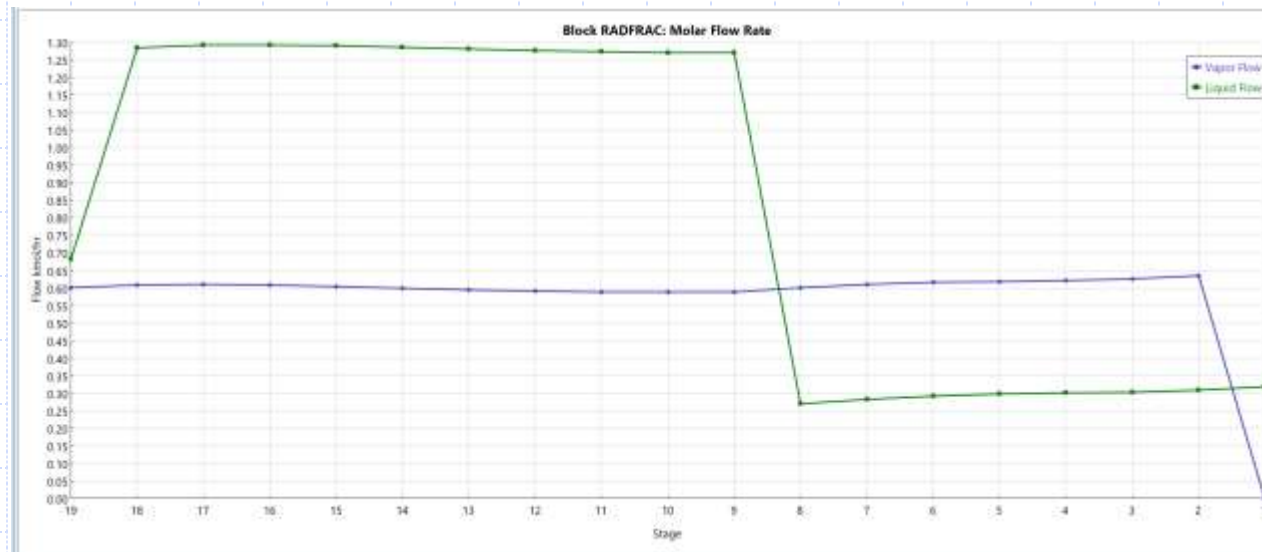


# Example: multicomponent distillation - column profiles

◆ Temperature



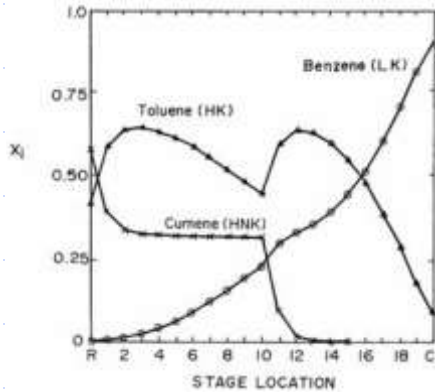
◆ Flow rates



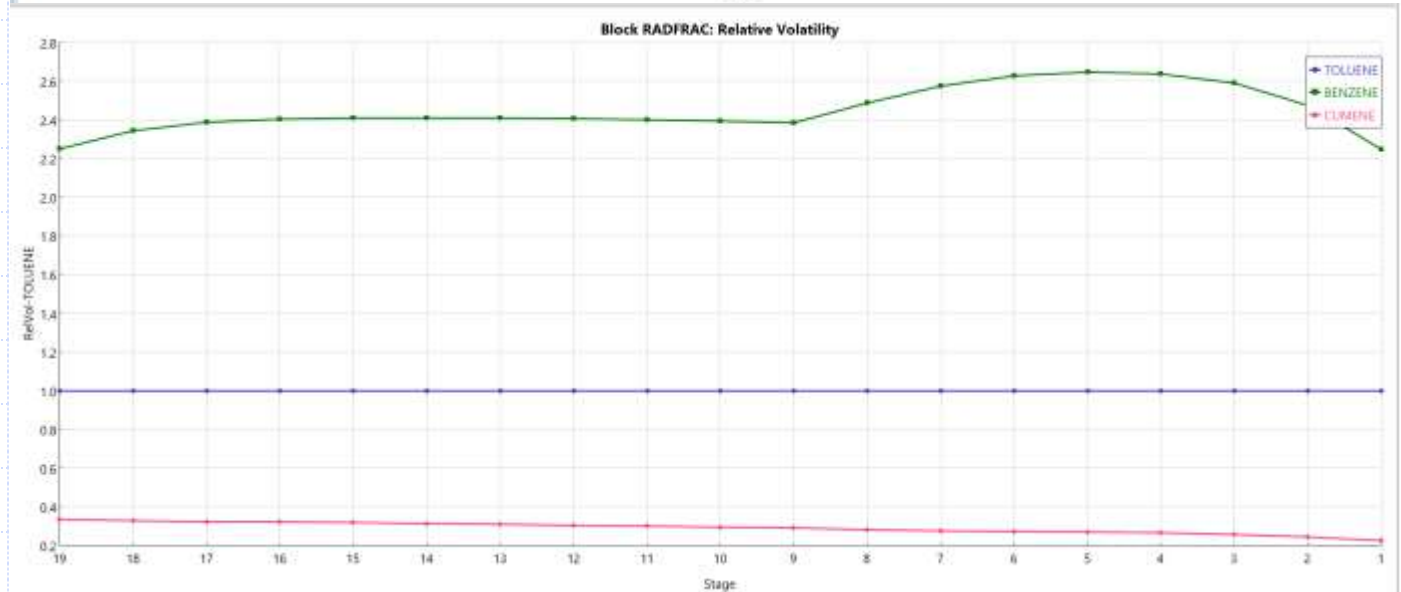
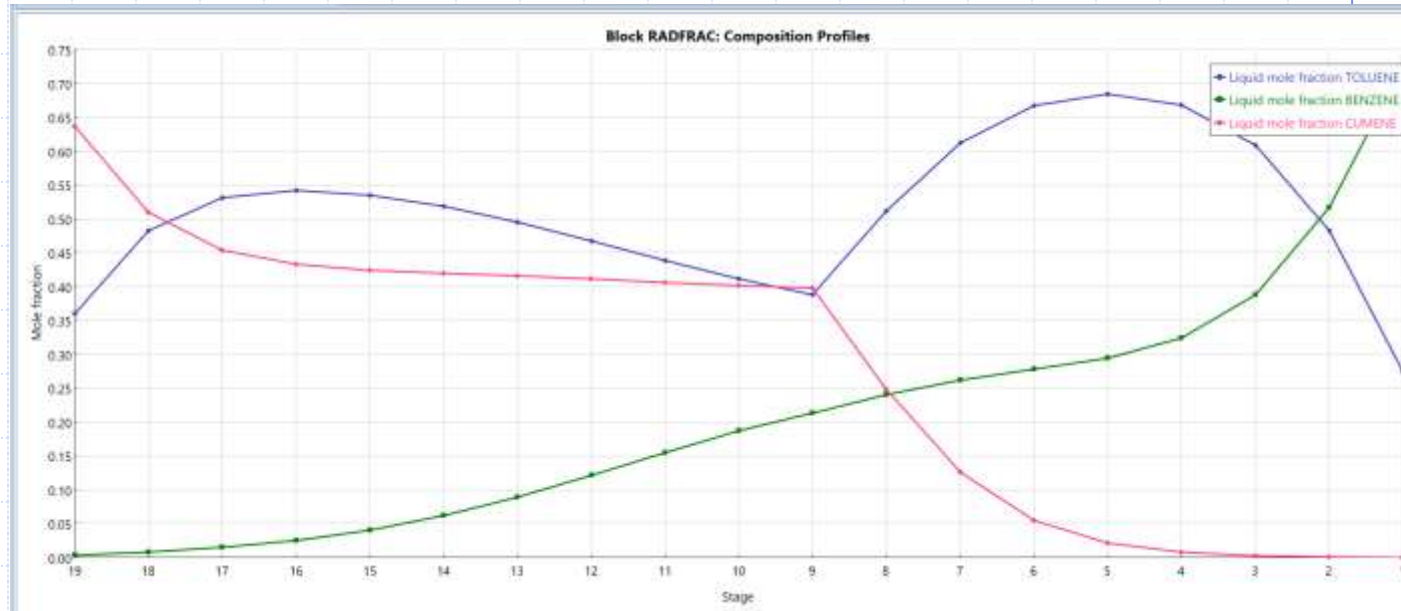


# Example: multicomponent distillation - column profiles

## Mole fractions



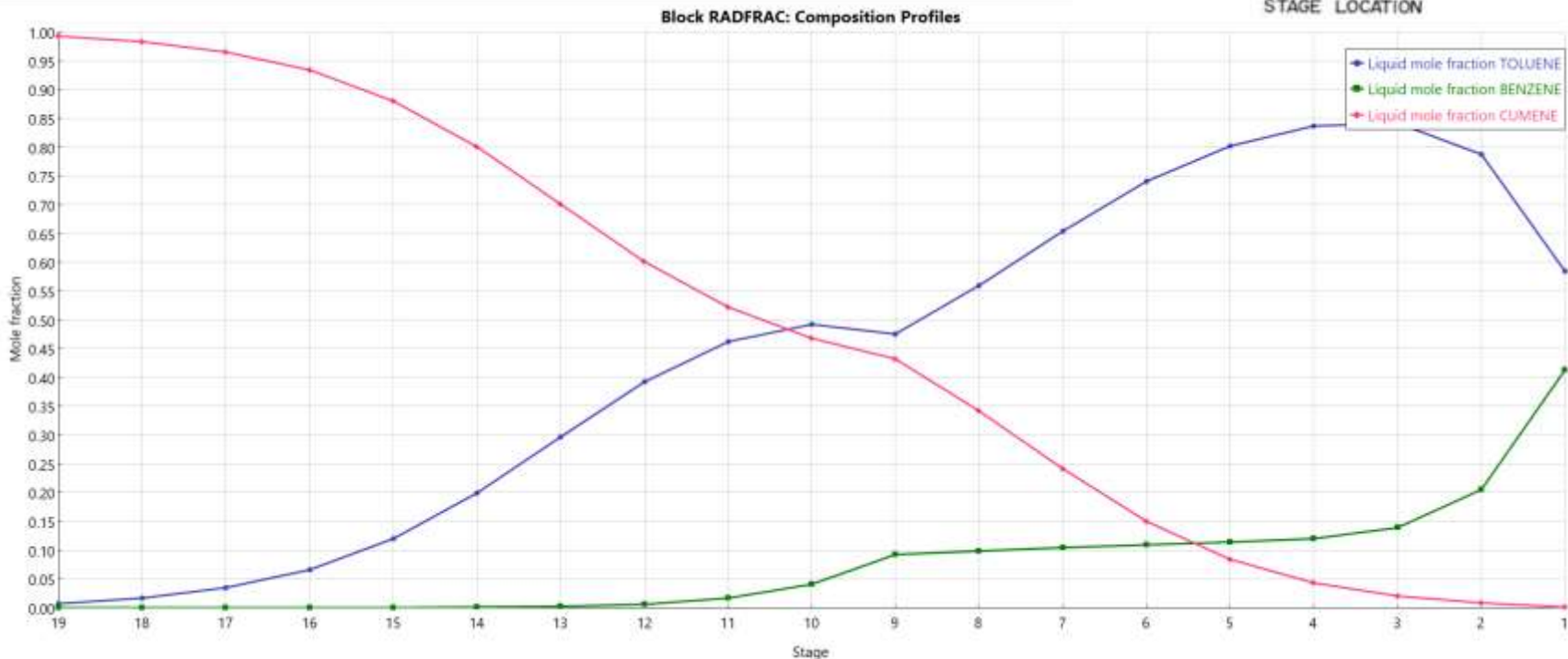
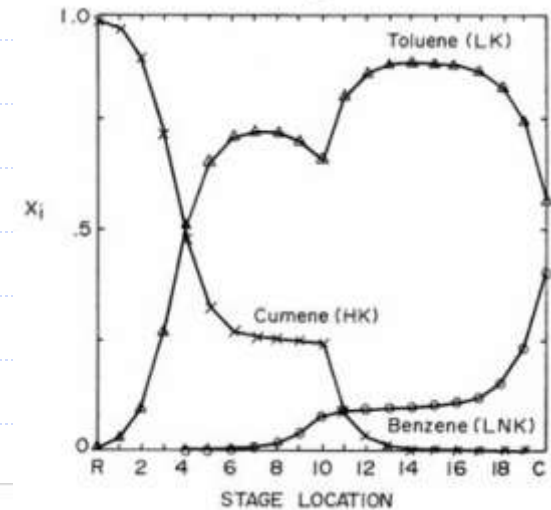
## Relative volatility



# Example: multicomponent distillation - column profiles for 99% recovery of toluene

◆ Mole fractions profiles for same distillation but with a 99% recovery of Toluene in the distillate

- Distillate flow rate = 0.563 kmol/hr



# Complex multicomponent distillation methods

Maurizio Fermeglia

[Maurizio.fermeglia@units.it](mailto:Maurizio.fermeglia@units.it)

Department of Engineering & Architecture

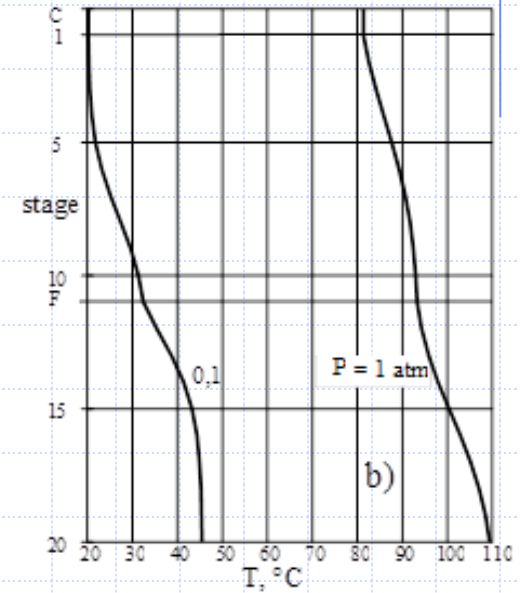
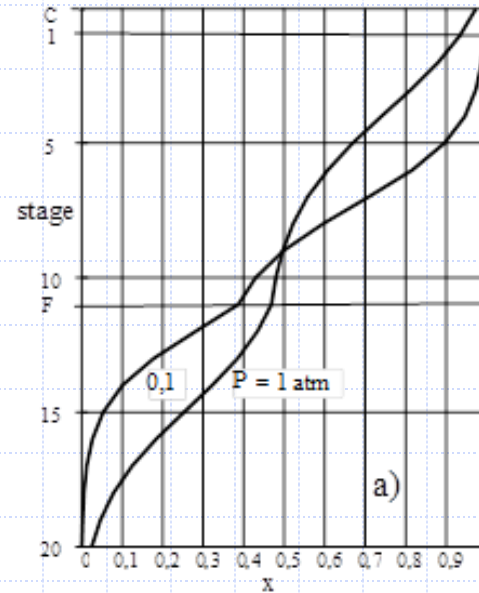
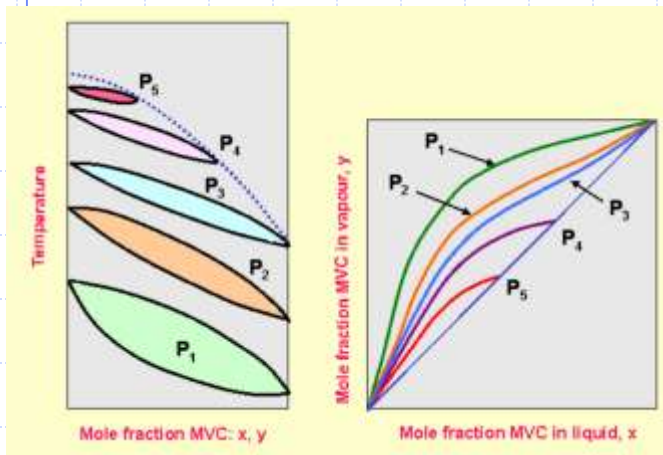
University of Trieste



# Pressure effect on distillation

## ◆ Distillation of a benzene-toluene mixture

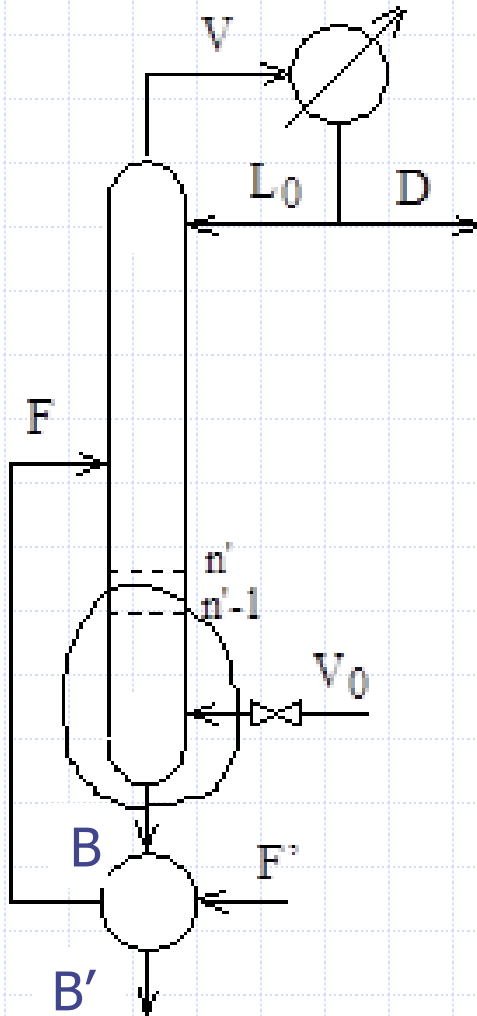
- $P = 0.1 \text{ atm}$  and  $P = 1 \text{ atm}$



- High pressure distillation (3 - 20 atm) usually occurs in
  - ◆ thermally integrated processes
  - ◆ when the normal boiling point of the vapor product is lower than the temperature of the cooling water required to condense it: it is cheaper to pressurize the column and raise the boiling point of the vapor product than to install a refrigeration system to condense it.
- Separability becomes less at higher pressures.
- High pressure VLE non ideality is high (both liquid and vapor)
- Above critical pressure distillation is not possible

# Energy integration

## ◆ Pre-heating of the feed with the residue



$$F(h_{F'} - h_F) = B(h_R - h_{R'})$$

$$F(T_{F'} - T_F) = B(T_R - T_{R'})$$

Equations may be solved with respect to  $T_F$  if we assume that  $T_{B'} = T_F + 15$ , where  $15^\circ\text{C}$  is the  $\Delta T_{min}$  in an shell and tube heat exchanger

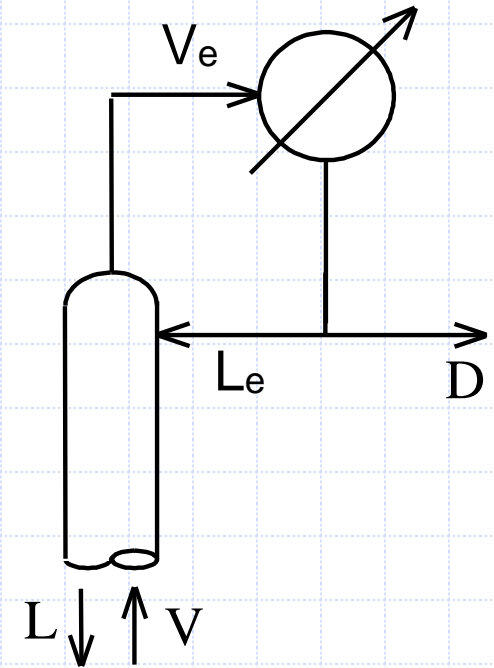
# Reflux sub cooling

- ◆ With reference to the figure we must distinguish between
  - External reflux ratio  $Re = L_e/D$
  - Internal reflux ratio  $R = L/D$
- ◆ Obviously it is:
  - $V_e = L_e + D$  and  $V = L + D$
- ◆ Relationship between  $V$  and  $V_e$  is similar to what done for sub cooled feed:

$$V_e - V = L_e - L = \phi_{Le} L_e$$

$$\phi_{Le} = -\frac{c_{p,L}}{\lambda} (T_{b,Le} - T_{Le})$$

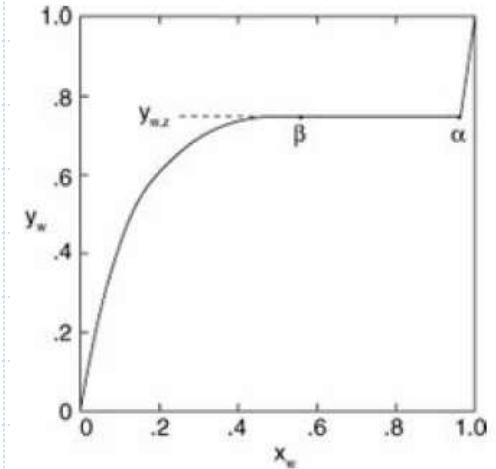
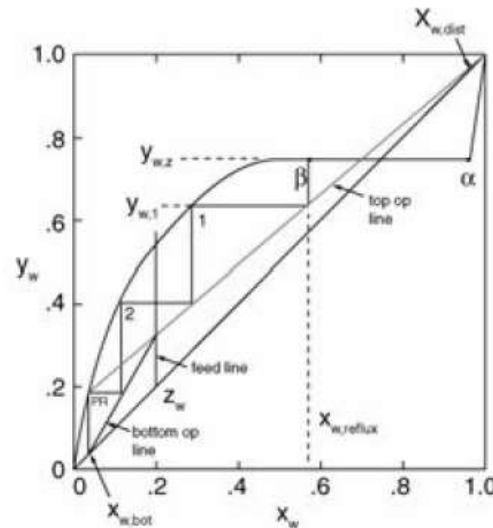
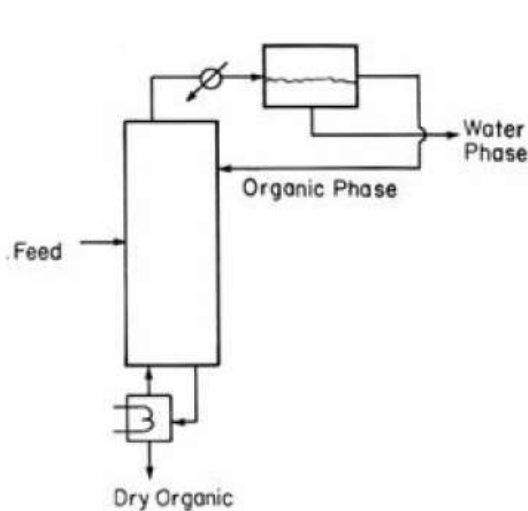
- ◆ A relationship exist between the reflux ratios:
  - $R = Re (1 - \phi_{Le})$
  - The stages construction is done in the usual way, considering internal reflux in the enrichment OL



# Binary azeotropic distillation processes

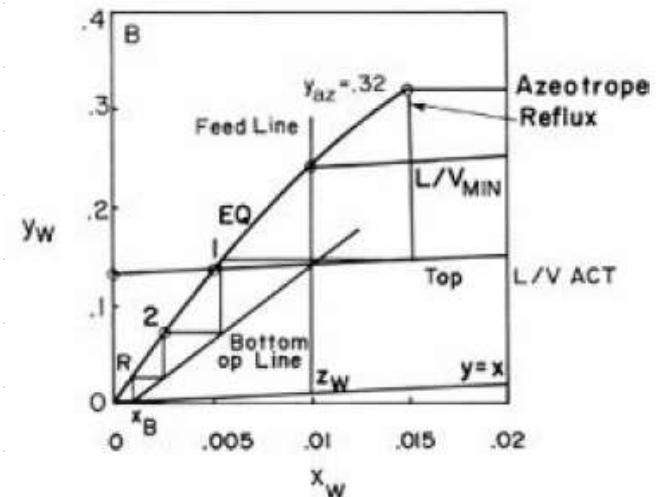
## Binary heterogeneous azeotropes

- Example: butanol - water



## Drying organic compounds (partially miscible with water)

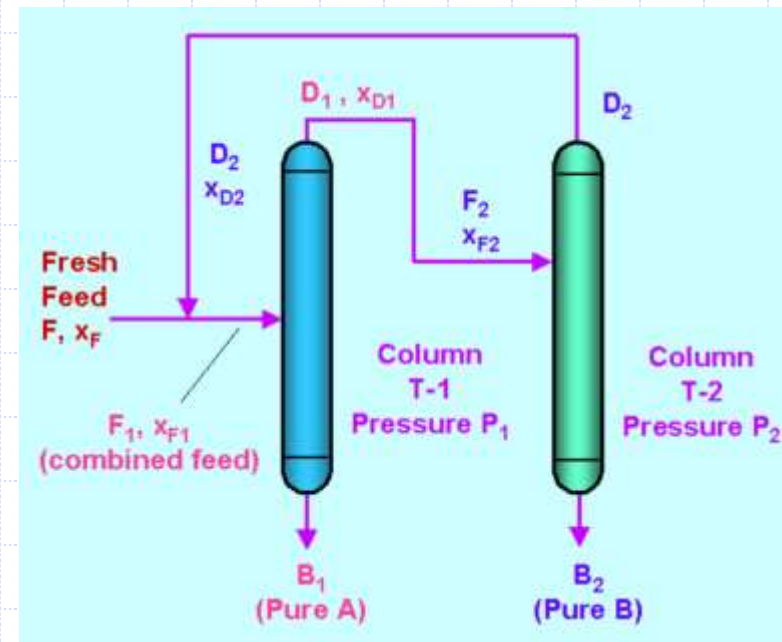
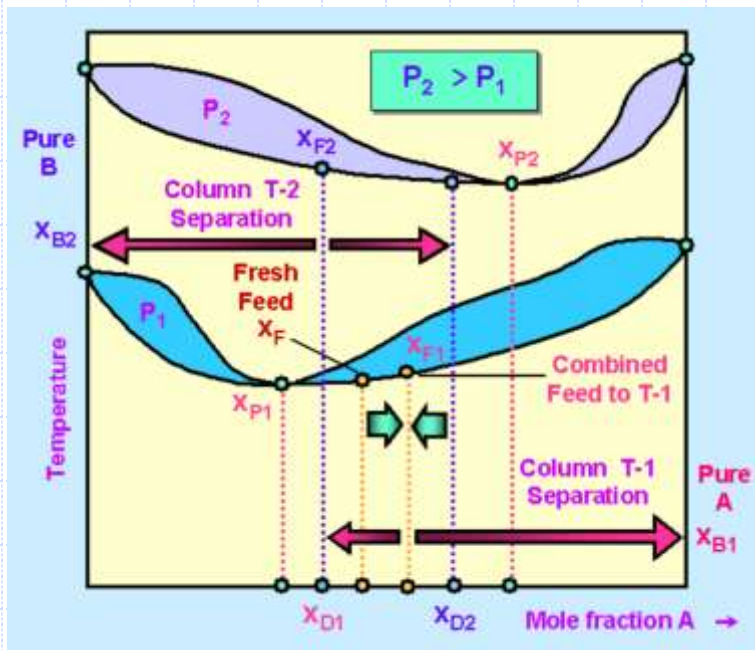
- Example: Benzene with small amount of water (0.001 mole fraction)





# Azeotropic systems distillation: 1. pressure swing distillation.

- ◆ Used if azeotropic composition is influenced by pressure
  - Two columns in series are used
  - Feed composition is between the two azeotropic compositions at the two different operating pressures
  - This is not very common in the industrial practice, which requires operating pressures not very high (not more than 50 bars)
  - An important example is the separation of H<sub>2</sub>O-HCl.



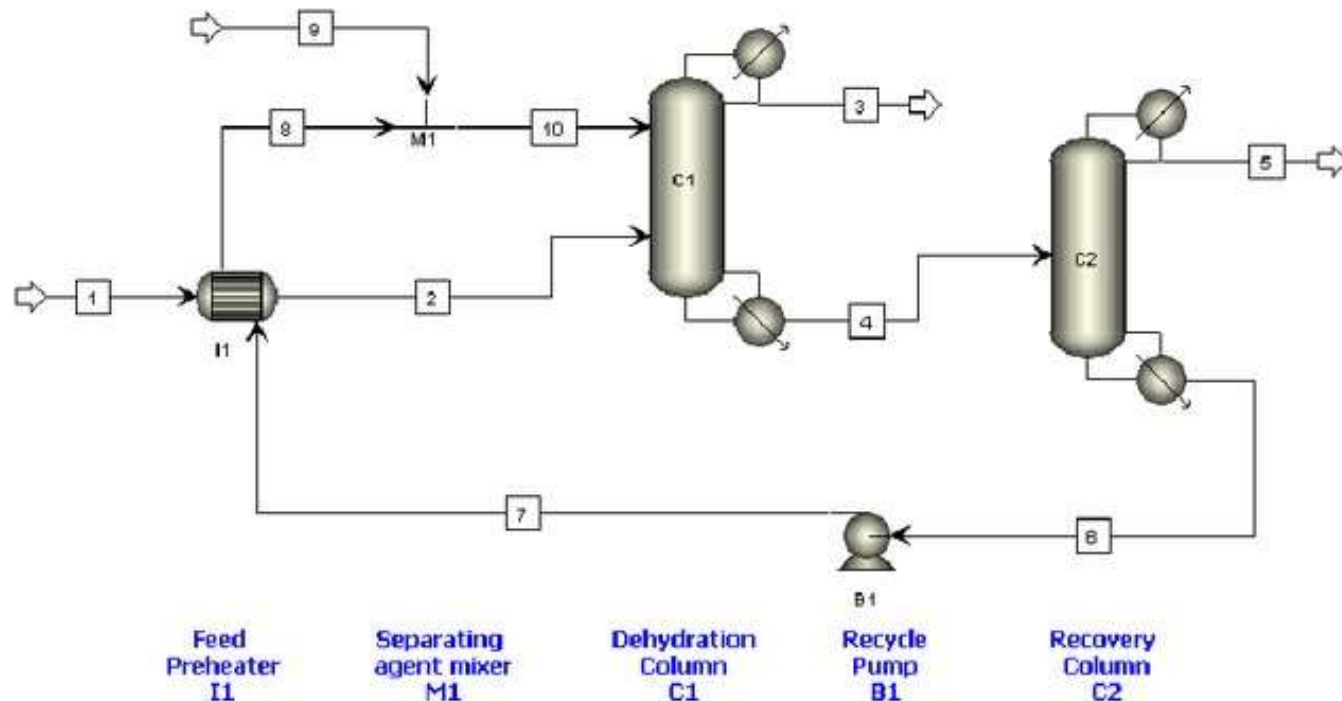


# Azeotropic systems distillation:

## 2. salt-effect distillation of aqueous systems

### ◆ Based on the salting-out effect

- The presence of a salt in the mixture can break the azeotrope
- A well known example is the possibility to break the Ethanol – Water azeotrope by adding NaCl.
- Rarely used due to many difficulties coming from the use of salts: crystallization and corrosion

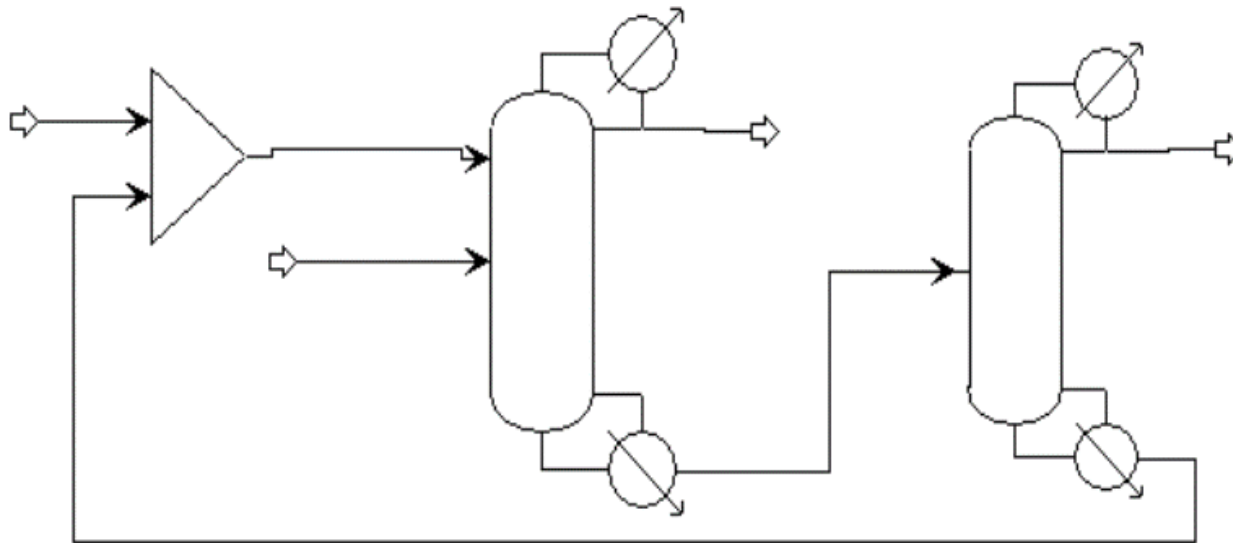


# Azeotropic systems distillation:

## 3. extractive distillation

### ◆ A liquid solvent is fed to the column

- At a different stage of the main feed.
- Solvent breaks the azeotrope by interacting with the mixture components
- Activity coefficients are modified by the addition of solvent and consequently volatility of one of the component is enhanced
- A second column is necessary for recycling the solvent
- Preferred technique in industry for azeotropic systems separation



# Azeotropic systems distillation

## 4. azeotropic distillation

- ◆ As for extractive distillation, a solvent is added
  - Solvent is chosen to create an azeotropic multicomponent mixture in which the pseudo-binary composition of the components to be separated is different from the corresponding azeotrope.
  - Typical example is the separation of ethanol water starting from a near azeotropic mixture (90% mole ethanol) using benzene as a solvent
  - The process schema is more complex and includes LLV equilibria

