Lecture 6: Separation process design, sizing & selection

Chapters 4, 7 (Textbook) plus additional material*

- **Part-1: Introduction**
- **Part-II: Two-phase (equilibrium) separations**
- **Part-III: Separation of azeotropic mixtures**
- **Part-IV: Other separation processes**

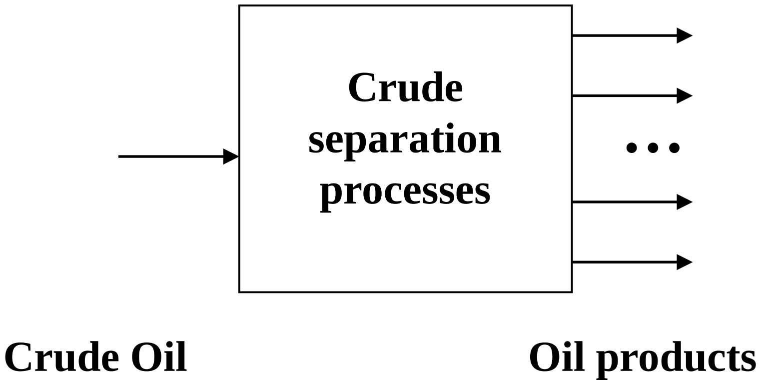
- **See also ”Separation Process Principles” by Henley, Seader & Roper Chapters 7, 11 & 13 of book for distillation & absorption, and chapter 14 for membrane based separation**

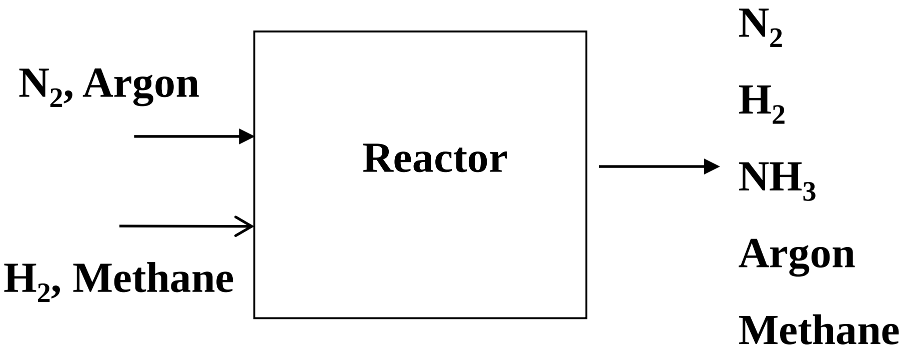
Downstream Separations: The main issues

- **When is separation necessary?**
- **What are the mechansims of separation?**
- **Which mechanisms and how many need to employed to achieve a desired separation?**
- **How to configure/select/design the separation tasks?**
- **How to verify if the desired separation can be achieved?**

This lecture will provide a quick overview of the above topics – more details can be found in courses on separation process principles

When is separation necessary?





Separating different oil products from crude oil

Recovery & purification of chemicals (products)

Two Examples

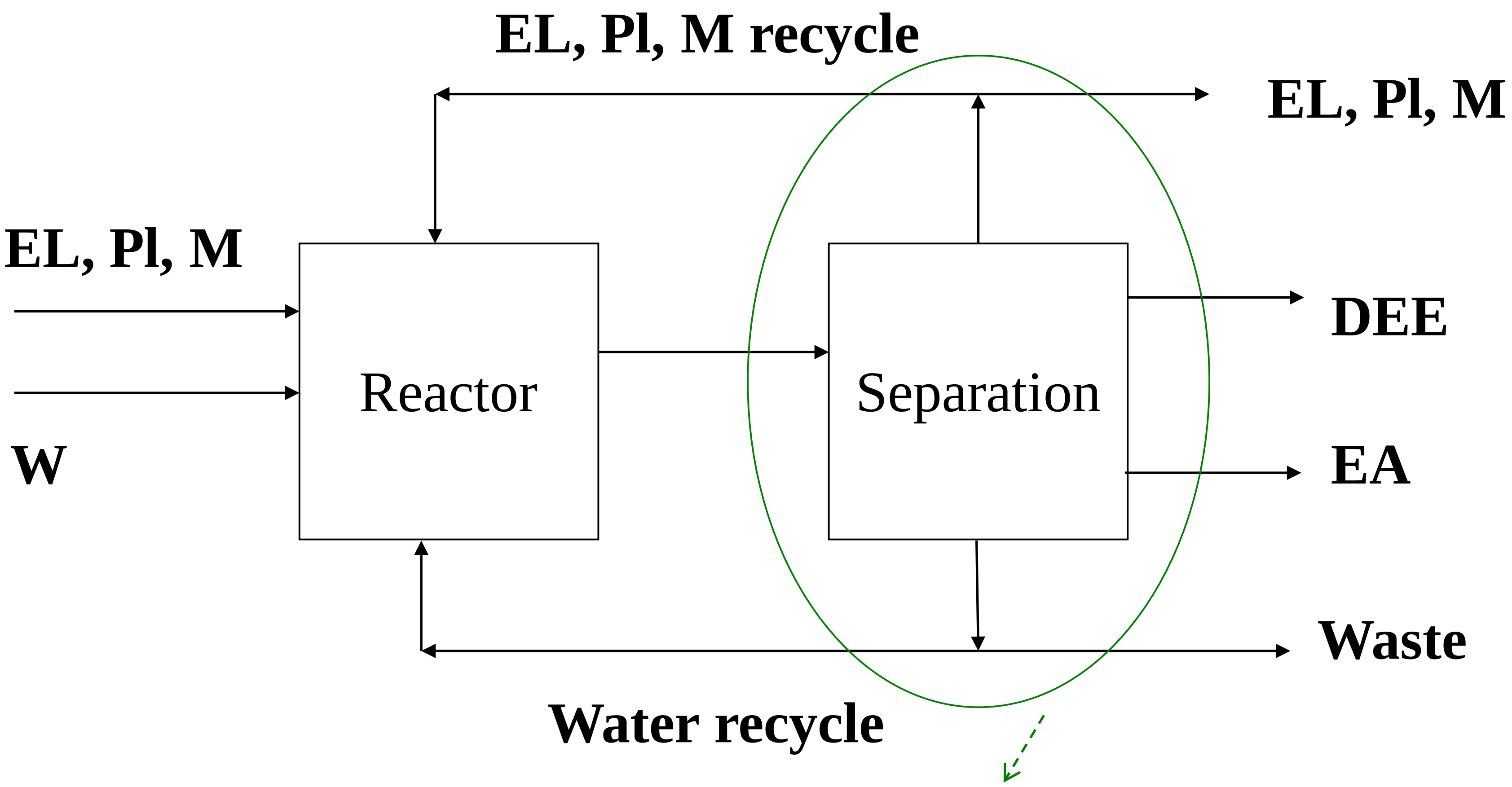
Downstream Separation in Chemical Process Design - I

Chemical processes without reaction

Extraction → **Recovery** → **Purification** → **Finishing**

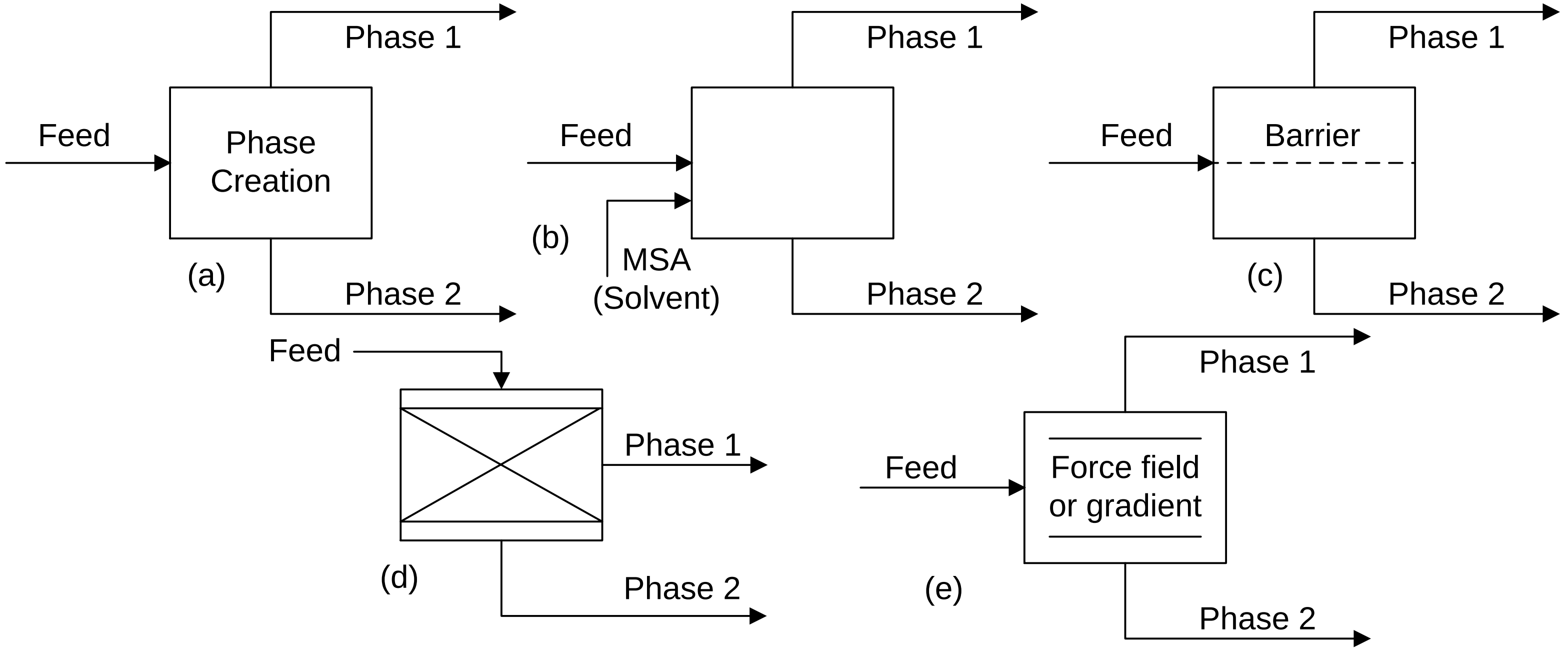
- **Crude oil based refinery for gasoline, and other fuel products**
- **Seeds and other biomass based edible oil extraction processes**
- **Herbs, plants based extraction of specialty chemicals**
- **………..**

Downstream Separation in Chemical Process Design - II



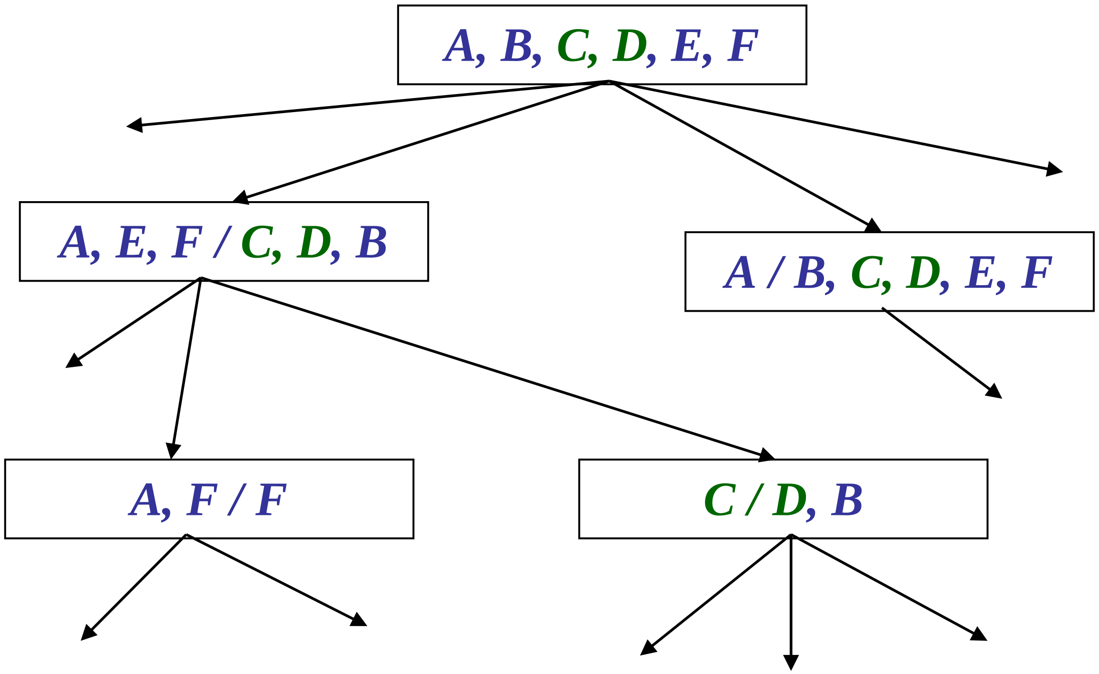
Identify and design the sequence of separation tasks that need to be performed in order to recover and purify the products, recycle the reactants and purge the inerts that enter the process

Which mechanisms of separation?



a) Phase Creation (eg, distillation); b) Agent-based separation (eg, extraction); c) Barrier (eg, pervaporation; filtration); d) Solid agent (eg, adsorption); e) Force field or Gradient (eg, ion-exchange; centrifuge)

How many mechanisms and which mechanisms?

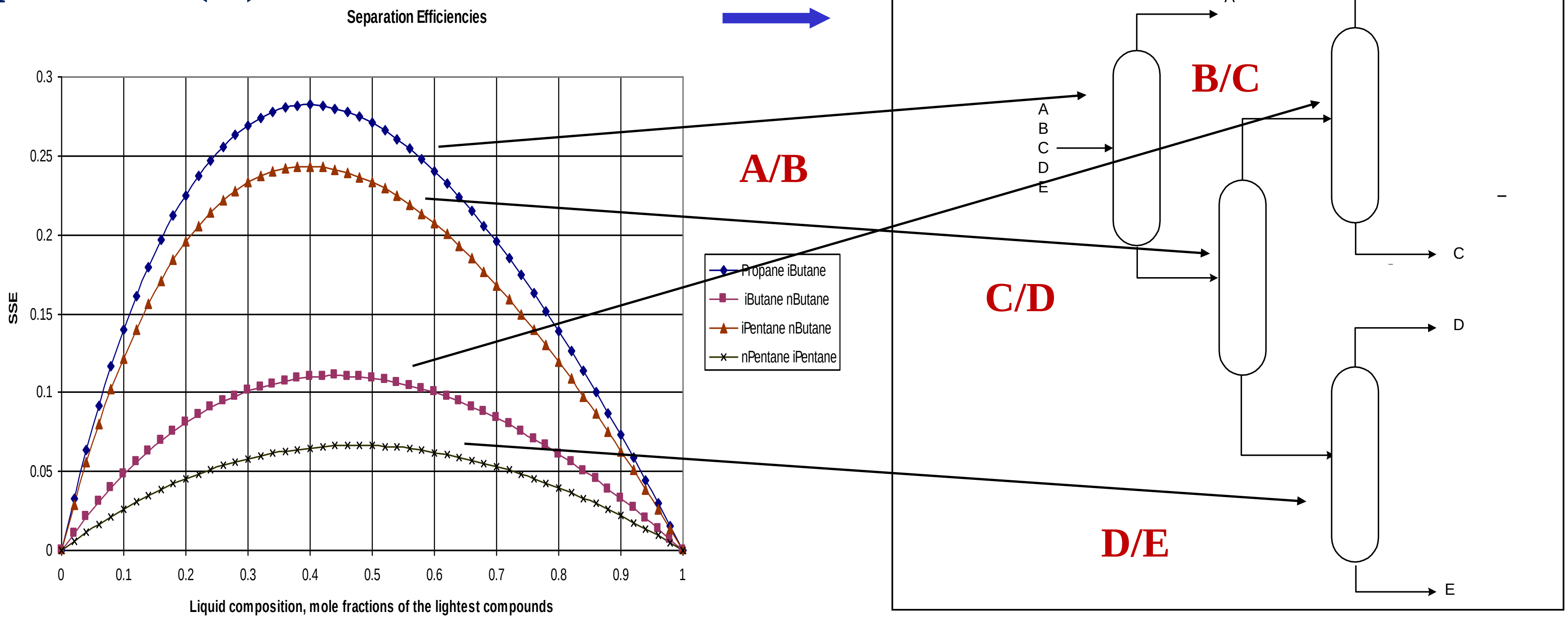


- **Depends on how many chemicals need to be separated (NS)?**
- **Minimum number of separation tasks is NS-1**
- **For each separation task, find the appropriate separation mechanism**

- **Analyze mixture to be separated (collect data or predict behaviour)**
- **Identify relation between mechanism and system property (separation principles)**
- **Generate and test alternatives (select, design, verify)**

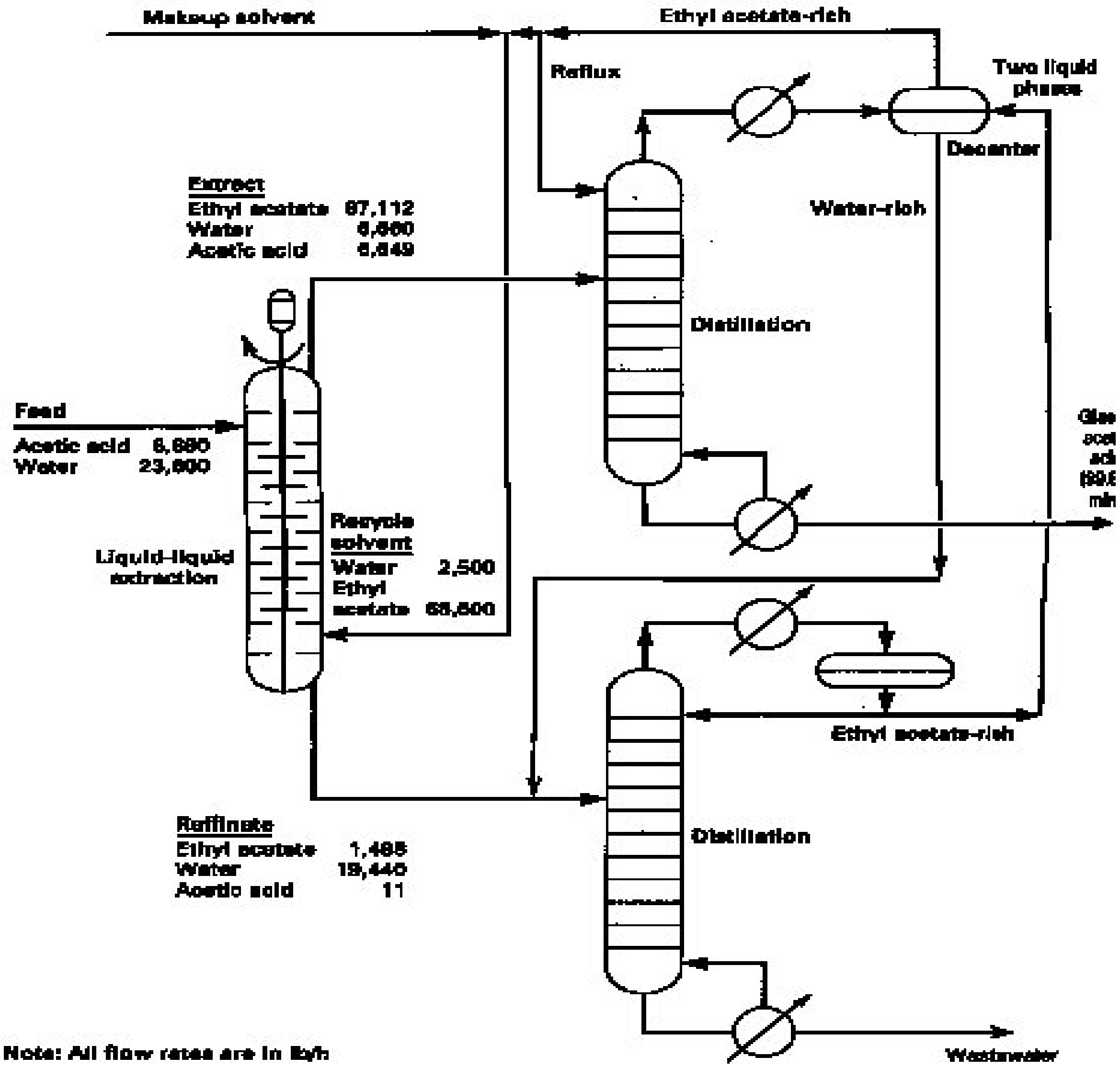
How to configure separation tasks? - Distillation Trains

Separation of propane (A), i-butane (B), butane (C), i-pentane (D), pentane (E)



- *Order the driving force diagrams in terms of* $f_{ij}|_{max} = abs(y_i - x_i)$;
- *Configure the distillation train in terms of* $f_{ij}|_{max}$ *(easiest separation first – largest driving force equivalent to minimum energy);*
- *Design each distillation column such that it uses the maximum driving force (note: only 4 separation tasks A-B; B-C; C-D; D-E)*

How to configure separation tasks? – Extraction plus recovery



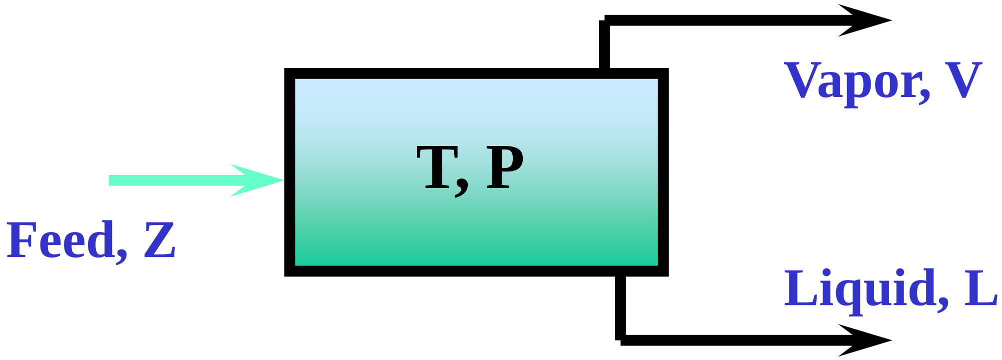
Note: All flow rates are in lb/h

Main Features:

- *Extraction (2-liquid phases); use of solvents*
- *Recovery of solvents & solute (requires energy for VL separation)*
- *Other forms of extraction could be membrane-based, ion-exchange, etc., that does not require the recovery step)*

Part-II: Two-phase (equilibrium) separations: Design issues

2-phase VLE based separation: design degrees of freedom?



Typical 2-Phase VLE-Model

Equilibrium relation $x_i \gamma_i \varphi_i^{sat} P_i^{sat} = y_i \varphi_i^{V} P \qquad i = 1,2,\ldots.c$

Condition $\Sigma_i x_i = \Sigma_i y_i = \Sigma_i z_i = 1$

Mass Balance $Z z_i = V y_i + L x_i \qquad i = 1,2,\ldots.c$

Degree of Freedom Analysis $F = c - p + 2$

For p = 2, F = c. There are 2c+3 Equations and 3c + 5 variables (not counting γ_i , φ_i , P_i^{sat}). **Therefore, *c + 2* variables need to be specified.** ***For example, specify Z, T, P and (c-1) z compositions.***

Some Definitions

Equilibrium Constant (VLE) $K_i = y_i/x_i$

- Ideal System $K_i = P_i^{sat}(T) / P$
- Non-ideal Liquid & Vapor $K_i = \gamma_i \varphi_i^{sat} P_i^{sat} /(\varphi_i^{V} P)$
- Non-ideal Liquid, ideal vapor $K_i = \gamma_i P_i^{sat} /P$
- Any P & T $K_i = \varphi_i^{L} / \varphi_i^{V}$

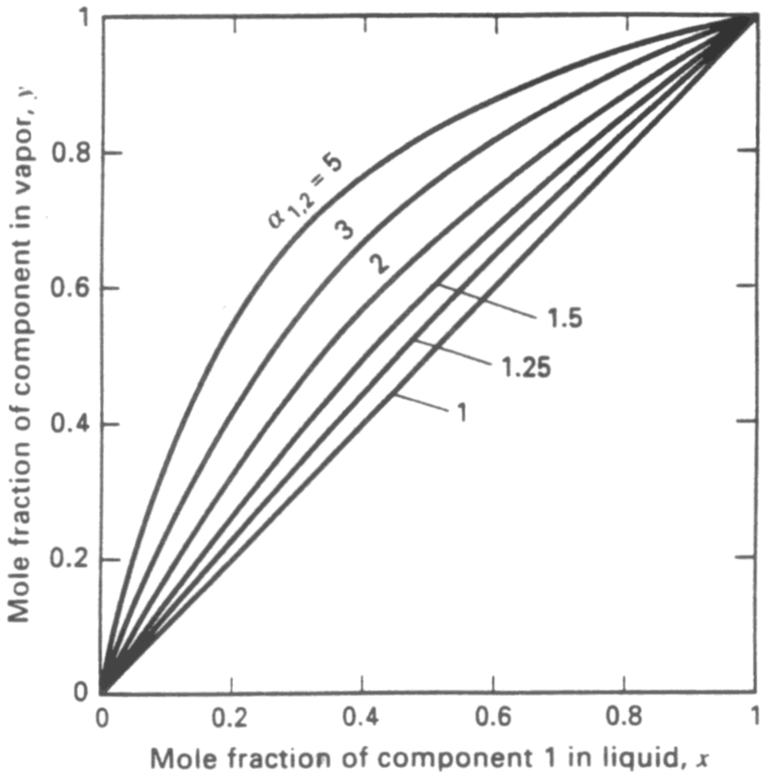
Relative volatility $\alpha_{ij} = y_j\, x_i / (x_j\, y_j) = P_i^{sat}/P_j^{sat}$

Rewriting in terms of y_i $y_i = x_i\, \alpha_{ij}/[1+ x_i(\alpha_{ij} - 1)]$

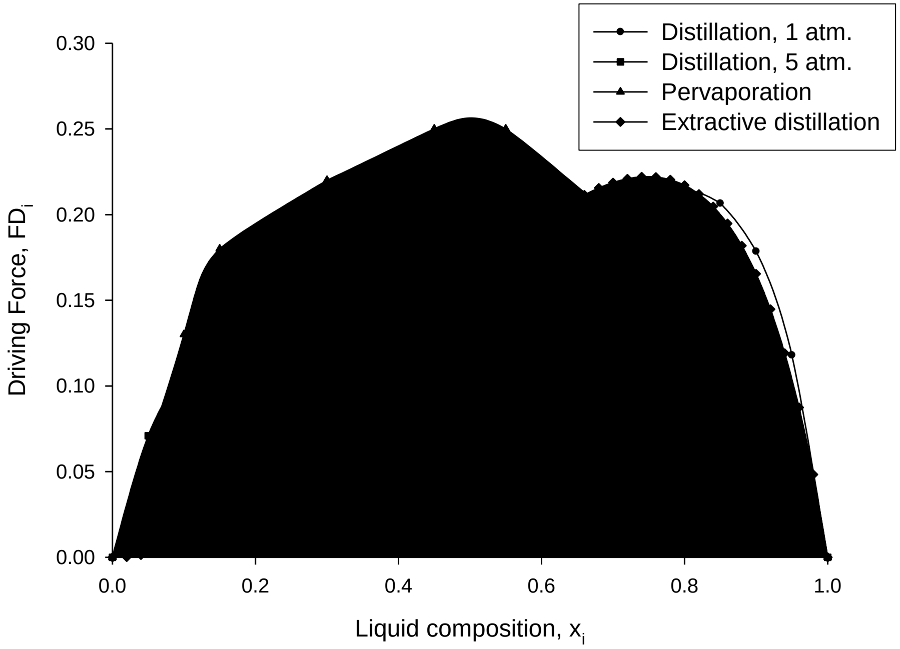
Driving Force $D_{ij} = y_i - x_i$

Rewriting in terms of y_i $D_{ij} = x_i\, \alpha_{ij}/[1+ x_i(\alpha_{ij} - 1)] - x_i$

Binary systems with different volatility

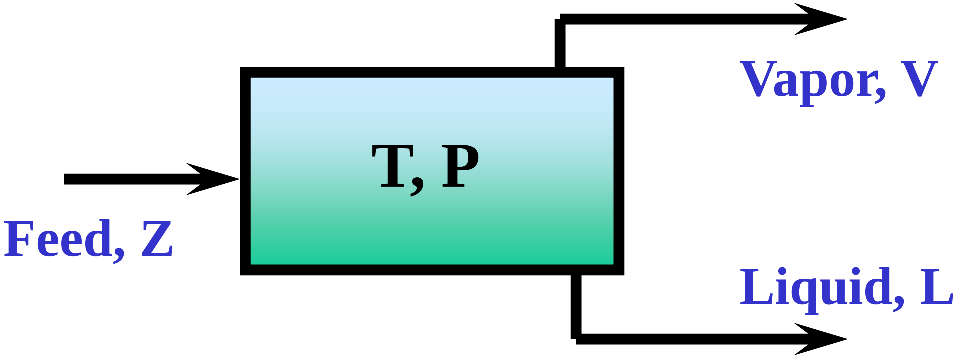


XY-(PT) phase diagram (in terms of relative volatility)



DX-(PT) phase diagram (in terms of driving force) – shown for different separation types)

VLE based separation: Model w.r.t. α_{ij} or D_{ij}



Typical 2-Phase VLE-Model

Equilibrium condition $y_i = x_i \alpha_{ij}/[x_i (\alpha_{ij} - 1) + 1]$ **w.r.t. relative volatility**

or (eq.1) $D_{ij} = x_i \alpha_{ij} /[x_i (\alpha_{ij} - 1) + 1] - x_i$ **w.r.t. driving force**

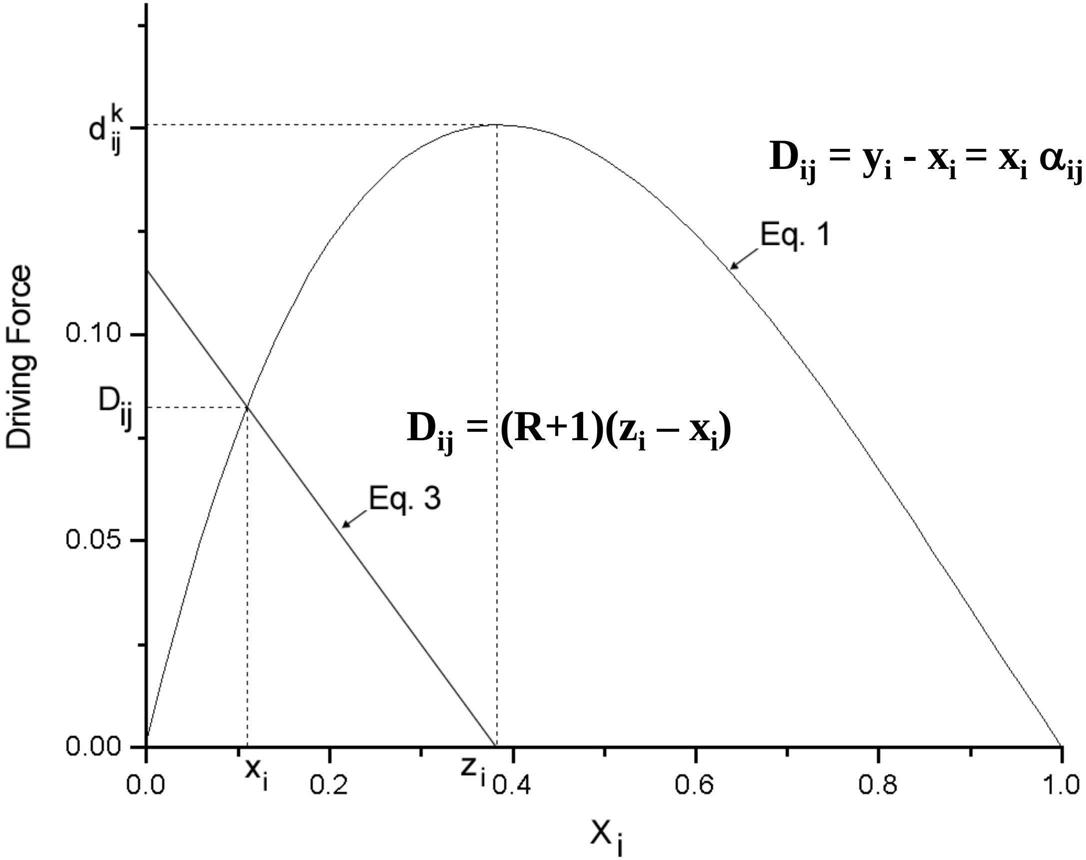
Mass Balance $Z z_i = V y_i + L x_i$ $i = 1,2,\ldots.c$

or $y_i = (R + 1) z_i - R x_i$ where $R = L/V$

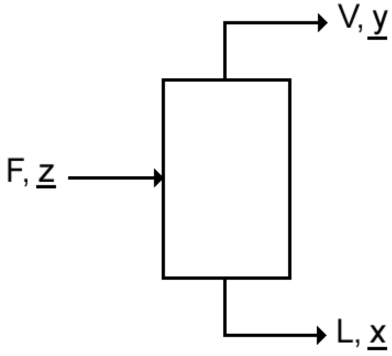
or (eq. 3) $D_{ij} = (R + 1) (z_i - x_i)$

Graphical calculation technique for V-L based separation

$$D_{ij} = y_i - x_i = x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1)) - x_i$$



$$D_{ij} = (R+1)(z_i - x_i)$$



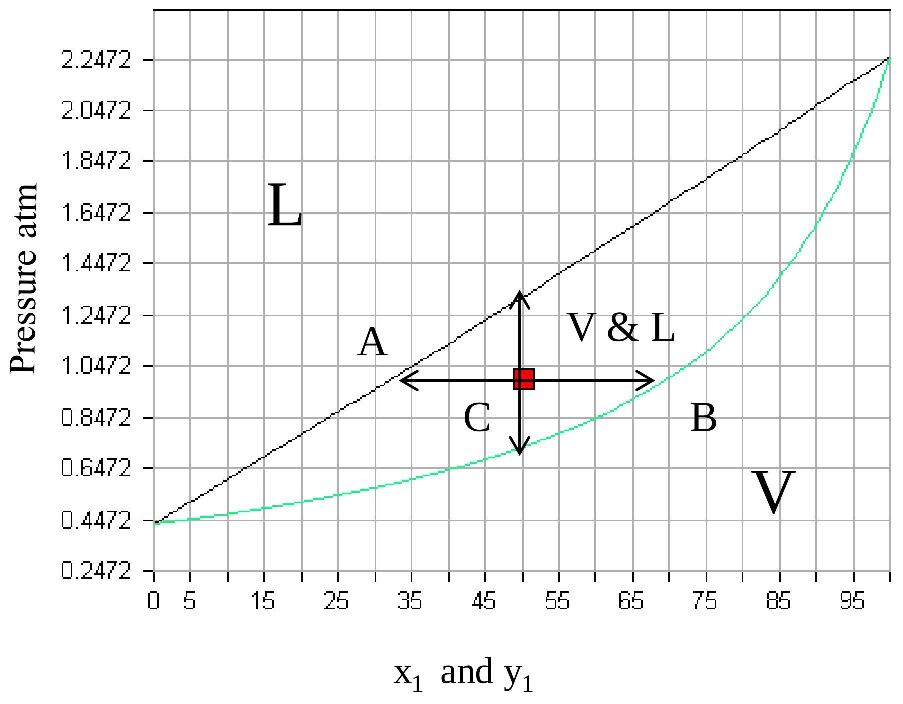
When $D_{ij} = 0$, there is no separation and $z_i = x_i$

When $x_i = 0$ or $L = 0$; $R = L/V = 0$ & $D_{ij} = y_i - x_i = z_i$ (everything is vaporized)

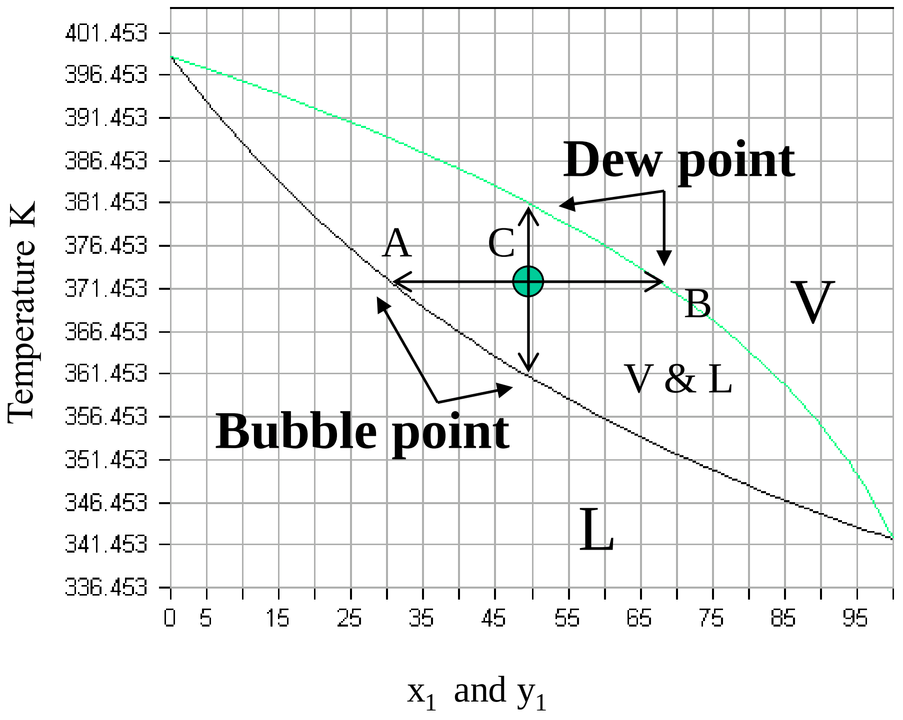
When R = specified; $x_i = D_{ij}/(R + 1) + z_i$ (point of intersection of Eqs. 1 & 3)

Visualization of 2-phase separations: P-XY & T-XY diagrams

P-xy diagram at constant T



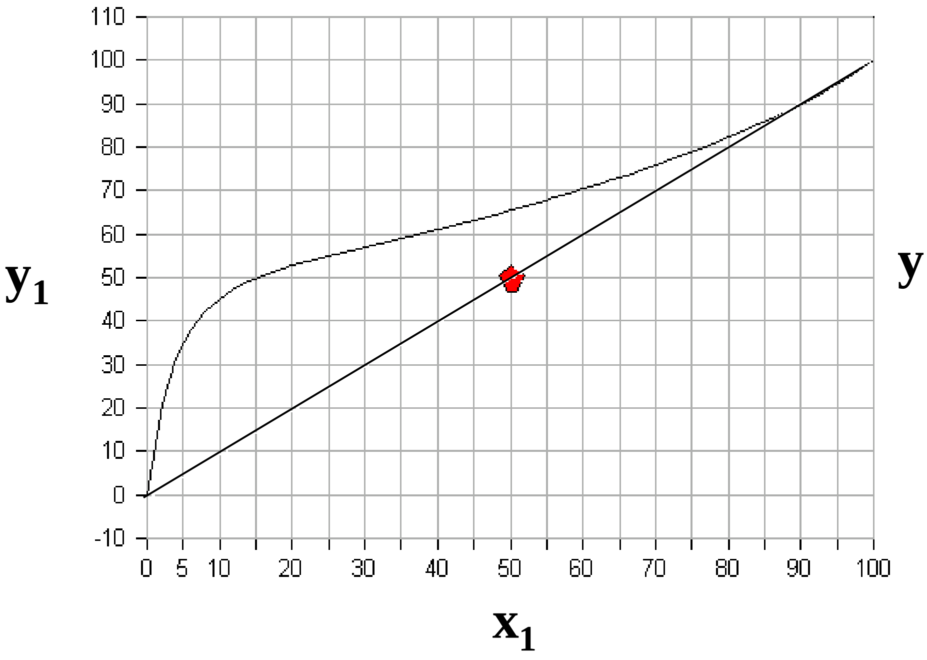
T-xy diagram at constant P



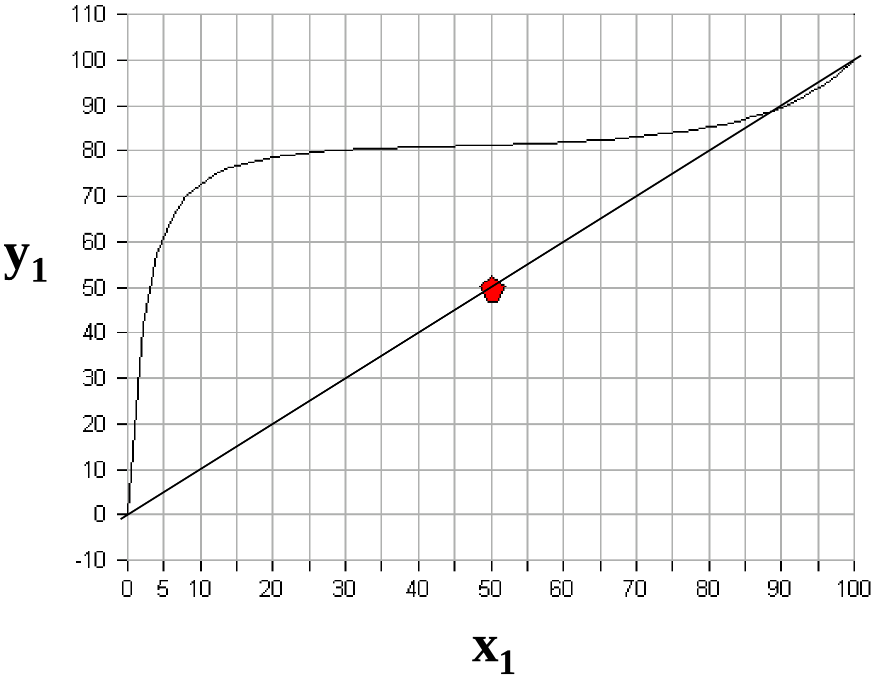
For a feed at C, L/V = CB/AC; at constant T, if you compress a vapor you get a liquid and vice versa. At constant P if you heat a liquid you get a vapor and vice versa. If you have a feed mixture in the 2-phase (V&L) region, it will split into a liquid and a vapor

VLE - Binary Systems: Azeotropic systems

Ethanol - Water

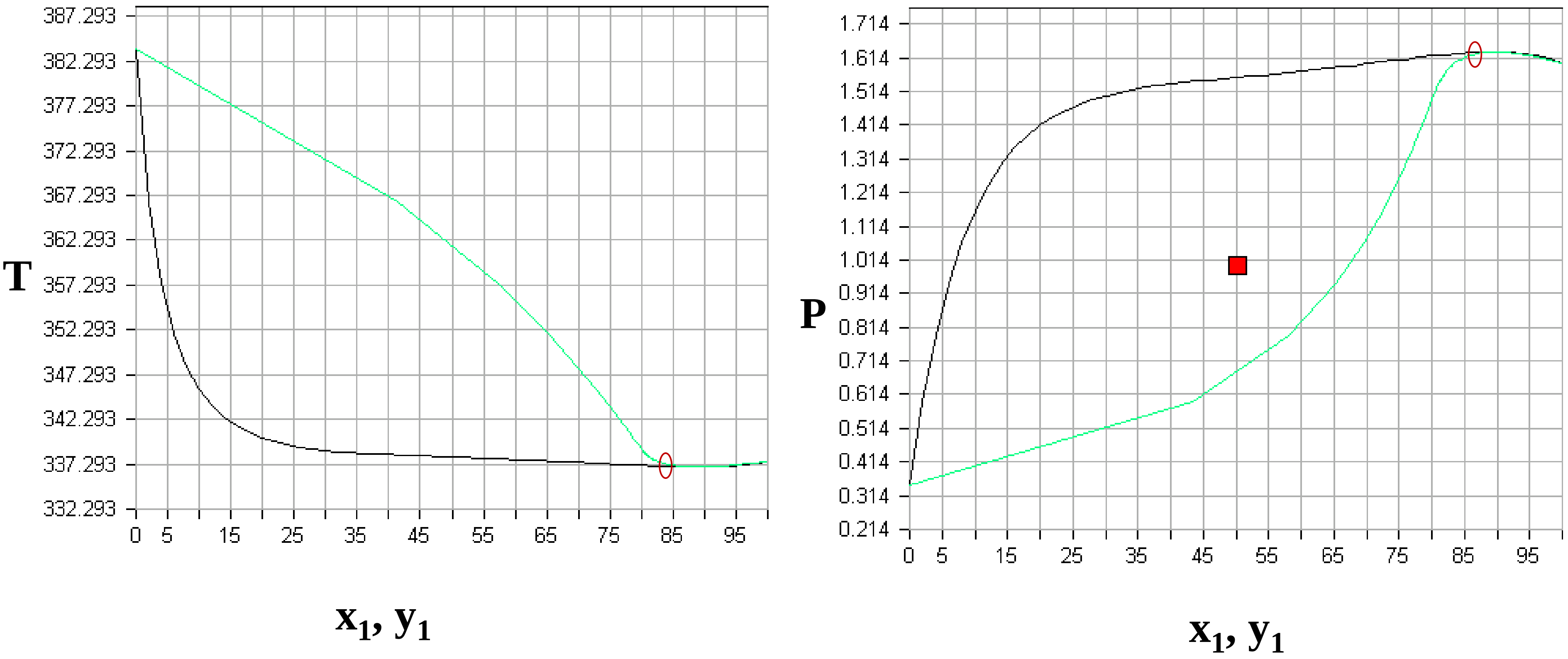


Methanol - Toluene



XY-PT phase diagrams. At the azeotrope, $x_i = y_i$, therefore, $K_i = 1$ and/or $\alpha_{ij} = 1$. Separation beyond the azeotropic point is not possible

Visualization of 2-phase separations: azeotrope systems



Methanol-Toluene T-xy & P-xy diagrams

Generate these diagrams as a function of P to see if the location of the azeotrope can be moved

Types of VLE-phase separation models & solution approaches

Problem Specification

Isothermal flash (T, P, F, z)

***Bubble-point T (P, x)**

***Dew-point T (P, y)**

***Bubble-point P (T, x)**

***Dew-point P (T, y)**

Adiabatic flash (Q=0, P, F, z)

Non-adiabatic flash (Q, P, F, z)

% Vaporization (V/F, P)

*** Note: Degrees of freedom = c + 1**

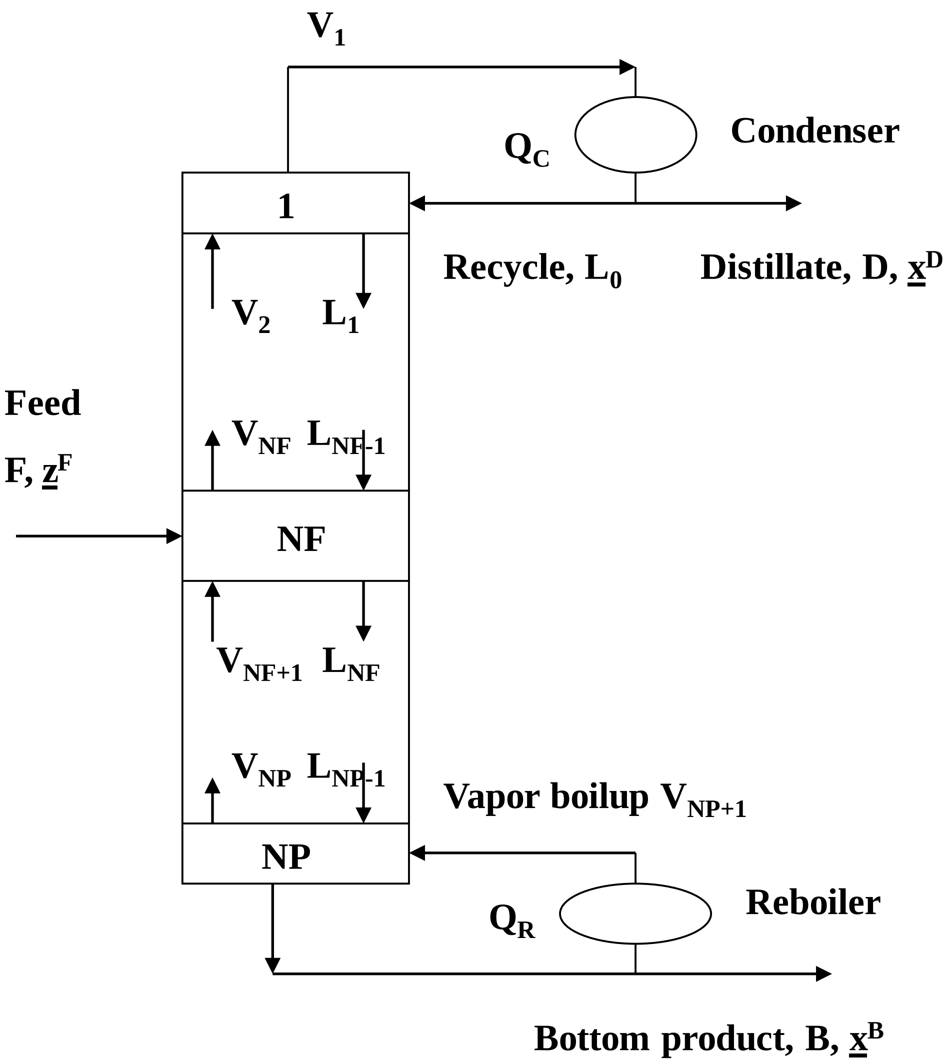
Isothermal flash: fast solution

Specified: $F, z_1, z_2, ..z_{c-1}, T, P$

Solve for $\Phi = V/F$ **with fixed** K_i

1. Calculate $K_i = P_i^{sat}(T)/P$
2. $f = \Sigma_i\, z_i(1-K_i)/[1+ \Phi(K_i-1)] = 0$
3. $V = F\,\Phi$; $L = F - V$
4. $x_i = z_i / [1+ \Phi(K_i-1)]$
5. $y_i = z_iK_i / [1+ \Phi(K_i-1)] = x_i K_i$
6. $Q = h^V V + h^L L – h^F F$

Separation of Binary Mixtures by Distillation: review



Component Mass Balance

Overall

$$F z^F = D x^D + B x^B$$

Rectifying section

$$y_{n+1} = L_n/V_{n+1} x_n + D/V_{n+1} x^D$$

$$y = [R/(R+1)] x + [1/(R+1)] x^D$$

Stripping section

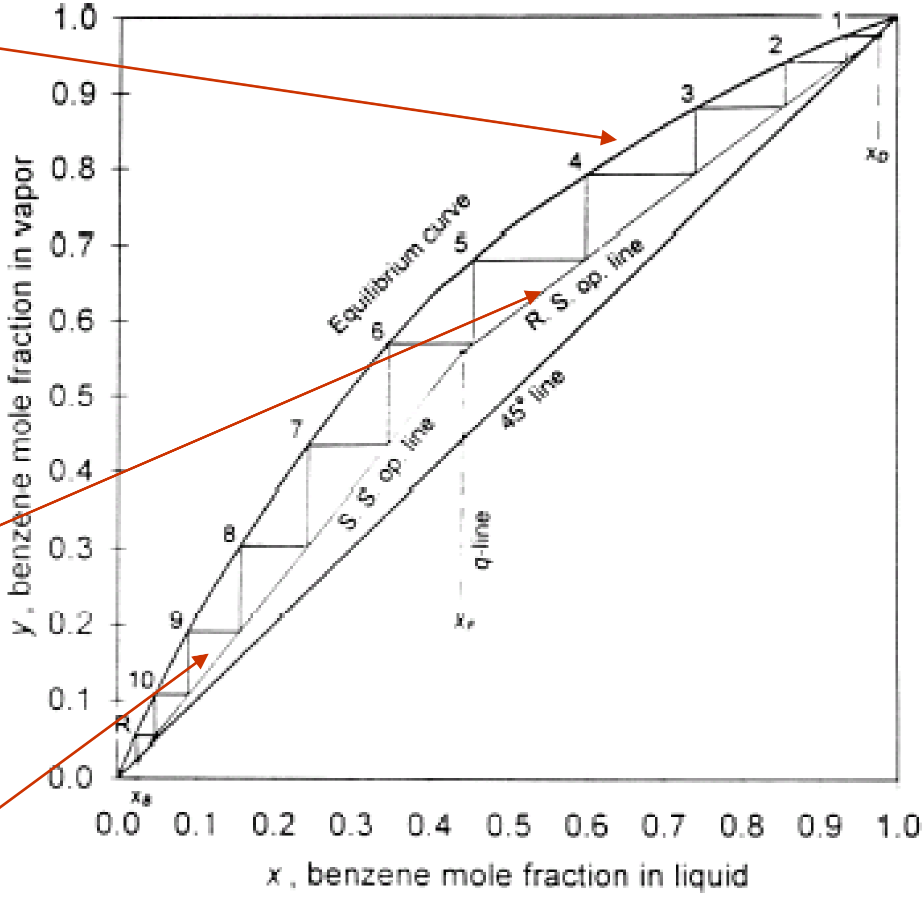
$$y_{m+1} = L_m/V_{m+1} x_m - B/V_{m+1} x^B$$

$$y = [(V_B+1)/V_B] x - 1/(V_B+1)] x^B$$

Equilibrium relation

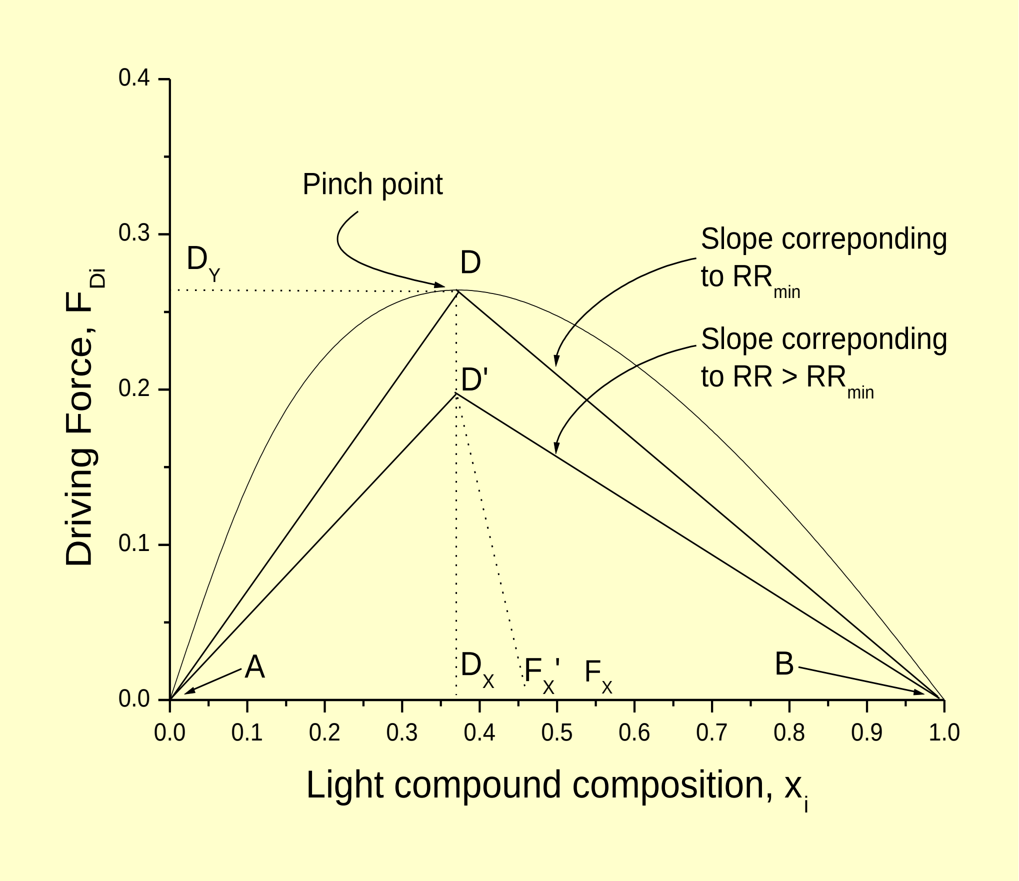
$$y_i = x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1))$$

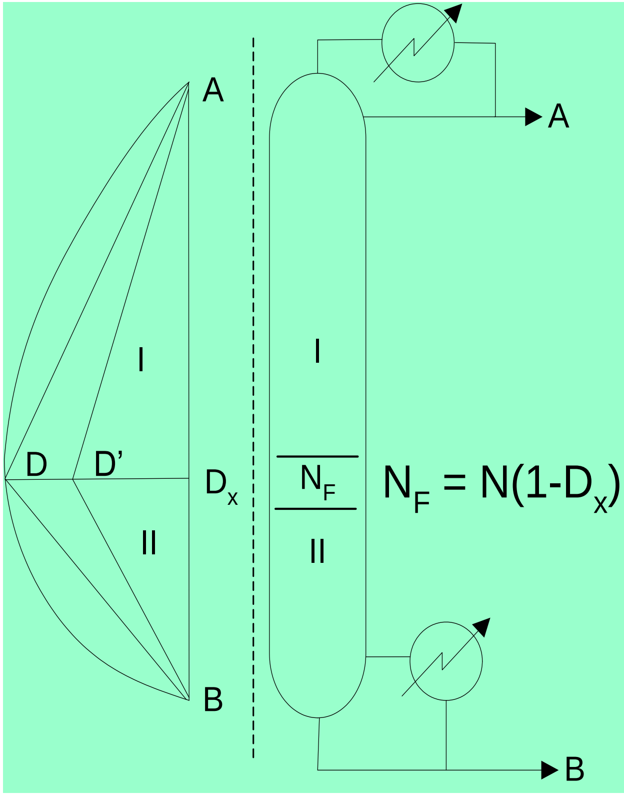
- **Equilibrium relation**
- $y_i = x_i \alpha_{ij} / (1 + x_i (\alpha_{ij} - 1))$
- **Component Mass Balance**
- **Overall**
- $F z^F = D x^D + B x^B$
- **Rectifying section**
- $y_{n+1} = L_n/V_{n+1} x_n + D/V_{n+1} x^D$
- $y = [R/(R+1)] x + [1/(R+1)] x^D$
- **Stripping section**
- $y_{m+1} = L_m/V_{m+1} x_m - B/V_{m+1} x^B$
- $y = [(V_B+1)/V_B] x - 1/(V_B+1)] x^B$



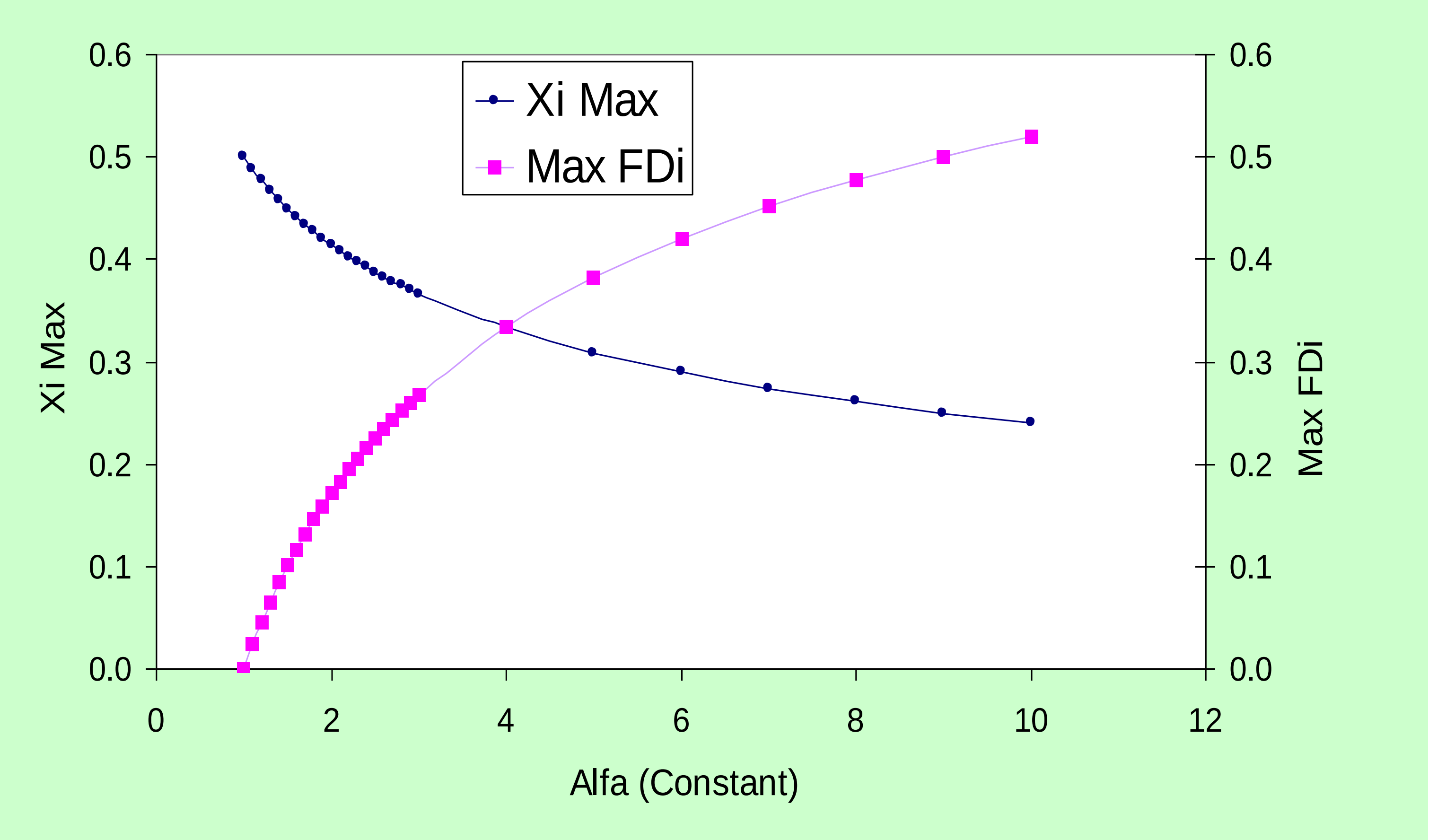
Driving force based design - I

- *Given a mixture to be separated into two products in a distillation column with N trays. What is the optimal (with respect to the costs of operation) feed plate location and the corresponding reflux ratio for different product purity specifications ?*

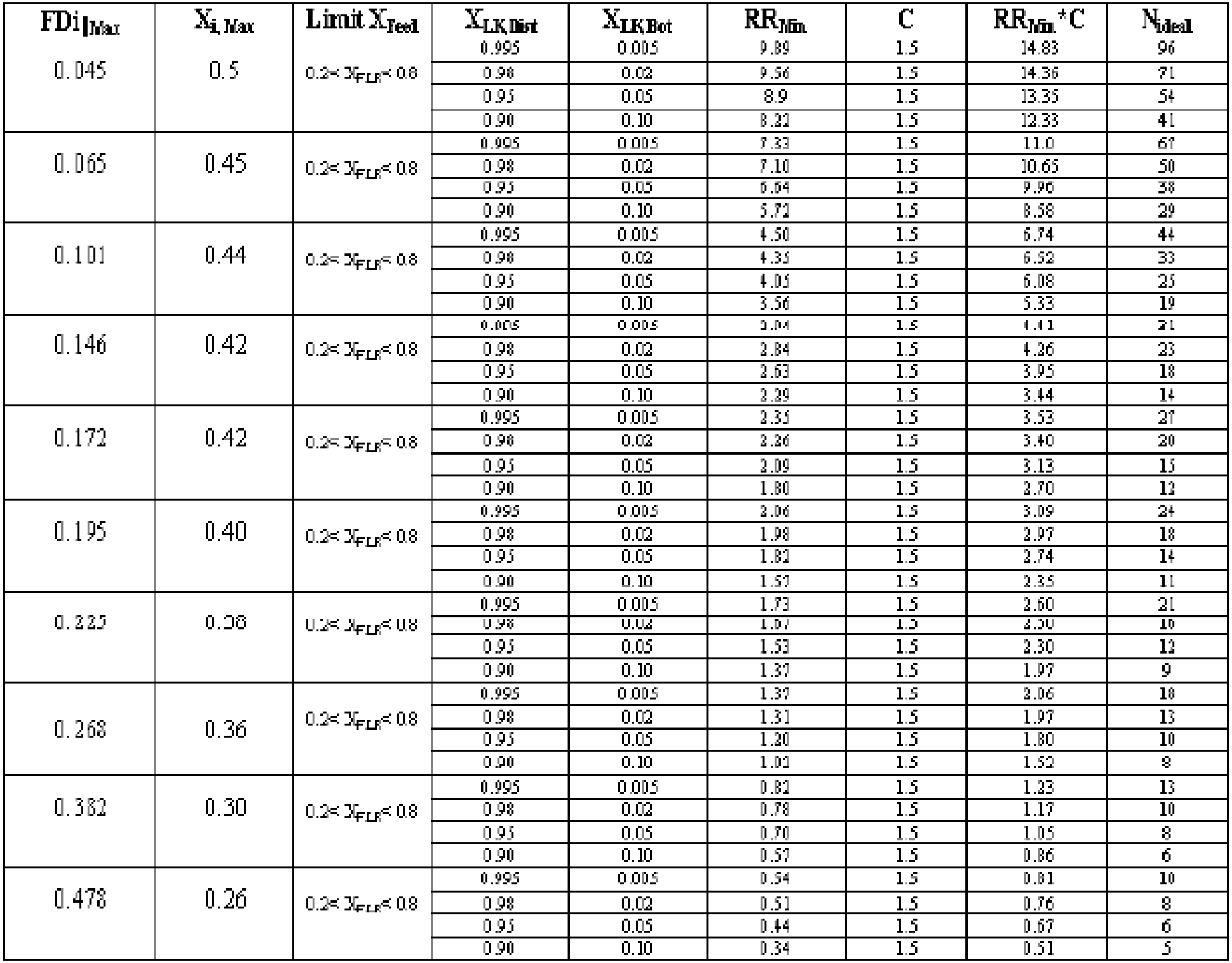




Relation between α_{ij}, D_{ij}(max), Xi (max)

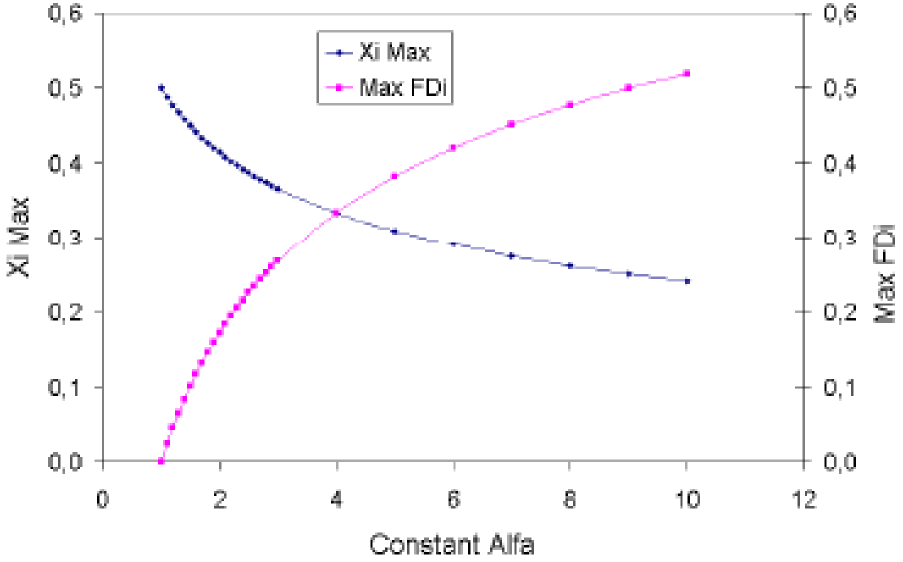


Identification of design targets



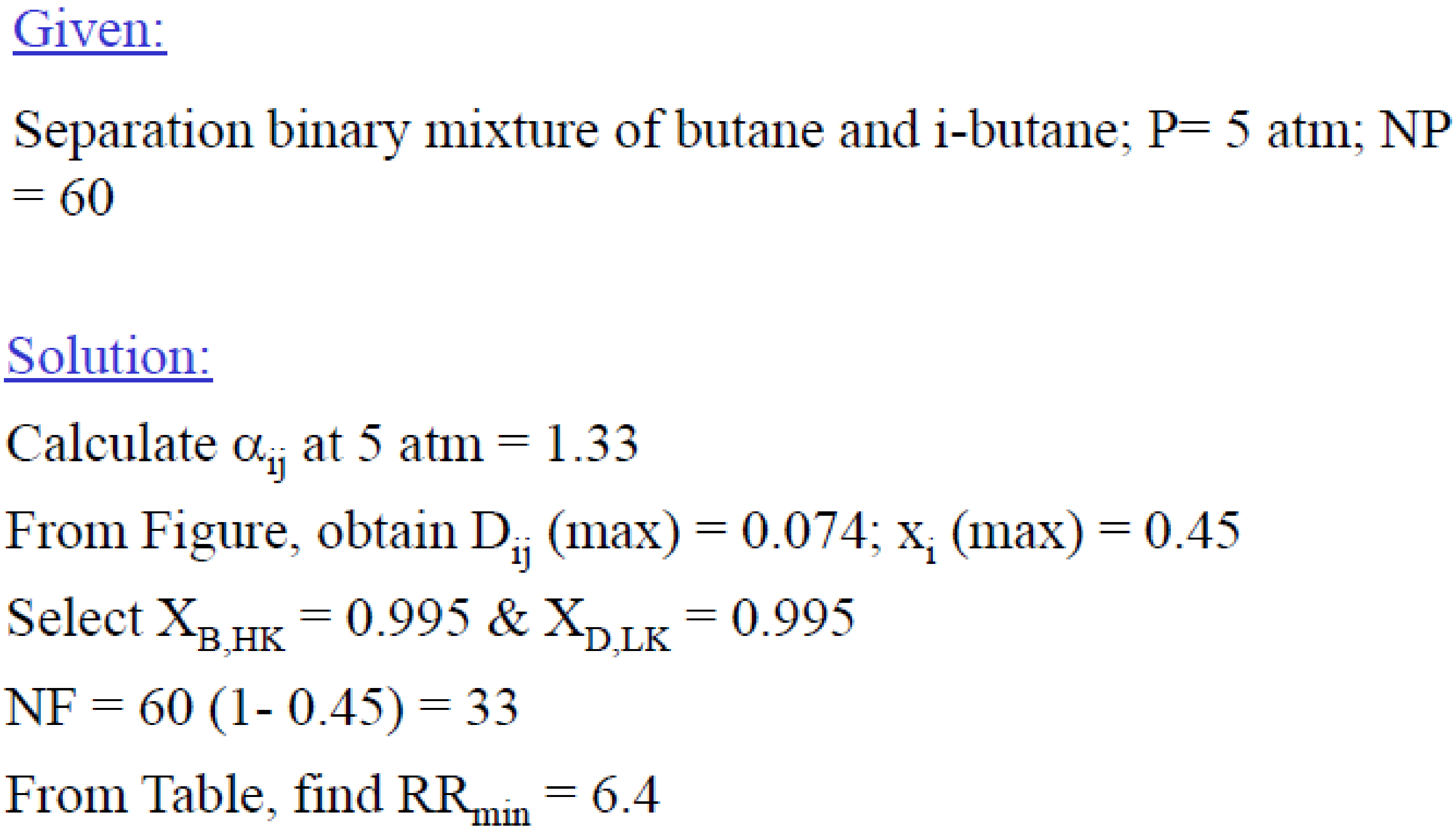
$FDi\|_{Max}$	$X_{i,Max}$	Limit X_{Feed}	$X_{LK,Dist}$	$X_{LK,Bot}$	RR_{Min}	C	RR_{Min}*C	N_{Ideal}
0.045	0.5	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	9.89	1.5	14.83	96
			0.98	0.02	9.56	1.5	14.36	71
			0.95	0.05	8.9	1.5	13.35	54
			0.90	0.10	8.22	1.5	12.33	41
0.065	0.45	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	7.33	1.5	11.0	67
			0.98	0.02	7.10	1.5	10.65	50
			0.95	0.05	6.64	1.5	9.96	38
			0.90	0.10	5.72	1.5	8.58	29
0.101	0.44	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	4.50	1.5	6.74	44
			0.98	0.02	4.35	1.5	6.52	33
			0.95	0.05	4.05	1.5	6.08	25
			0.90	0.10	3.56	1.5	5.33	19
0.146	0.42	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	2.94	1.5	4.41	31
			0.98	0.02	2.84	1.5	4.26	23
			0.95	0.05	2.63	1.5	3.95	18
			0.90	0.10	2.29	1.5	3.44	14
0.172	0.42	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	2.35	1.5	3.53	27
			0.98	0.02	2.26	1.5	3.40	20
			0.95	0.05	2.09	1.5	3.13	15
			0.90	0.10	1.80	1.5	2.70	12
0.195	0.40	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	2.06	1.5	3.09	24
			0.98	0.02	1.98	1.5	2.97	18
			0.95	0.05	1.82	1.5	2.74	14
			0.90	0.10	1.57	1.5	2.35	11
0.225	0.38	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	1.73	1.5	2.60	21
			0.98	0.02	1.67	1.5	2.50	16
			0.95	0.05	1.53	1.5	2.30	12
			0.90	0.10	1.37	1.5	1.97	9
0.268	0.36	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	1.37	1.5	2.06	18
			0.98	0.02	1.31	1.5	1.97	13
			0.95	0.05	1.20	1.5	1.80	10
			0.90	0.10	1.01	1.5	1.52	8
0.382	0.30	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	0.82	1.5	1.23	13
			0.98	0.02	0.78	1.5	1.17	10
			0.95	0.05	0.70	1.5	1.05	8
			0.90	0.10	0.57	1.5	0.86	6
0.478	0.26	$0.2\le X_{FLK}\le 0.8$	0.995	0.005	0.54	1.5	0.81	10
			0.98	0.02	0.51	1.5	0.76	8
			0.95	0.05	0.44	1.5	0.67	6
			0.90	0.10	0.34	1.5	0.51	5

Simple and fast reverse design method



1. Given a mixture to be separated by distillation
2. Select a pressure and calculate the D_{ij} for all pairs of binary mixtures (ordered w.r.t. boiling point)
3. Identify the αij and from it, D_{ij} (max), x_i (max) for specific products xD_i and xB_i
4. Use the table of α_{ij} , D_{ij} (max), x_i (max), NP, NF, …. To read out the remaining design variables

Problem Solution



Given:

Separation binary mixture of butane and i-butane; P= 5 atm; NP = 60

Solution:

Calculate α_{ij} at 5 atm = 1.33

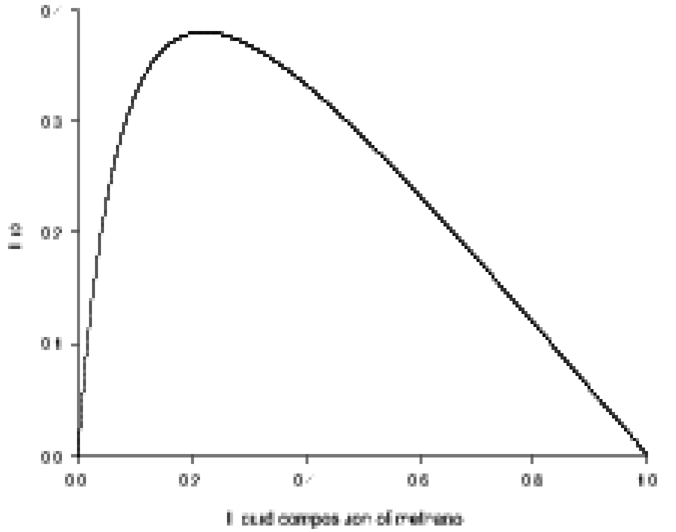
From Figure, obtain D_{ij} (max) = 0.074; x_i (max) = 0.45

Select $X_{B,HK} = 0.995$ & $X_{D,LK} = 0.995$

NF = 60 (1- 0.45) = 33

From Table, find $RR_{min} = 6.4$

Driving force based design - II

Feed: **Methanol-Water**, $x_{MeOH} = (0.80, 0.50, 0.22, 0.15)$		
Pressure, $P = 1$ atm, Number of stages, $N = 22$		
Algorithm	**Action**	
Step 1,2	Calculate driving force curve	
Step 3	Identify D_x	$D_x = 0.22$
Step 4	Determine N_F	$N_F = 22(1 - 0.22) = 17$
Step 5	Check for scaling	Case 4; factor 1a, $N_F = 16$
Step 7	Determine RR_{min}	1.02
Step 7a	Give specification 1	$x_{Methanol} = 0.9995$
Step 7b	Give specification 2	$x_{Water} = 0.9995$

Part-III: Separation of azeotropic mixtures (chapter X of textbook, see also chapter 11 of Seader & Henley book)

Separation of an azeotropic mixture

- Mixture analysis
  - Identification of an azeotrope.
- Possible separation techniques
  - Pressure swing.
  - Extractive/azeotropic distillation.
- Solvent identification and validation
- Flowsheet configuration

Mixture analysis

Whenever you have the problem of separating a mixture, a good starting point is always to do a mixture anaysis.

This can include both pure component and mixture properties.

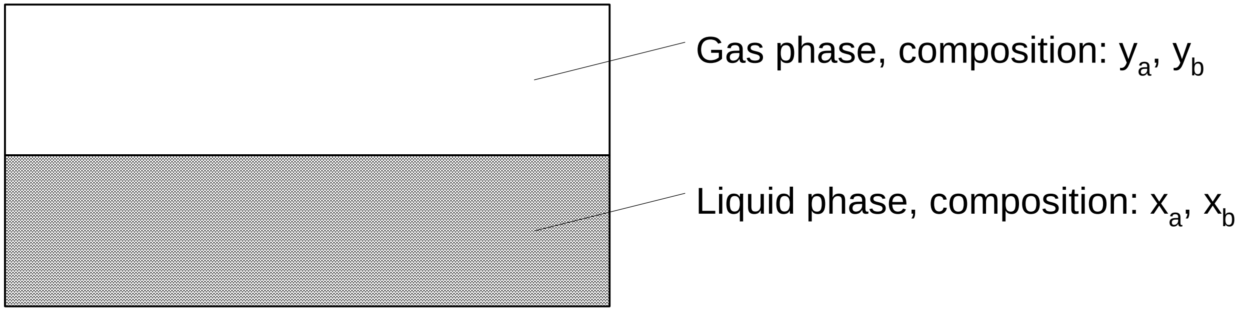
The mixture analysis will imediately give information both intuitively and to a computer aided system on what kind of separation is possible.

Binary Azeotrope:

A binary azeotrope is when a 2 component, 2 phase system of gas and liquid in chemical equilibrium has the same composition in both phases.

Azeotropic condition:

$x_a = y_a$, $x_b = y_b$

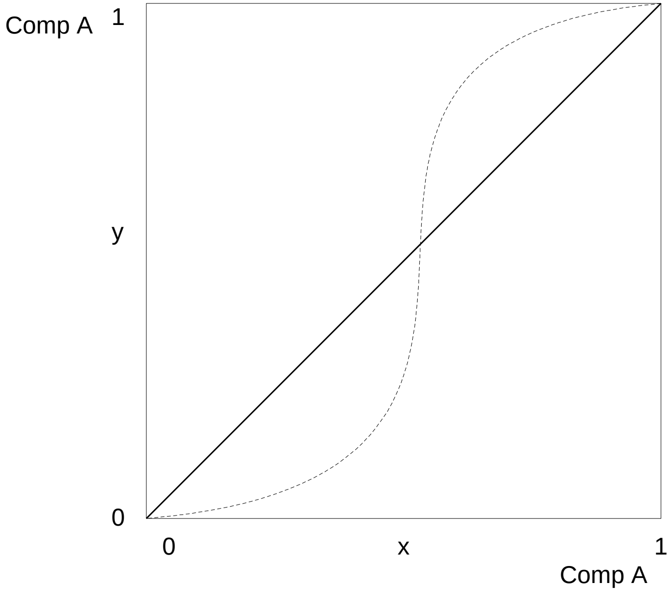


Identification of an azeotrope

Azeotropes is found by VLE (Vapor-Liquid Equilibria) mixture analysis.

This can be either database lookup for VLE datapoints or the datapoints can be calculated with a thermodynamic model.

By the definition of an azeotrope, in a x-y plot the curve crosses the diagonal, at the azeotrope composition.



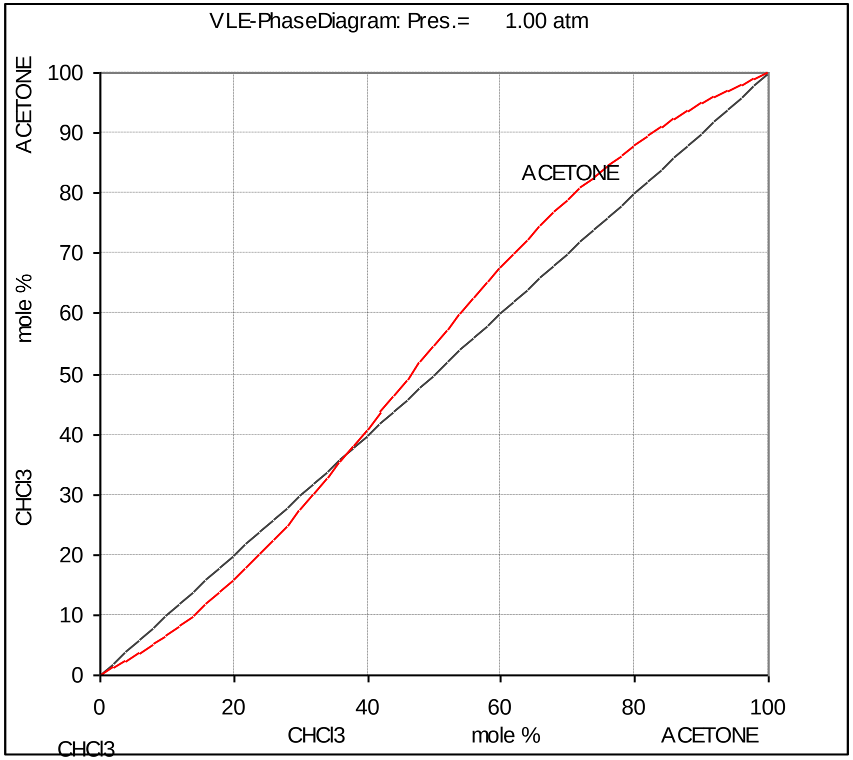
Possible separation techniques

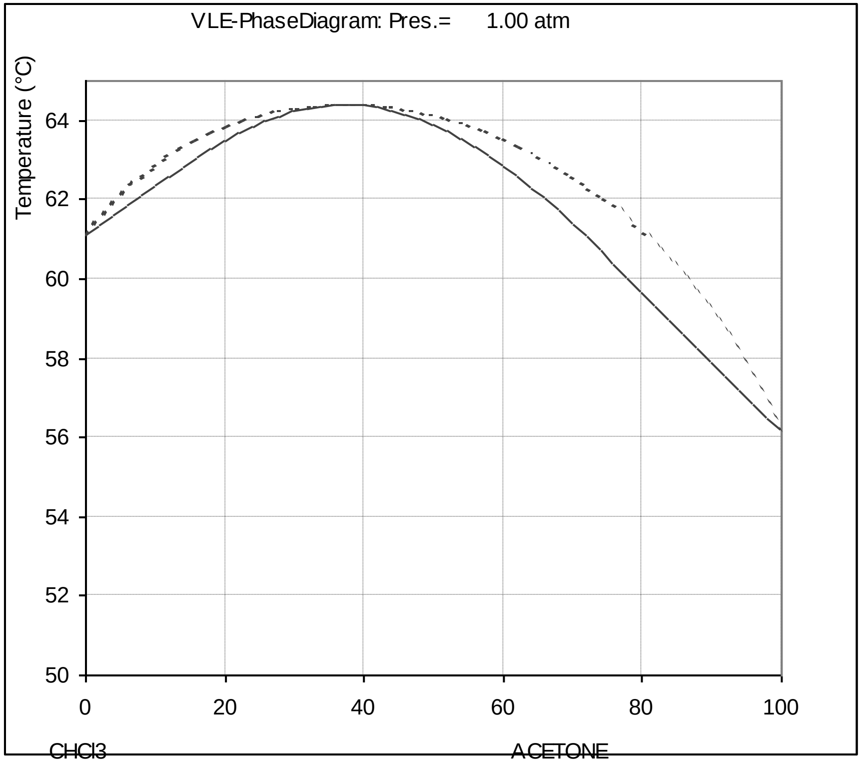
Conventional distillation not possible, if 2 pure products are desired.

Possible solutions to this problem:

- Use separation techniques which are not exploiting differences in vapor vs. liquid phases, i.e. membranes or liquid-liquid extraction.
- Pressure swing.
- Extractive / azeotropic distillation.

Acetone - chloroform

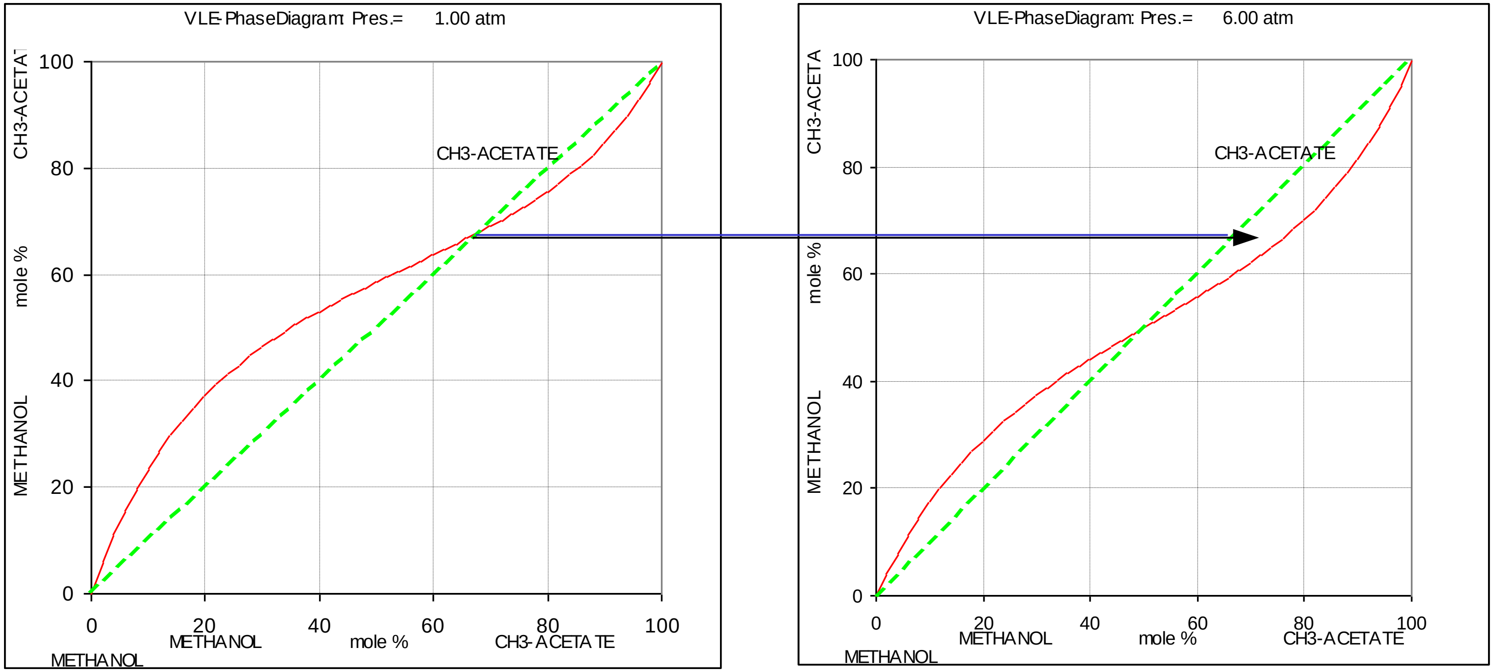




Azeotrope ~ 38 mole% acetone, 64.5 °C, maximum boiling

Pressure swing

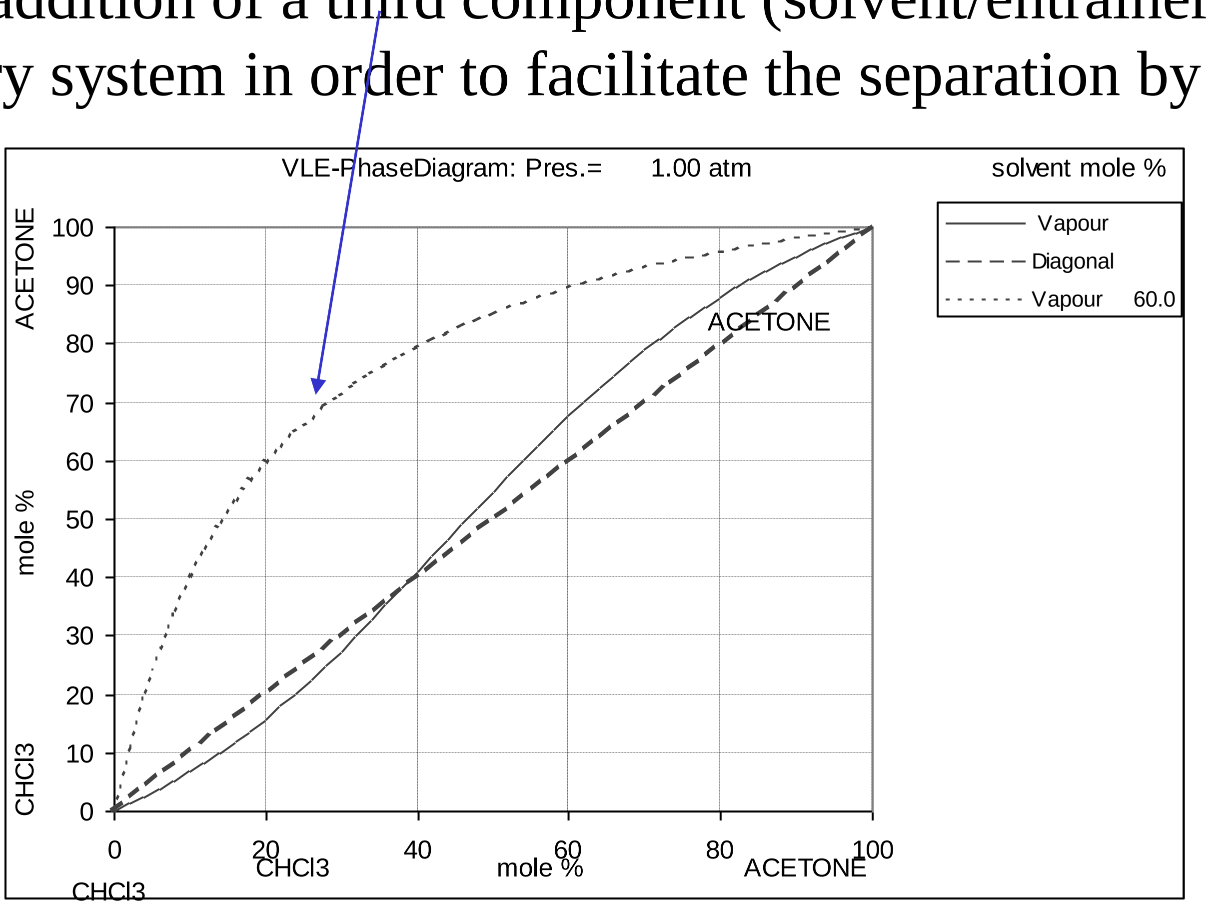
Pressure swing distillation is exploiting the fact that for some azeotropes the composition changes with pressure



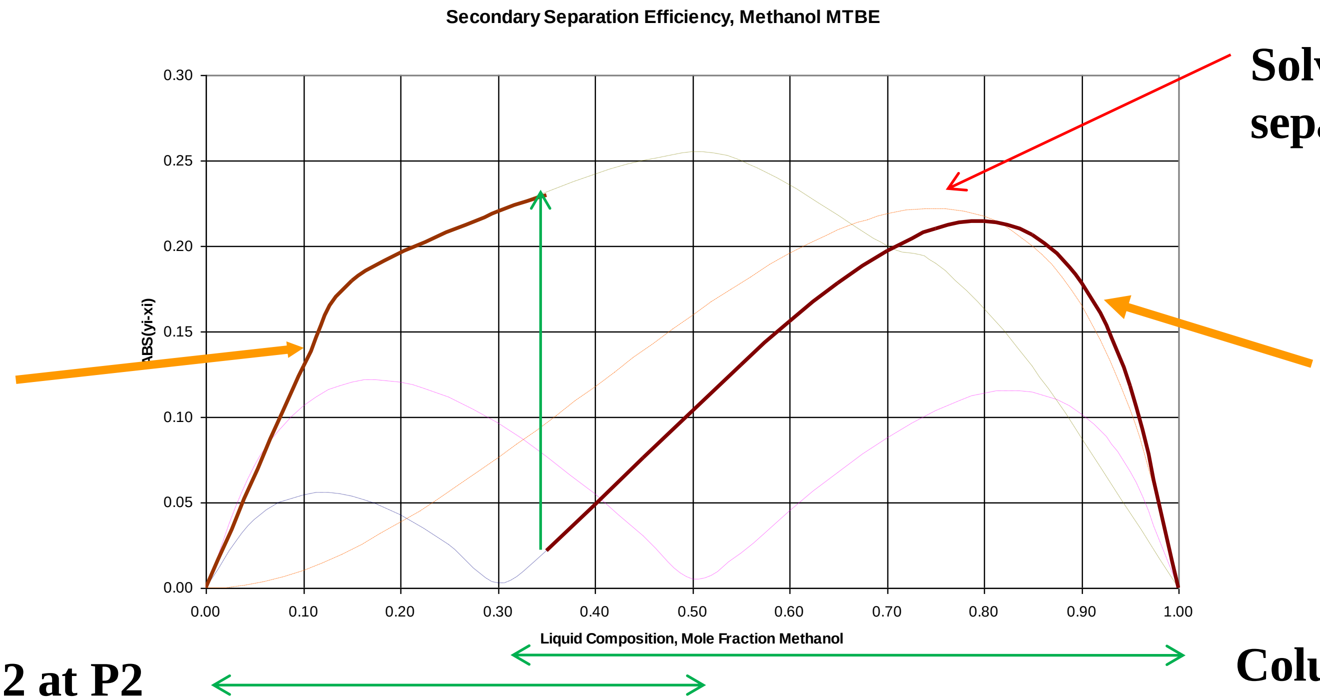
System: methanol – methyl acetate

Extractive distillation

The addition of a third component (solvent/entrainer) to the binary system in order to facilitate the separation by distillation.



Hybrid Separation: Driving force



Solvent based separation

Pervapo-ration

Distillation column 1

Column 2 at P2

Column 1 at P1

Separation by single distillation operation not feasible; hybrid separation schemes (solvent based extraction or distillation plus pervaporation or pressure swing distillation) feasible

Solvent identification (I)

The solvent can be found in a solvent database or by the use of a computer tool.

The computer tool must be able to solve the following problem:

Given: A set of desired properties (pure and mixture)
Needed: Description of compounds with these properties

Computer Aided Molecular Design (CAMD) programs can solve this.

General functionality:

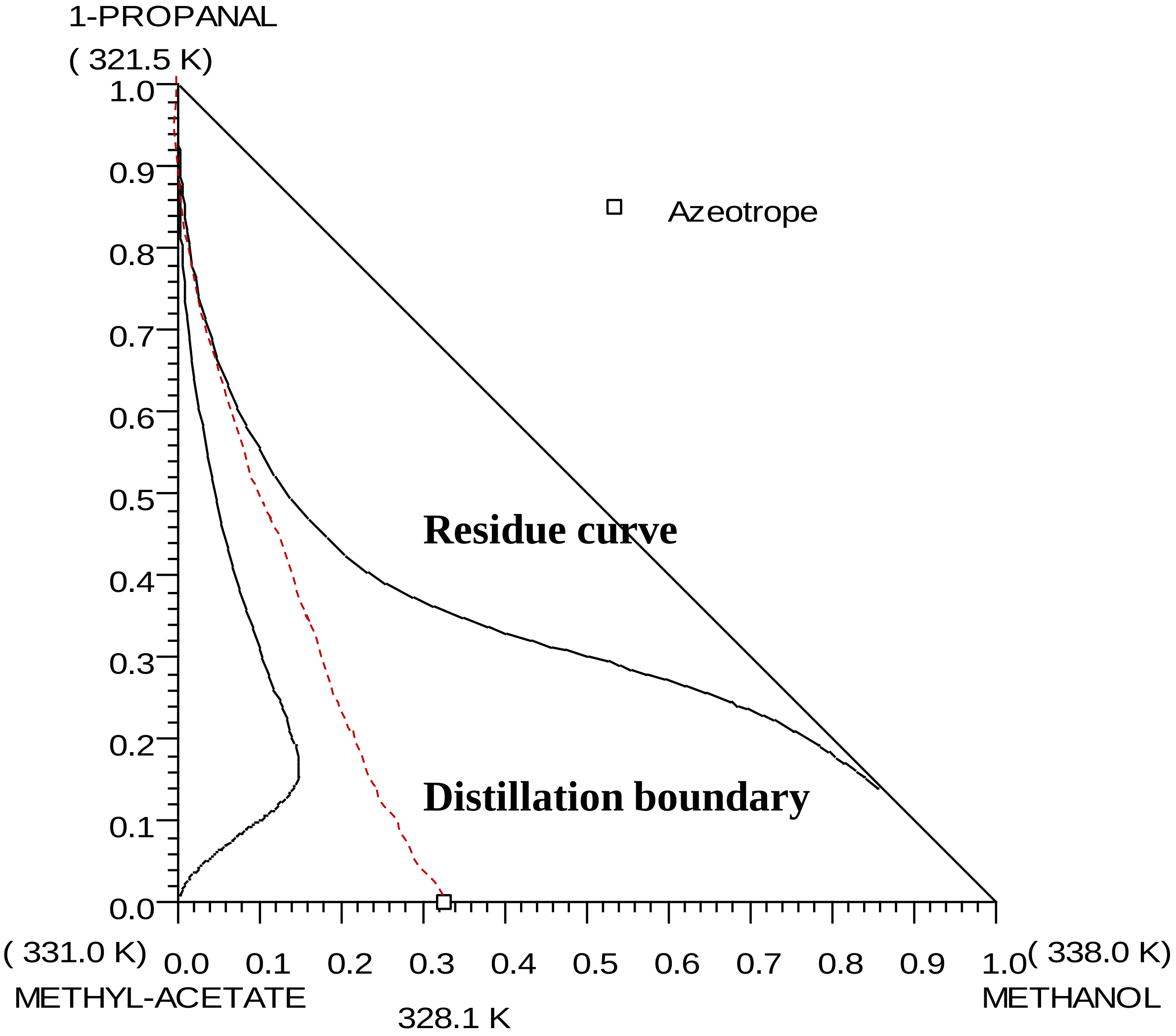
1. Combine molecular fragments to describe complete molecules
2. Predict the properties of the molecular descriptions
3. Reject descriptions with undesired properties

Solvent identification (II)

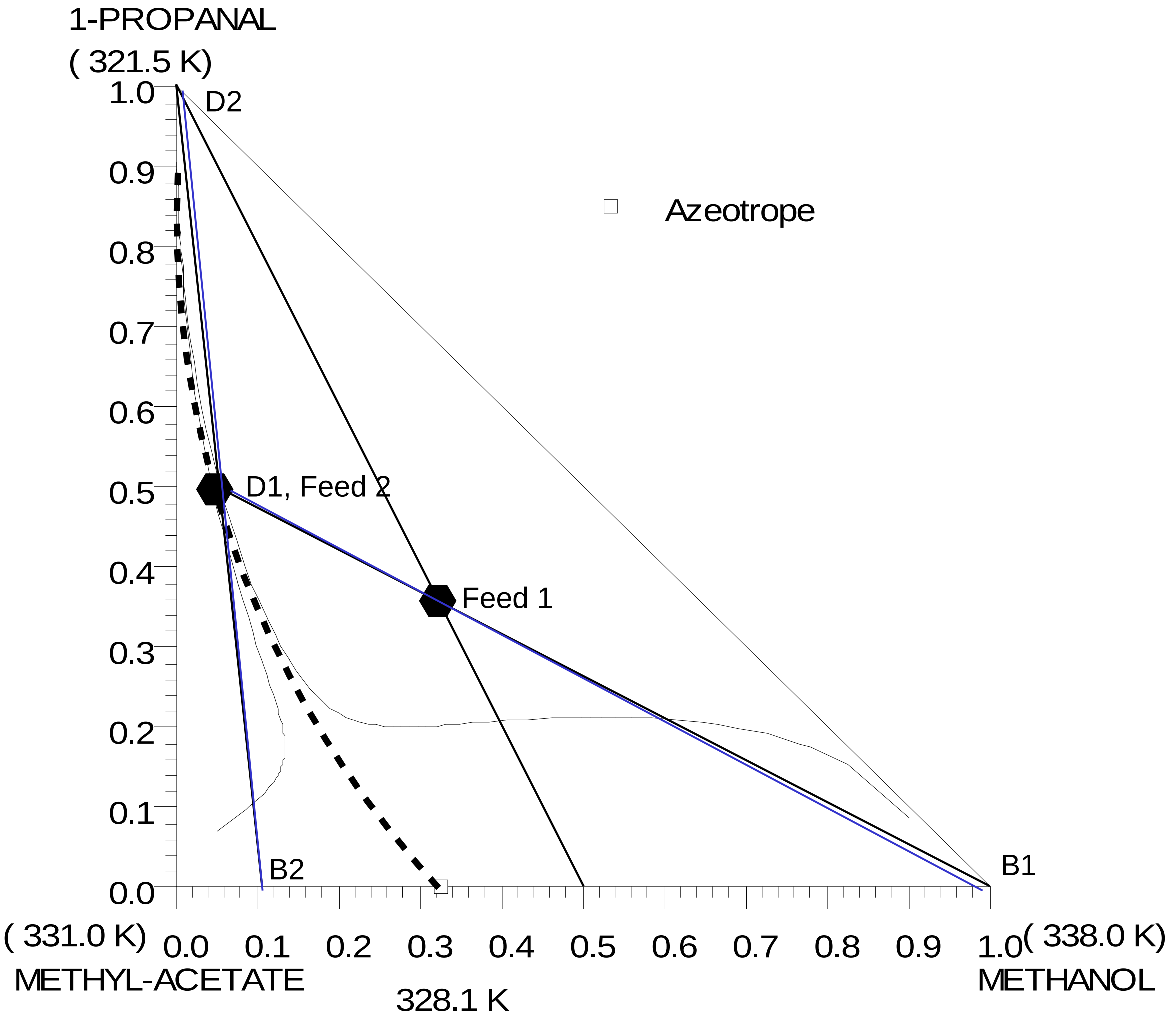
Desired properties for the entrainer:

1. If it is a minimum boiling azeotrope the boiling point of the entrainer should be lower than the azeotropic temperature and vice versa.
2. The boiling point should not be to high in order to have small energy consumption.
3. Should not be harmful to the environment.
4. Should not form azeotropes with any of the two compounds.
5. High selectivety: $S_s = \frac{\gamma_{jS}^{\infty}}{\gamma_{iS}^{\infty}}$
6. Low solvent loss: $S_{sv.L} = \frac{1}{\gamma_{sJ}^{\infty}}$
7. ...

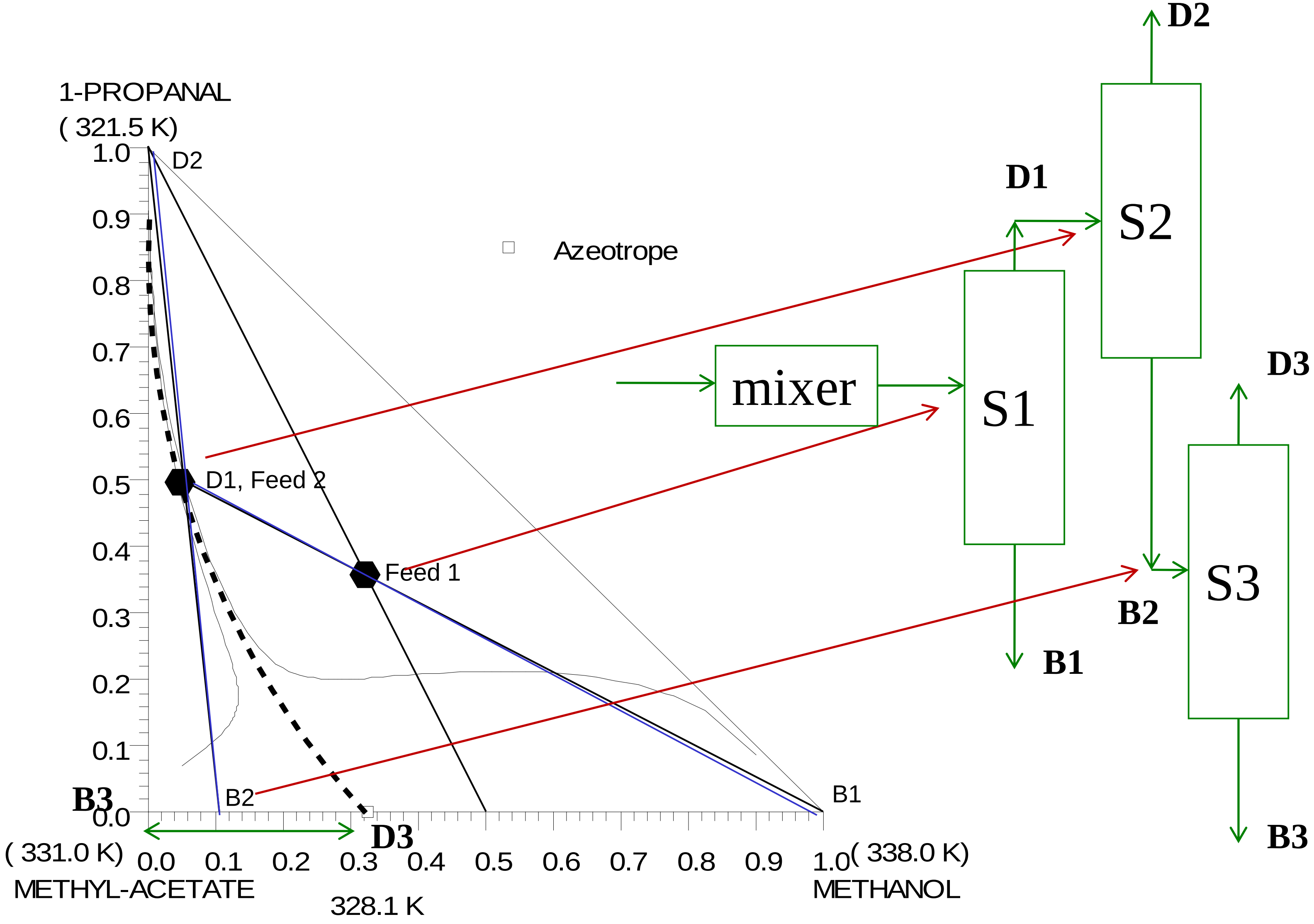
Solvent validation (I): Identify distillation boundaries



Solvent validation (II): Separation feasibility

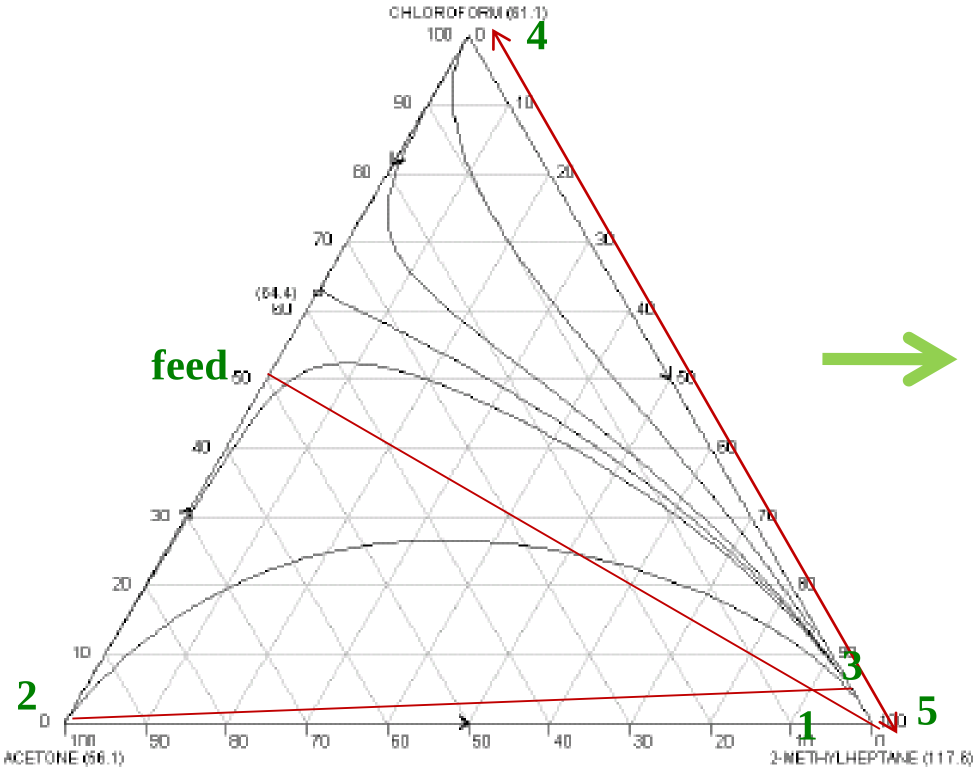


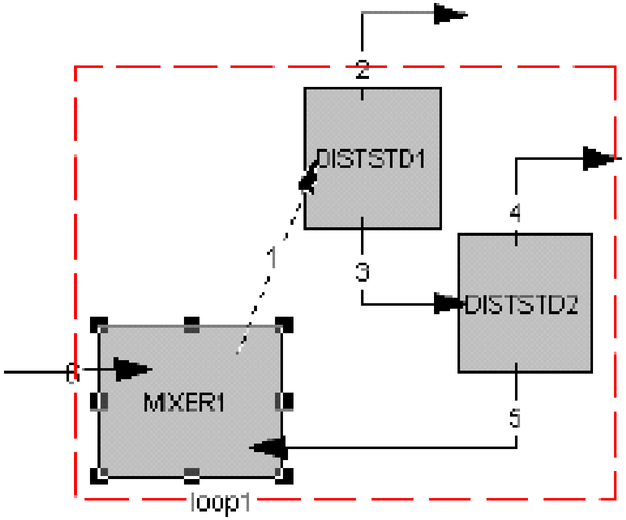
Solvent validation (III): Flowsheet configuration



Another flowsheet configuration: High boiling azeotrope

How to identify feasible configurations & design?



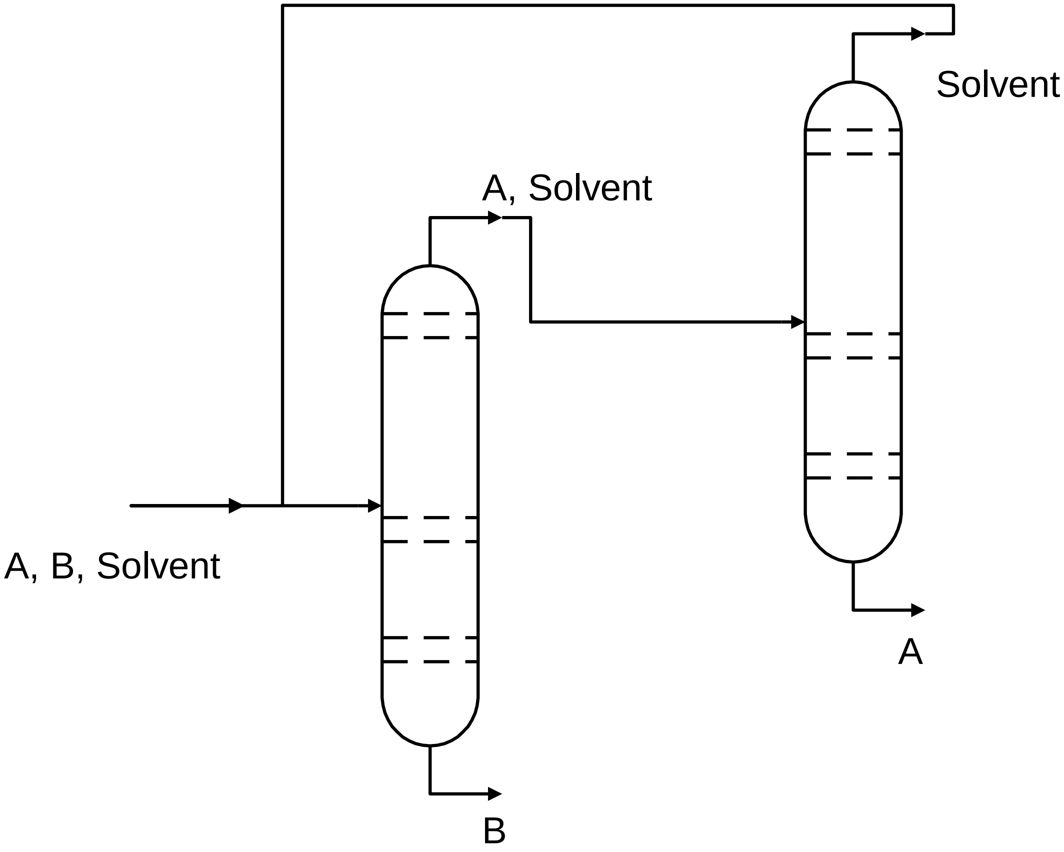


Identify the azeotropes, determine the distillation boundaries, generate the residue curves, design and analyze the separation scheme

Other flowsheet configurations

For different types of ternary diagrams, the flowsheet can be fixed in advance, consisting of minimum two distillation columns.

What kind of distillation boundary and residue curves are needed to get the flowsheet shown on the right?

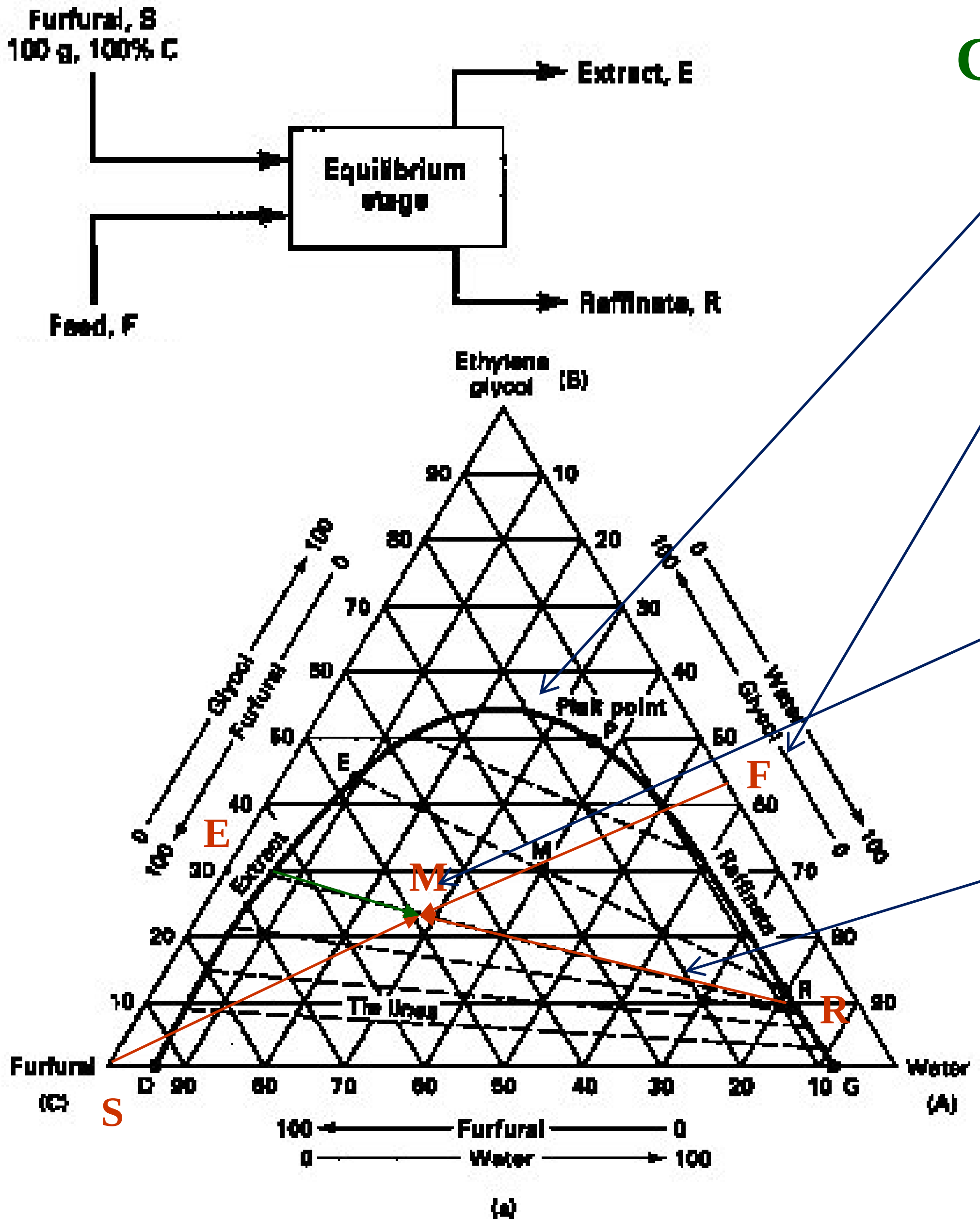


Part-IV: Other separation processes

Table 8.5 Analogy between Distillation and Extraction

Distillation	Extraction
Addition of heat	Addition of solvent
Reboiler	Solvent mixer
Removal of heat	Removal of solvent
Condenser	Solvent separator
Vapor at the boiling point	Solvent-rich solution saturated with solvent
Superheated vapor	Solvent-rich solution containing more solvent than that required to saturate it
Liquid below the boiling point	Solvent-lean solution, containing less solvent than that required to saturate it
Liquid at the boiling point	Solvent-lean solution saturated with solvent
Mixture of liquid and vapor	Two-phase liquid mixture
Relative volatility	Relative selectivity
Change of pressure	Change of temperature
D = distillate	D = extract product (solute on a solvent-free basis)
B = bottoms	B = raffinate (solvent-free basis)
L = saturated liquid	L = saturated raffinate (solvent-free)
V = saturated vapor	V = saturated extract (solvent-free)
A = more volatile component	A = solute to be recovered
C = less volatile component	C = carrier from which A is extracted
F = feed	F = feed
x = mole fraction A in liquid	X = mole or weight ratio of A (solvent-free), $A/(A + C)$
y = mole fraction A in vapor	$Y = S/(A + C)$

Graphical Design Technique



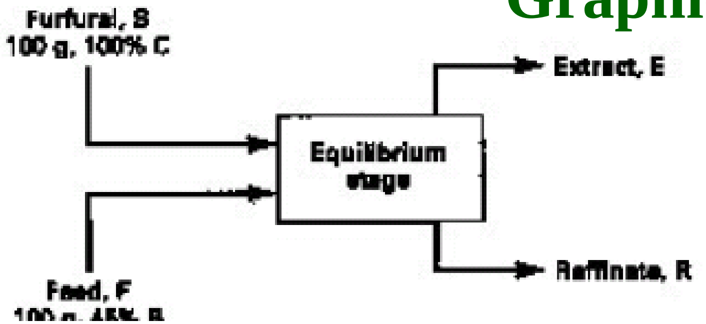
Draw the ternary LLE diagram

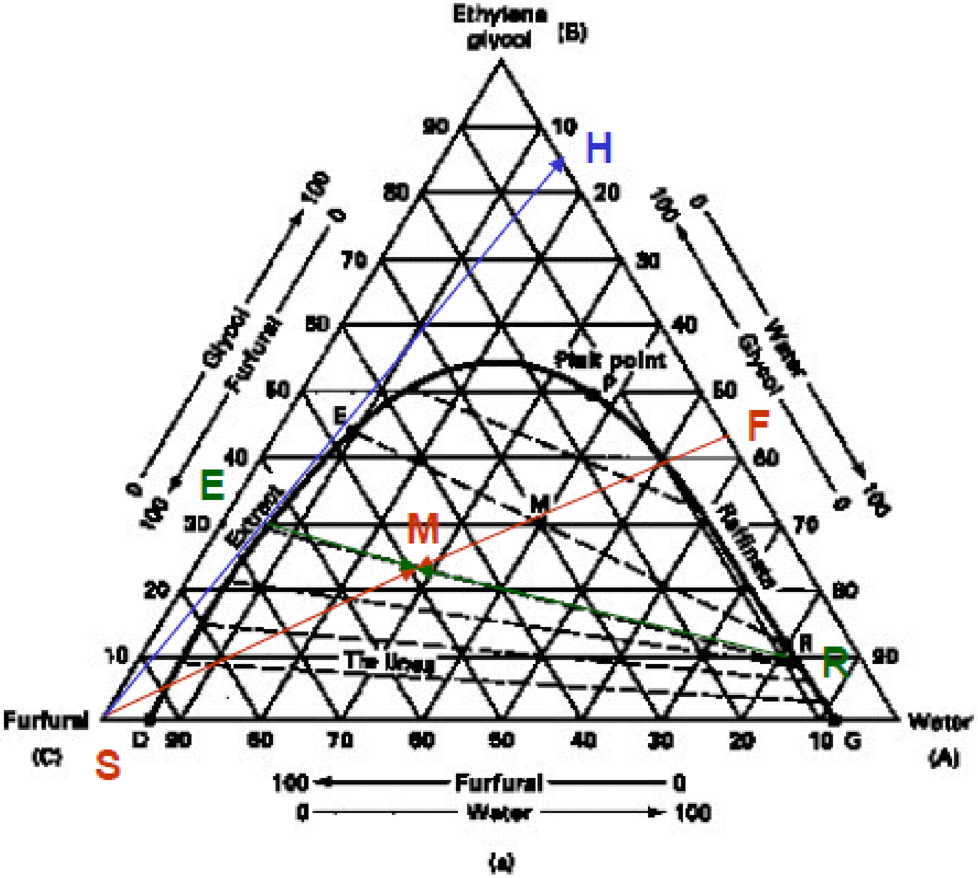
Locate F (feed) & S (solvent) streams & join them in a straight line

Locate any point M that determines the mixing point between F and S.

Locate a tie-line that passes through M. The end-points of the tie-line indicates the composition of E and R streams

Graphical Design Technique for LL-extraction





Calculate the compositions of streams E & R

Draw the ternary LLE diagram

Step 1:Locate F & S

Step 2: Define M = F+S=E+R

Step3: Locate M by inverse lever-arm rule; F/S = 1=SM/MF

Step4: If M is within the 2-phase region, find the tie-line passing through M to locate E & R

Step 5: Use the inverse lever-arm rule to calculate E=M(RM/ER) & then R=M-E

Step6: Find the solvent-free composition of E. Join points C & E and extend to H.

Modelling and design of counter-current LL-extraction systems

Figure 8.13 Countercurrent-flow, N-stage liquid-liquid extraction cascade.

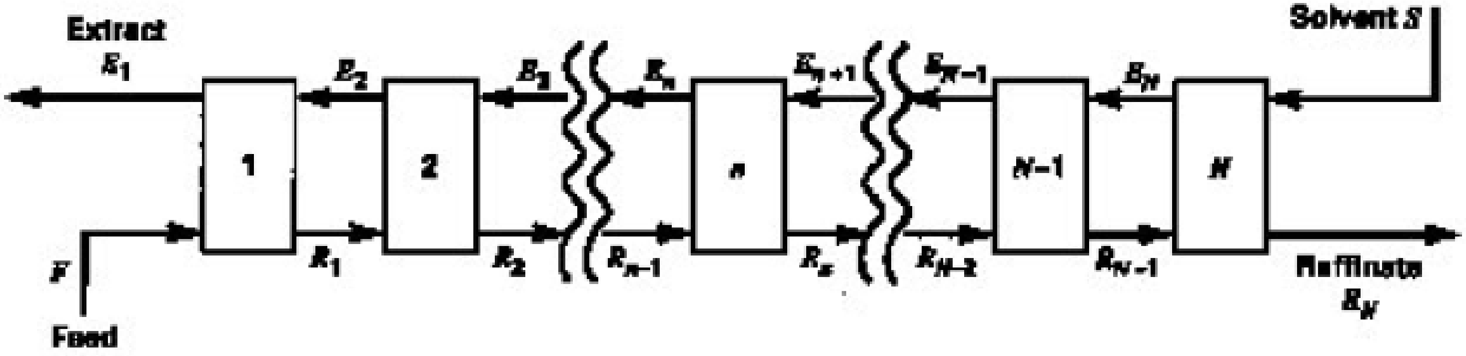
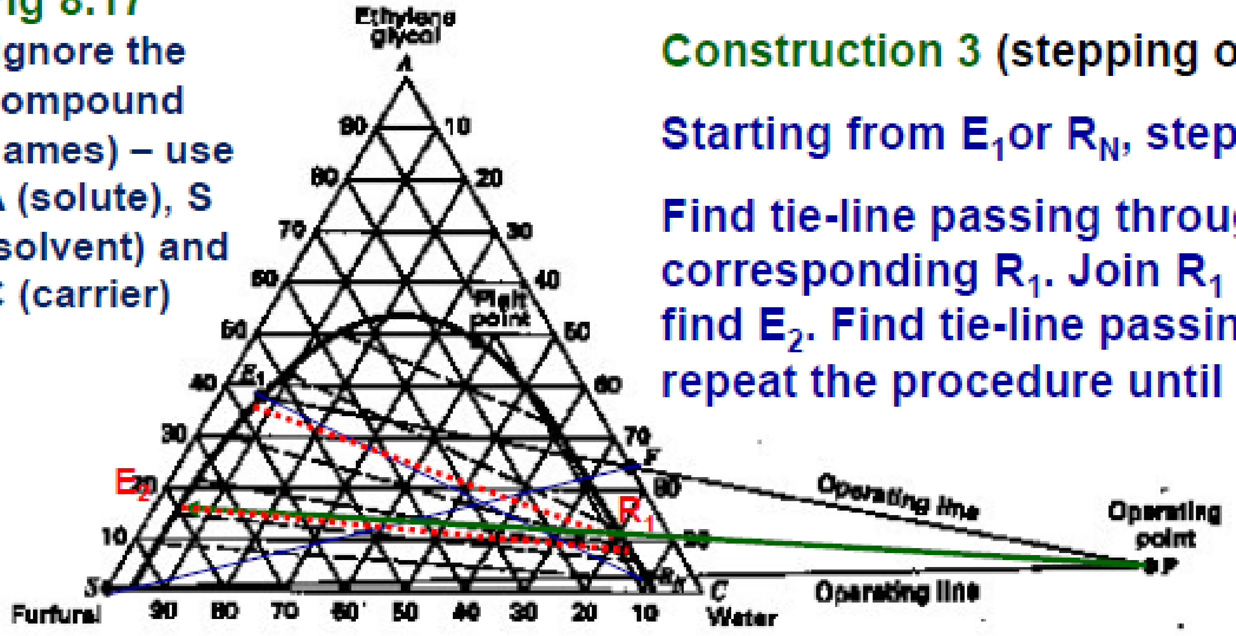


Fig 8.17
(ignore the compound names) – use A (solute), S (solvent) and C (carrier)



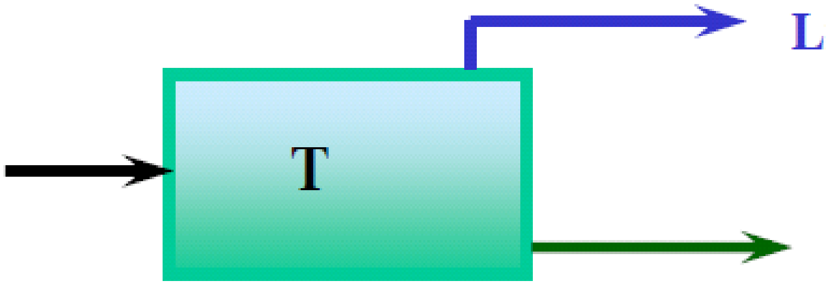
Number of equilibrium stages

Construction 3 (stepping of stages)

Starting from E_1or R_N, step of stages as follows

Find tie-line passing through E_1. Mark out the corresponding R_1. Join R_1 with P and extend to find E_2. Find tie-line passing through E_2 and repeat the procedure until R_N is reached

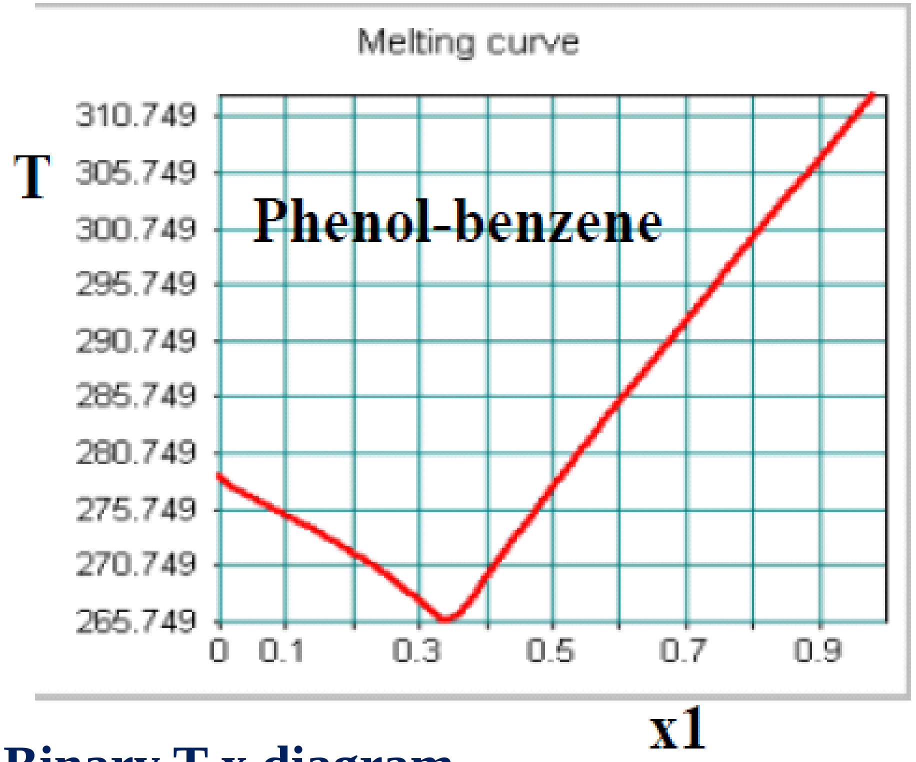
SLE Phase diagrams: Non-electrolytes



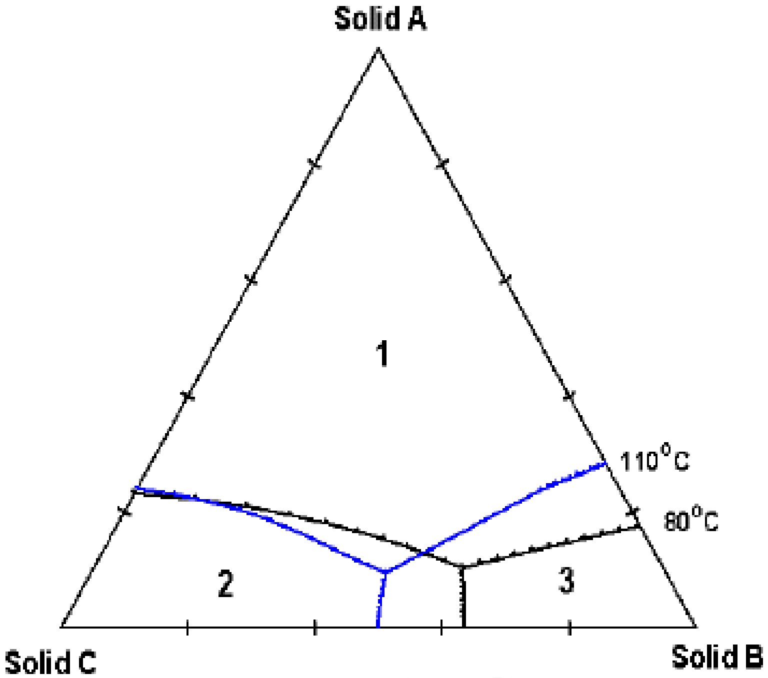
T

Liquid, L

Solid, S



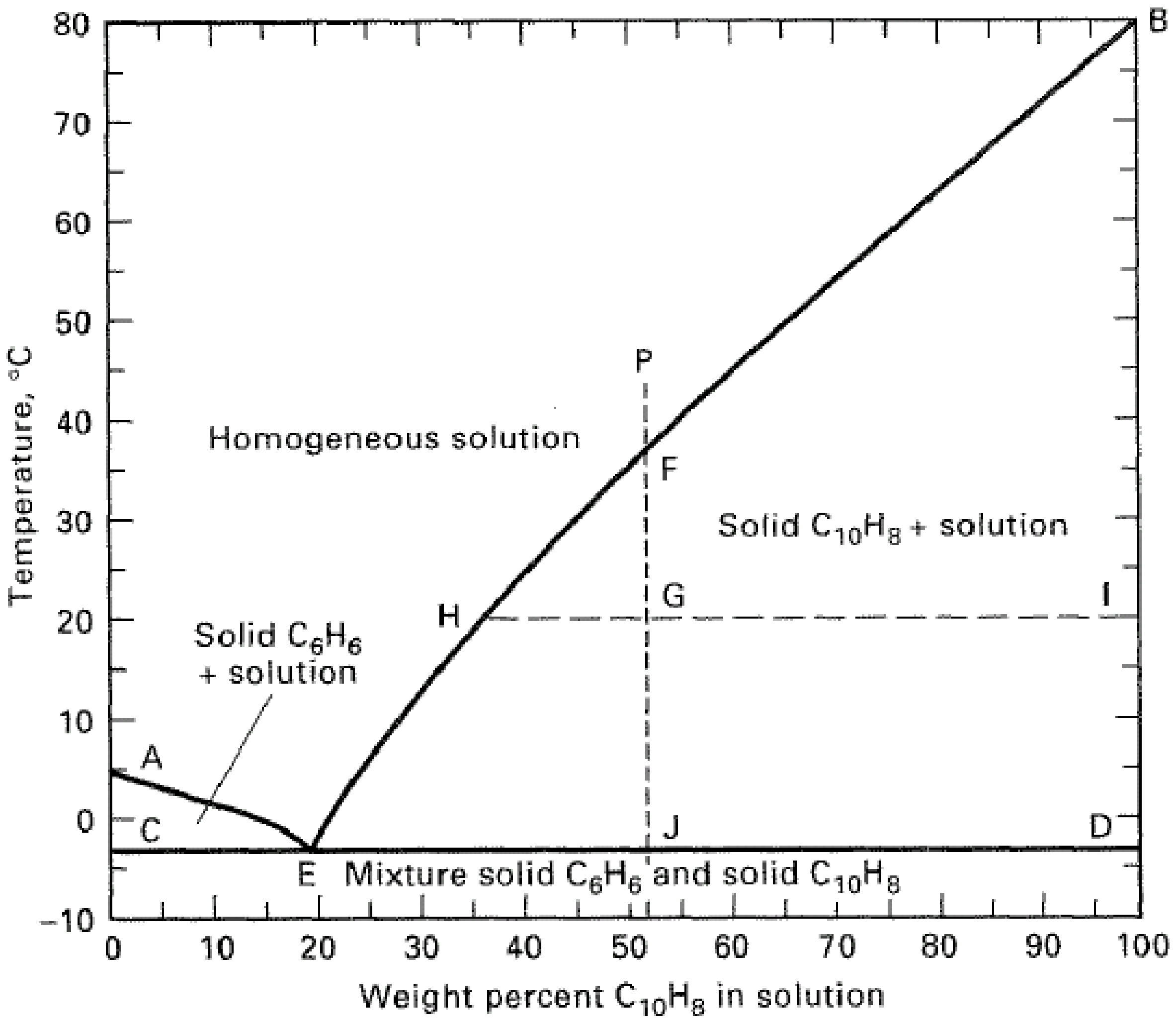
Binary T-x diagram



Ternary saturation diagrams at constant T & solvent-free

Crystallizer operation

Solubility of naphthalene in benzene.



Cool a liquid mixture from point P.

When temperature at point F is reached, solid crystals of naphthalene starts to form

Further reduction of temperature to G gives a liquid of composition H and solids of amount GH per original solution (HI) is obtained

At J or below, only solids exist

Equipment design parameters (to be covered in next lecture)

- **Distillation Column Design - Determine, Reflux ratio, Number of stages, Column diameter, Tray height, Heat duties for reboiler & condenser (*following the example in the book*)**
  - **Use the $\alpha_{lk/hk}$, ξ_{lk}, ξ_{hk} to calculate N_i & R_i**
  - **Calculate $N_t = 0.8 \max_i(N_i) + (1-0.8) \min_i(N_i)$; use efficiency of 80%**
  - **Calculate $R = 0.8 \max_i(N_i) + (1-0.8) \min_i(N_i)$**
  - **Calculate L´ and V´ and from it, F_{lv}**
  - **Use F_{lv} and Fig 4.4 to obtain $C_{sb,t}$ (for a selected tray spacing)**
  - **Calculate flooding velocity, U_{nf}, and from it, the area A and diameter D of the column (use Eqs. 4.7 or 4.8 and 4.9)**
  - **Determine Tray stack height, extra feed space, disengagement space (top & bottom), skirt height**
  - **$Q_{cond} = H^V V - h^L L$**
  - **Calculate Q_{reboil} from total energy balance**

- **Distillation Column Design - Determine, Reflux ratio, Number of stages, Column diameter, Tray height, Heat duties for reboiler & condenser (*Using PRO-II*)**
  - **Use Short-Cut Fractionation (for column design)**
  - **Use rigorous simulation model to obtain the final design**
  - **Use the “sizing” calculation option for the column design**
  - **Select the column diameter, tray spacing, etc., from the output of PRO-II**
  - **For condenser duty = Q_{cond} (given by PRO-II), size a heat exchanger (determine area A)**
  - **For reboiler duty = Q_{reboil} (given by PRO-II), size a heat exchanger (kettle-type) – determine area**
  - **Determine Tray stack height, extra feed space, disengagement space (top & bottom), skirt height**

- **Absorption Column Design - Determine, absorption factor, Number of stages, Column diameter, Tray height, Heat duties for reboiler & condenser**
  - **Use the $\alpha_{lk/hk}$, ξ_{lk}, ξ_{hk} to calculate N_t**
  - **Calculate N_t from Kremser equation (approx = 10)**
  - **Use efficiency of 20%**
  - **Calculate L´ and V´ and from it, F_{lv}**
  - **Use F_{lv} and Fig 4.4 to obtain $C_{sb,t}$ (for a selected tray spacing)**
  - **Calculate flooding velocity, U_{nf}, and from it, the area A and diameter D of the column (use Eqs. 4.7 or 4.8 and 4.9)**
  - **Determine Tray stack height, extra feed space, disengagement space (top & bottom), skirt height**
  - **Packed columns can also be calculated from the number of transfer units and height of transfer units**

- **Pumps, Compressors, Heat Exchangers, ….**
- **The sizing parameters for each of these equipments can be obtained from PRO-II or calculated through the method used in the book (see the ethanol case study in chapter 4)**
- **Pump – find the power needed (based on work)**
- **Compressor - find the power needed (based on work)**
- **Tank – volume (area and height) based on residence time**
- **Heat Exchangers – area of the heat exchanger based on U, ΔT, Q, Flowrate**
- **…..**

•Ethanol Process: Case Study (from Textbook)

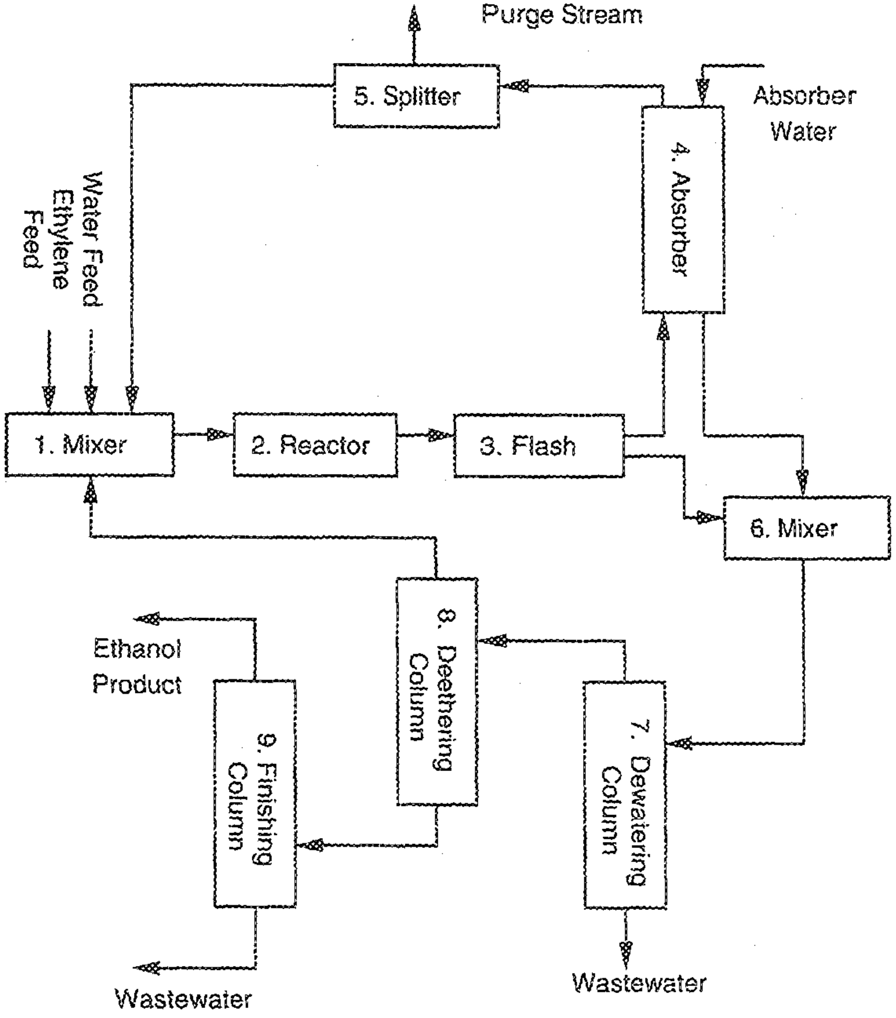


FIGURE 3.1 Ethanol flowsheet.

- **We have now performed mass and energy balance.**
- **We have added pumps/compressors, heat exchangers wherever necessary.**
- **Now we need to do the sizing calculations for all unit operations in the flowhseet.**
- **Costing & Economic analysis**

•Sizing & Costing Calculations

- **Prepare a list of unit operations found in the flowsheet**
- **For each unit operation, find a design that matches the calculated input-output conditions to obtain the sizing parameters**
- **Use the sizing parameters to determine the cost of each unit operation**

•Decisions that need to be made

- **Choice of equipment type**
- **Choice of pressure (already made)**
- **Choice of material**
- **Other parameters specific to the unit operation**