Complex distillation systems. Theory and models.

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PASI 2008

Outline

1.- Introduction.

2.- Theory in simple columns design.

3.- Reversible distillation columns and sequences.

4.- Optimal synthesis distillation columns sequences.

1.- Introduction.

Mathematical models in Distillation⇒ predict values:

Product composition for F (x_F)
Minimum energy demand Rmin
Minimum number of stages Nmin
Relationship R/Rmin vs N/Nmin

Mathematical models for:

Process optimization, design, synthesis.
Process control.
Process fault diagnosis.

Interest in Distillation grows because of:

Energy intensive process: Petrochemical, Biofuels.
New processes.
Complex sequences: energy intensive.
Reactive distillation: equipment intensive.
Reactive-extractive distillation.

High improvement potentials in distillation processes.

1.- Introduction.

Different mathematical models according to their sizes:

Aggregated (reduced): minimal information. Simple analytical formulae.

Short cuts: few equations but require numerical solution.

Rigorous: conservation laws, thermodynamics and constitutive models.

Trade off: size and complexity vs. information.

Limitations:

Rigorous models $\Rightarrow$ general purpose.

Simple and reduced models $\Rightarrow$ especial cases.

1.- Introduction

Fundamental concepts in distillation

Models components:
Mass balances
V-L equilibrium
Energy balances

Very exact descriptions using rigorous models for distillations

Concepts derived from distillation theory:

- Pinch points
- Residue curves
- Distillation points

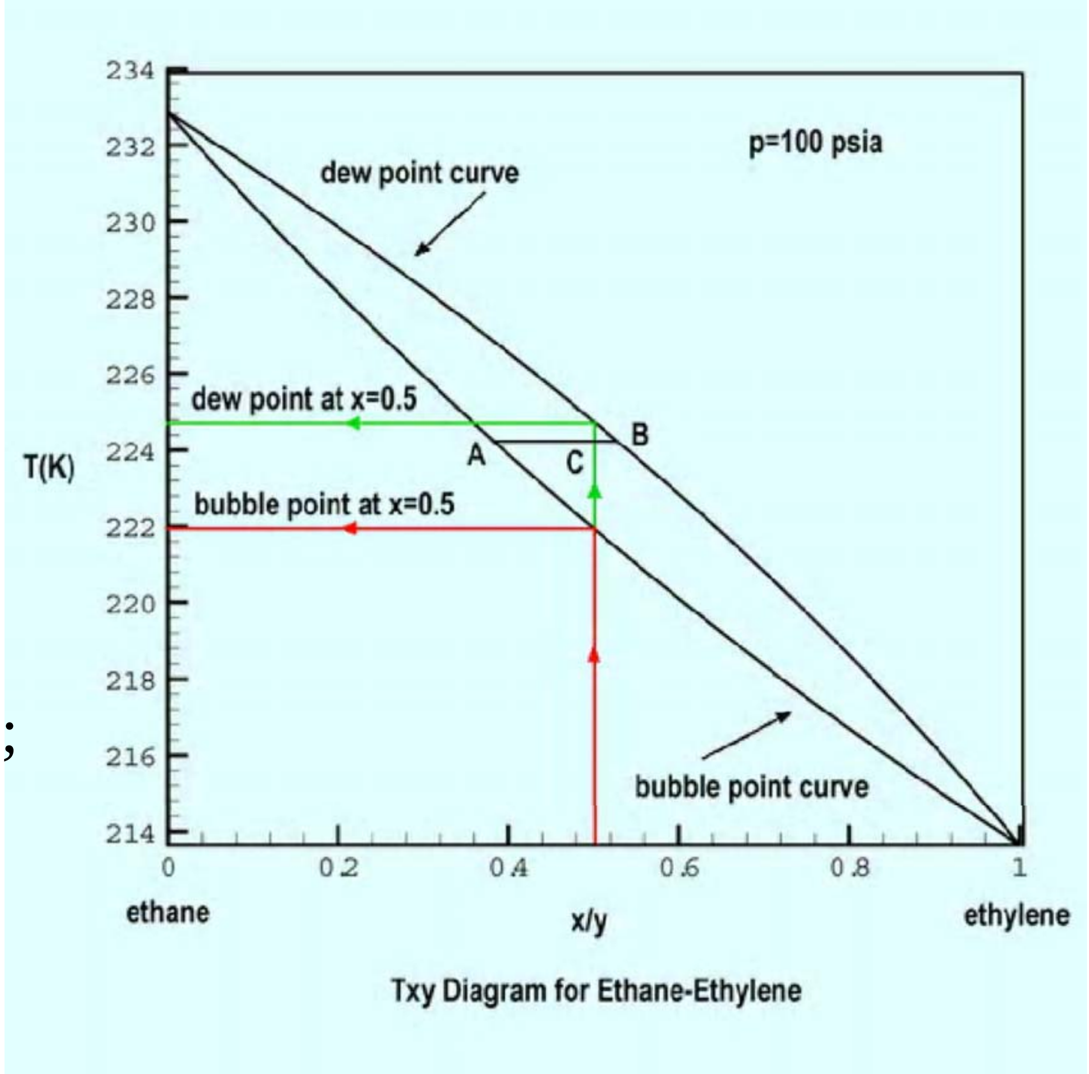
2.- Theory in simple columns design.

Mathematical models.
Minimum energy demand.
Minimum number of stages.

Thermodynamic aspects
V-L Equilibrium
Ideal Mixtures
T vs X(Y), P=cte. diagram

$$K_i = K_i\,(x, y, T, P) = P_i(T);$$
$$i = 1, \ldots NC$$

$$y_i = K_i(T)\; x_i$$



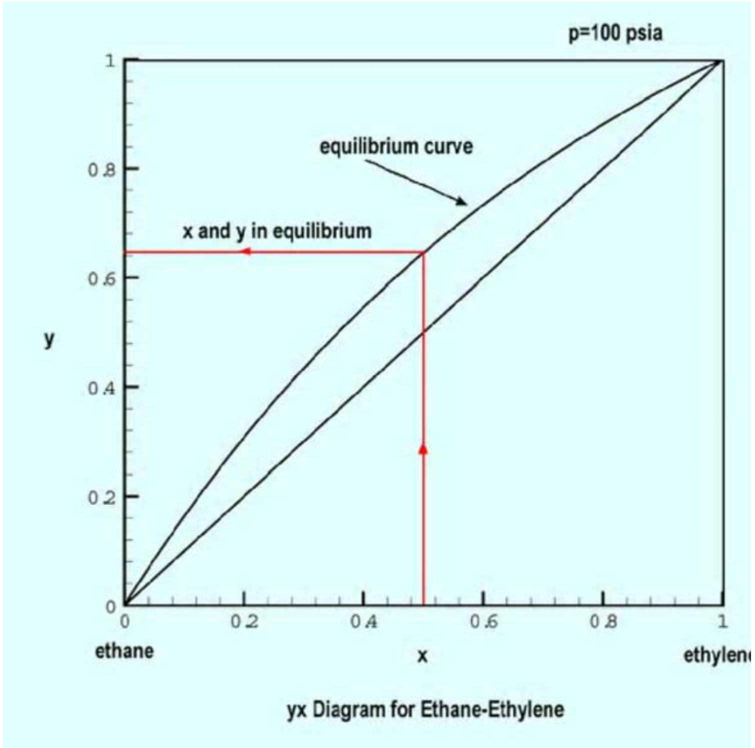
2.- Theory in simple columns design.

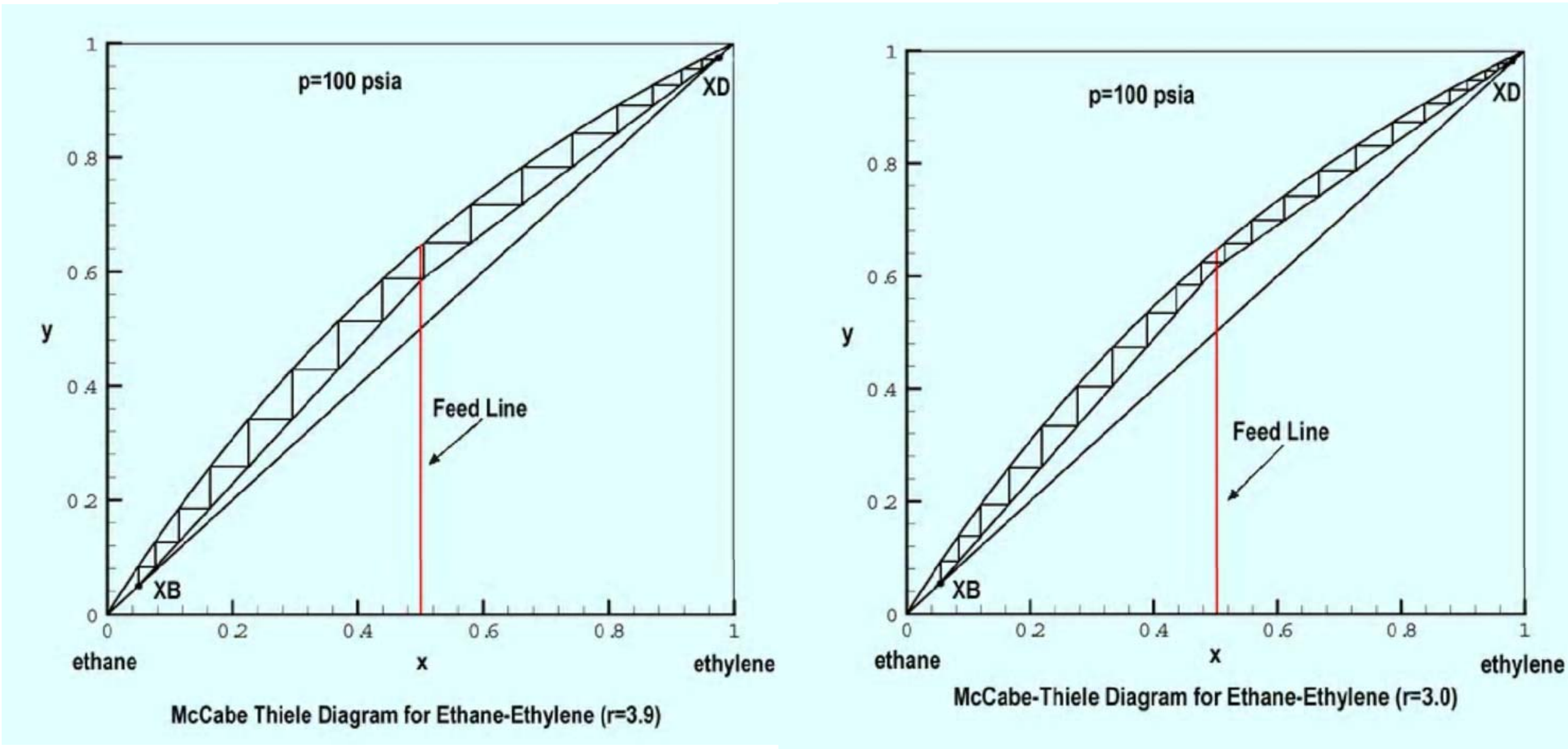
Simple columns. Mathematical models.

Minimum energy demand.
Minimum number of stages.

Assumptions:
Constant relative volatility and
Constant difference in vaporization enthalpy
⇓
Constant Molar Overflow (CMO)
⇓
Straight operating line, decoupling mass and energy balances

Y vs X diagram



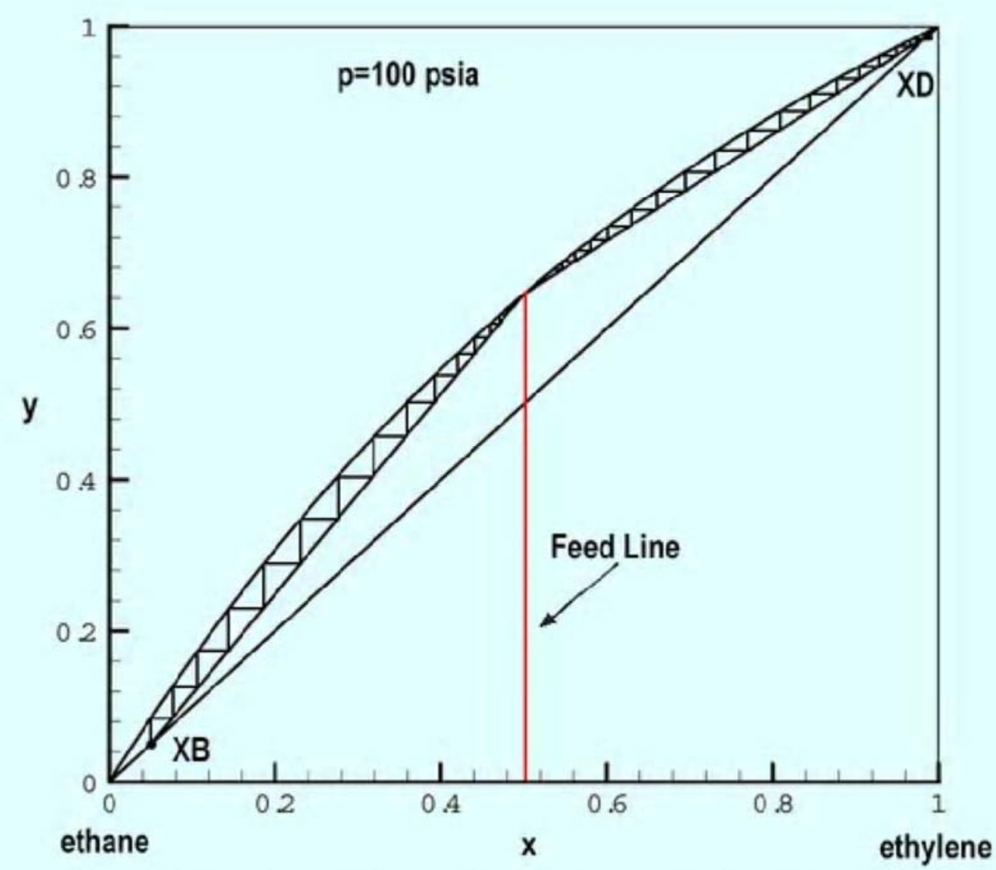


Computing minimum energy demand.

Constant molar overflow $\Rightarrow$ Operating points belong to Straight lines

Tray by tray calculations, equilibrium stages

Minimum energy demand.
Pinch at Feed tray.
The number of stages increases
at the feed location.

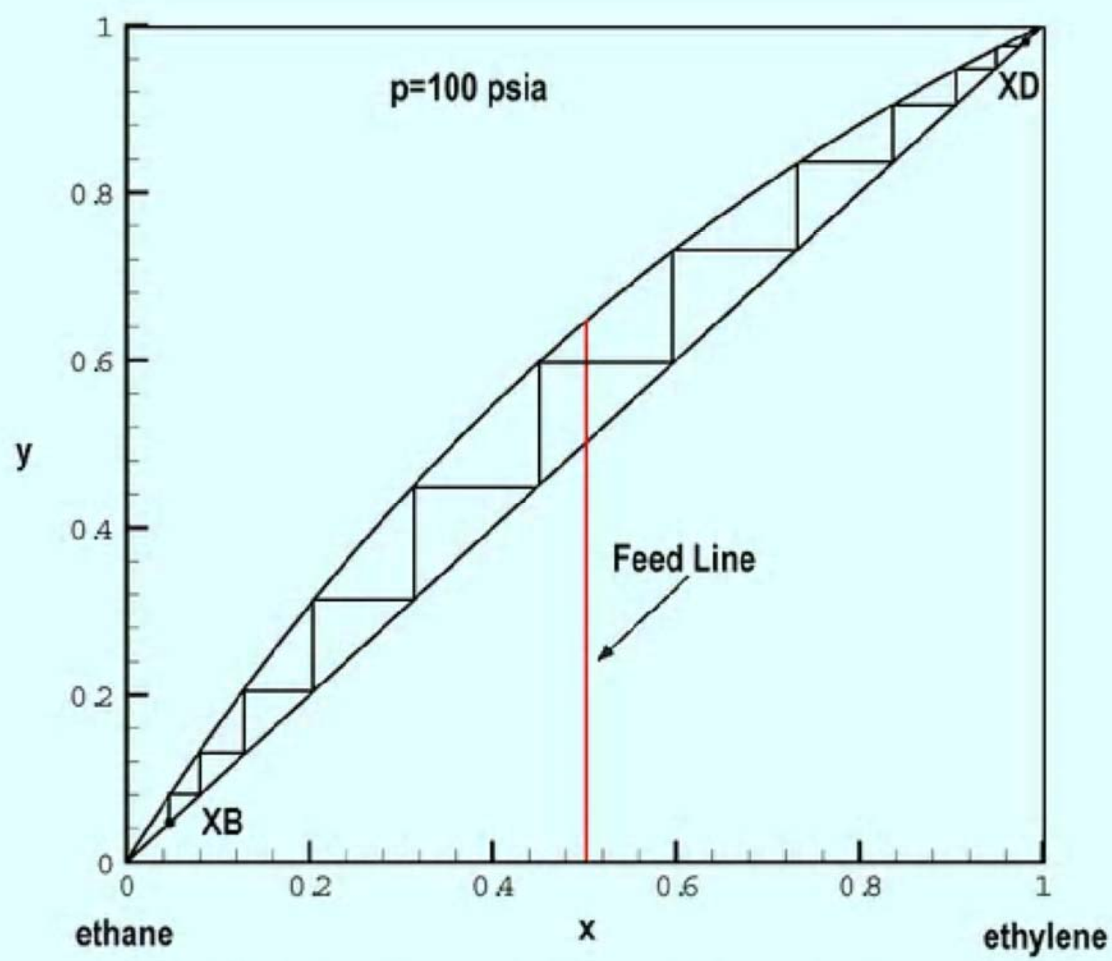


McCabe-Thiele Diagram for Ethane-Ethylene with Feed Pinch

Minimum number of stages.

Total reflux = Distillation points

$X_k \Rightarrow VLE \Rightarrow Y_k^* = X_{k+1} \Rightarrow VLE \Rightarrow Y^*_{k+1} = X_{k+2} \ldots$



McCabe-Thiele Diagram for Ethane-Ethylene at Total Reflux

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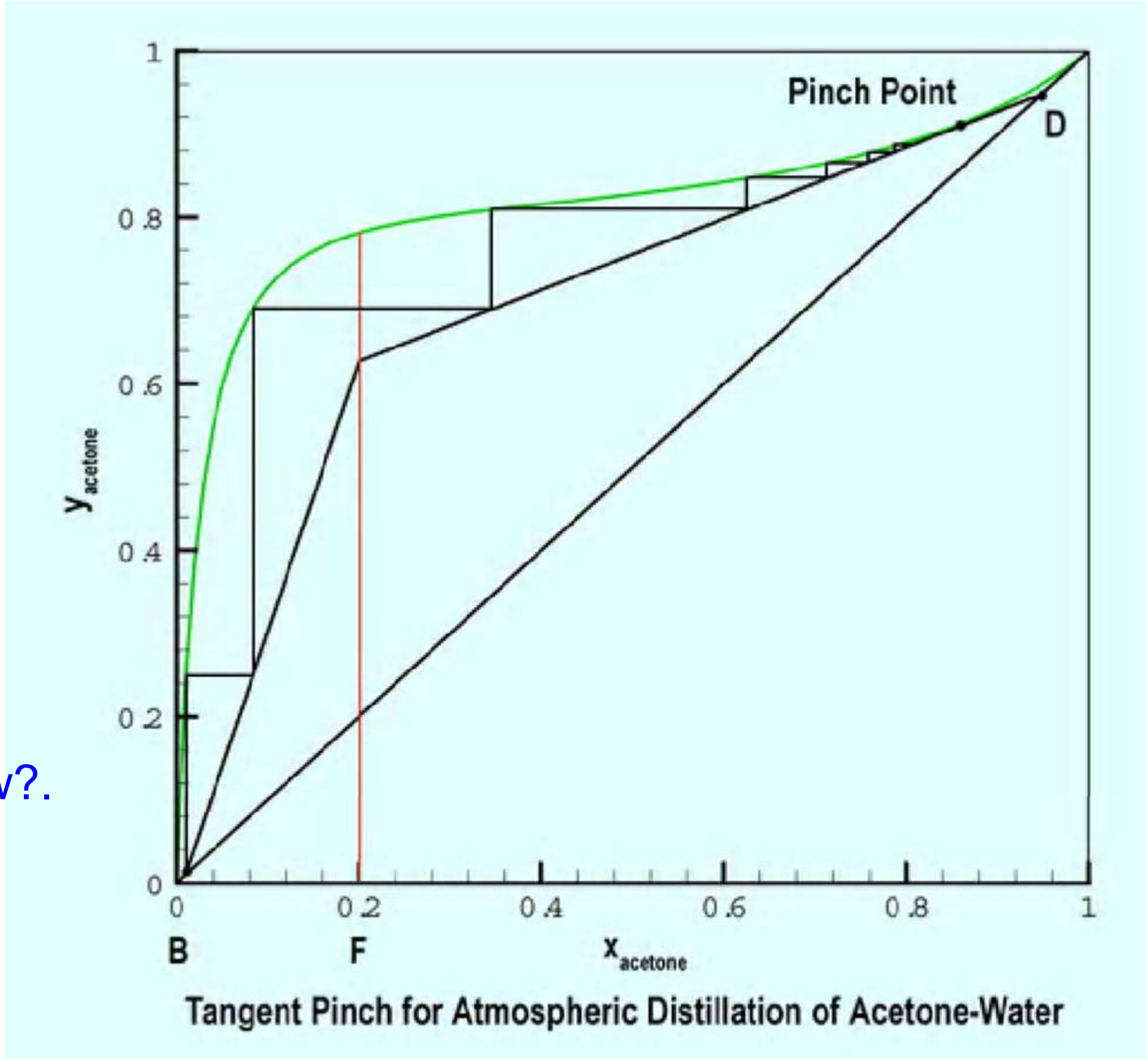
V-L Equilibrium

Non- Ideal Mixtures

X vs Y ; P=cte. diagram

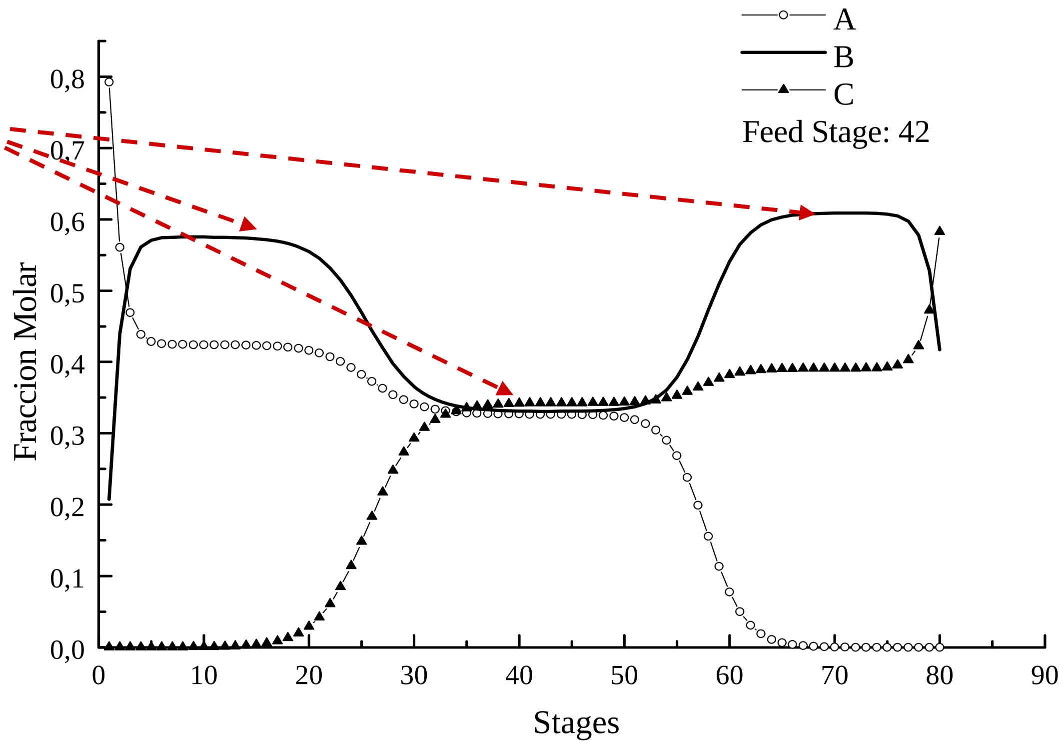
$$K_i = K_i\,(x, y, T, P)$$
$$= \gamma_i(x,T)P_i(T);$$

Constant molar overflow?.



Multicomponent systems. Adiabatic Column. Constant pressure. Rigorous simulation.
Liquid composition profiles

Pinch points?

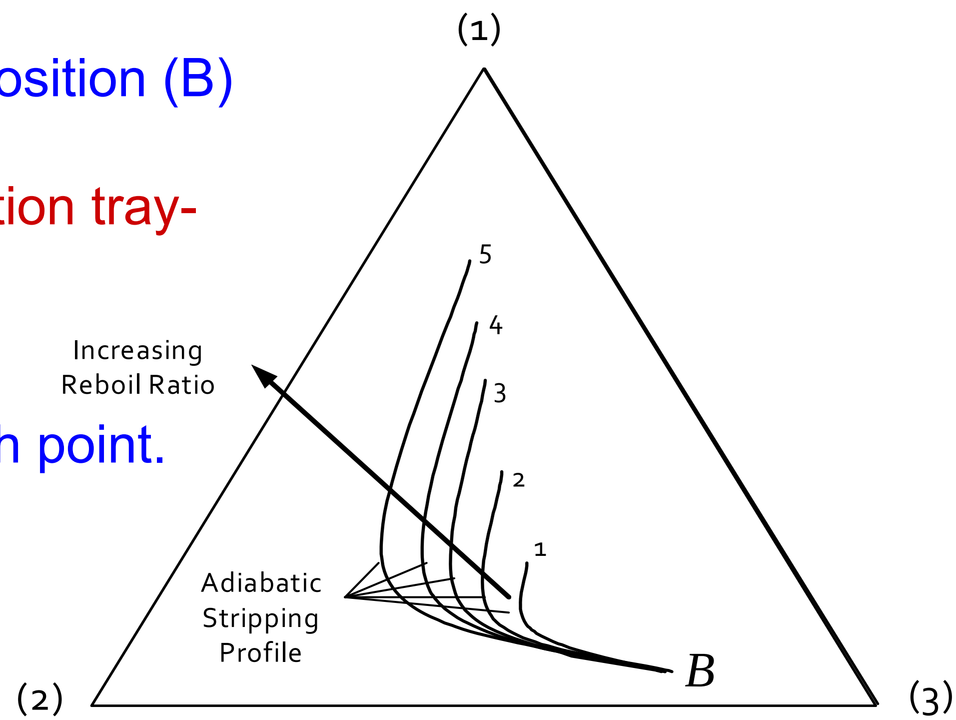


Composition profiles (*F, i* = 0.33/ 0.33/ 0.34 - *D, i* = 0.7946/ 0.205/ 0 - *B, i* = 0/0.4184/0.5815 - *p* = 101.3 *Kpa*)
n-pentane, n-hexane and n-heptane

Ternary systems. Adiabatic Column. Constant pressure.
Liquid composition profiles.

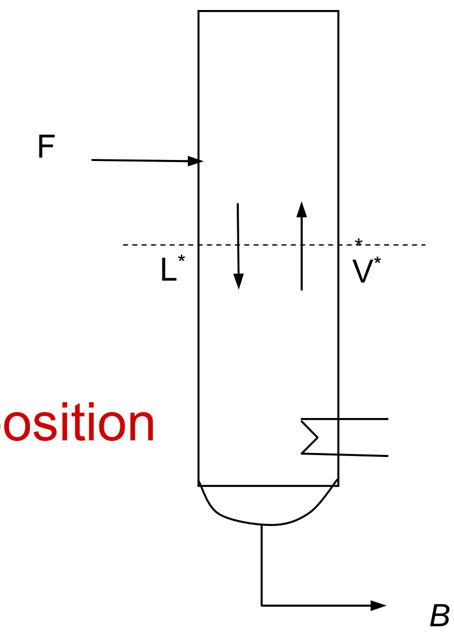
Rigorous simulation.
Specifying a liquid product composition (B) and the reboil ratio,
the succession of liquid composition tray-tray profile can be computed.

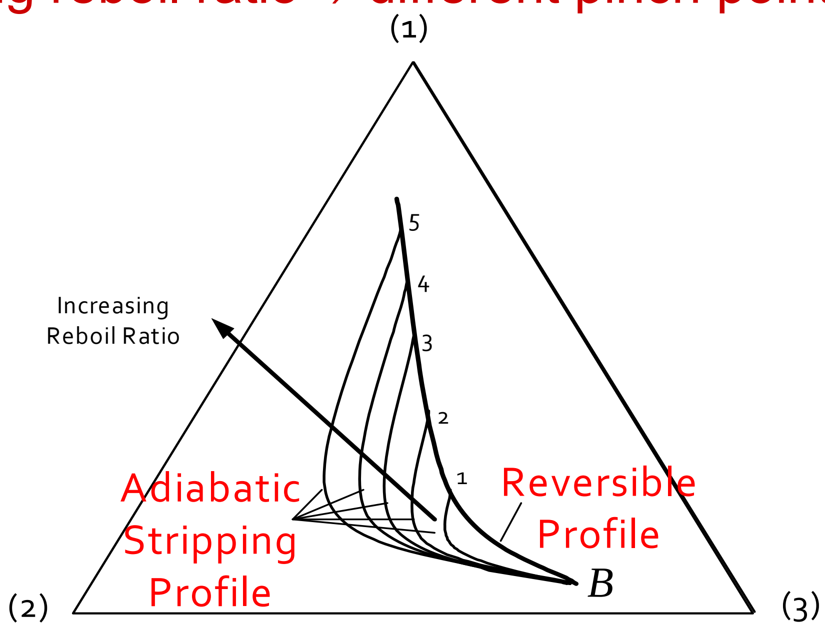
The liquid profile approaches a pinch point.
The number of stages ⇒ ∞ at each point: 1, 2, …



Ternary systems. Adiabatic Column. Constant pressure.
Liquid composition profiles

Specifying:
1) liquid product composition (B)
2) reboil ratio value
3) equilibrium between L* and V*,
a liquid composition can be computed.
Changing reboil ratio⇒ different pinch point composition





Reversible Profile = Collection of Pinch

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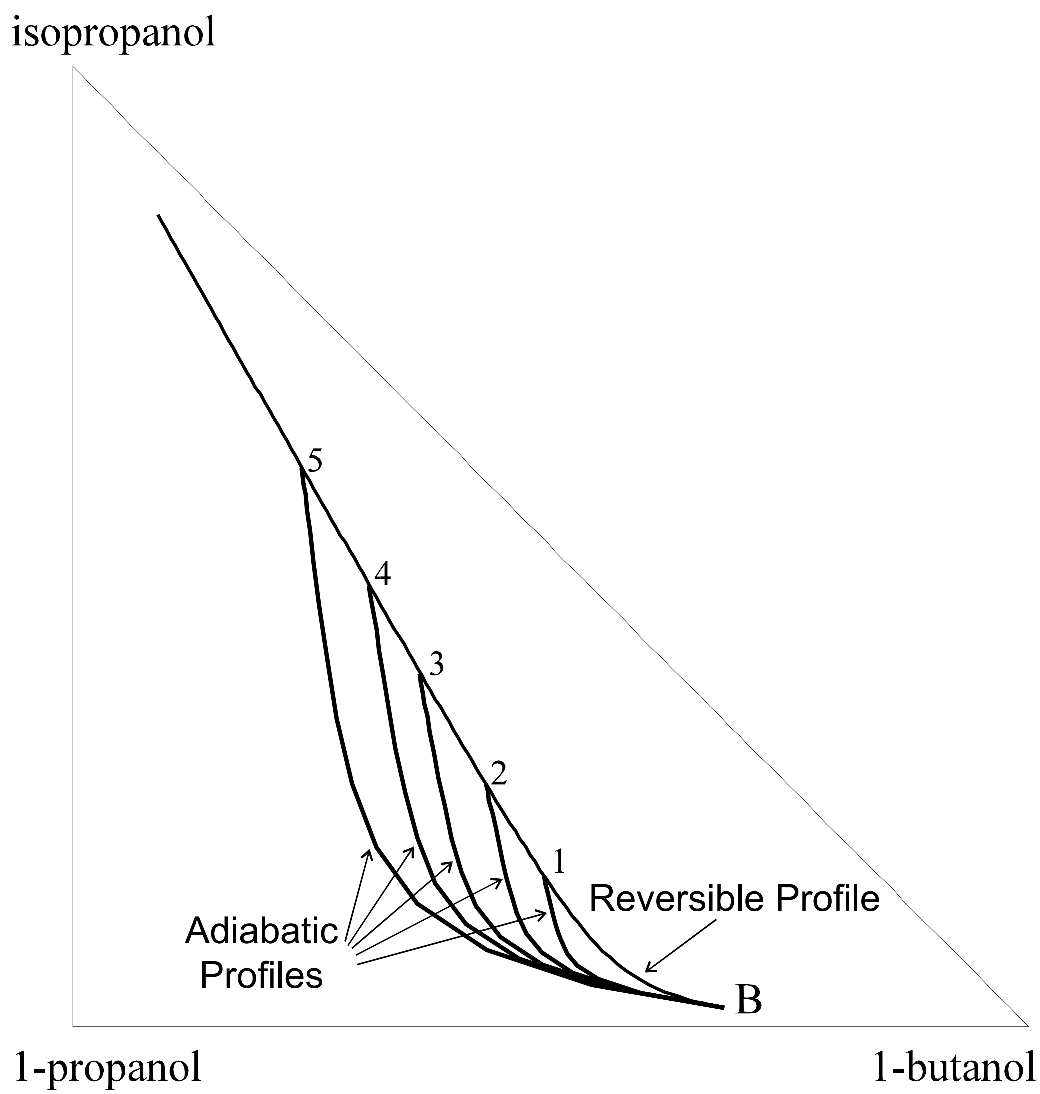
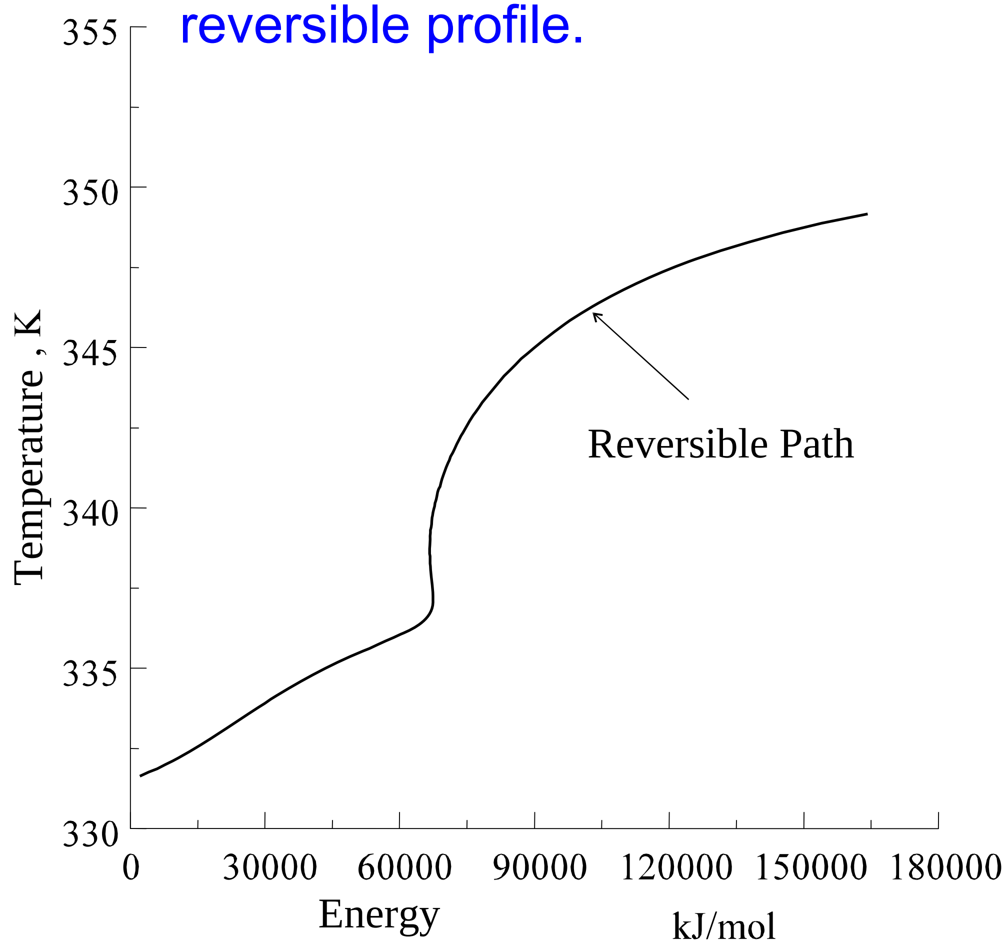
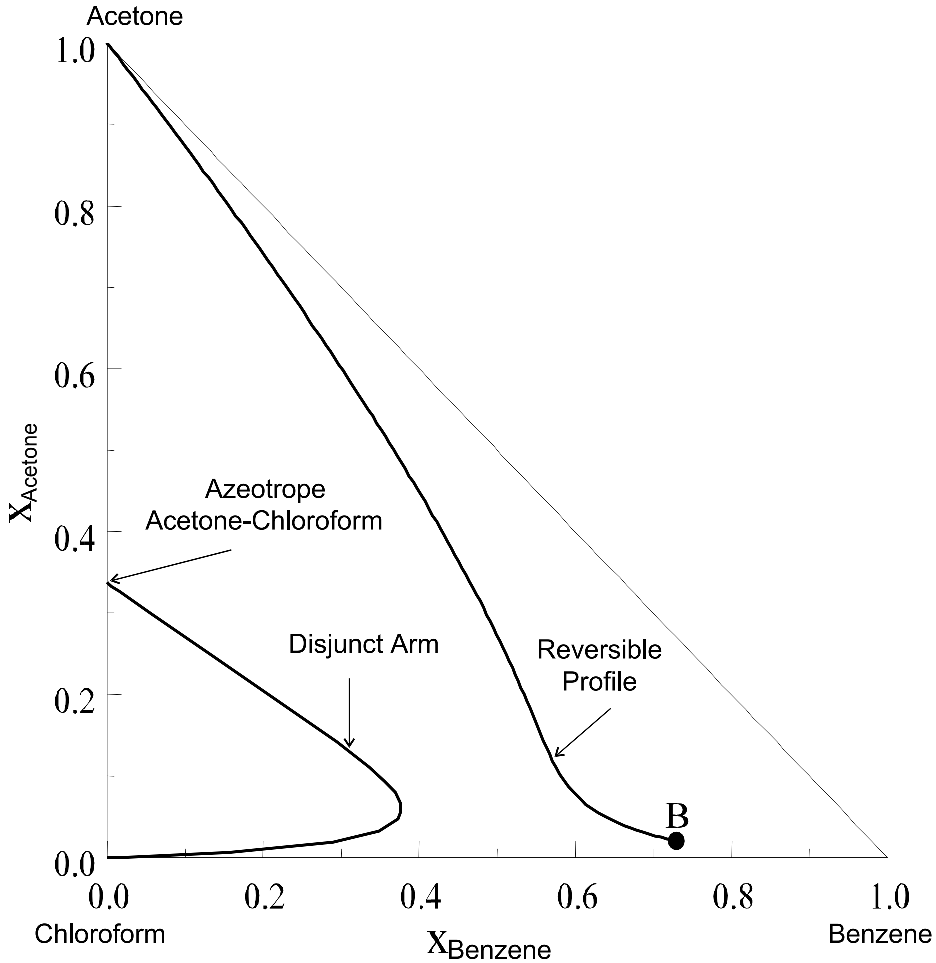
Reversible path for a bottom: distillative alcoholic mixture.



Reversible path for a bottom: distillative alcoholic mixture.

Starting from product D (T_D) and increasing reboil ratio, the profile is computed. Temperature and Energy results from the reversible profile.





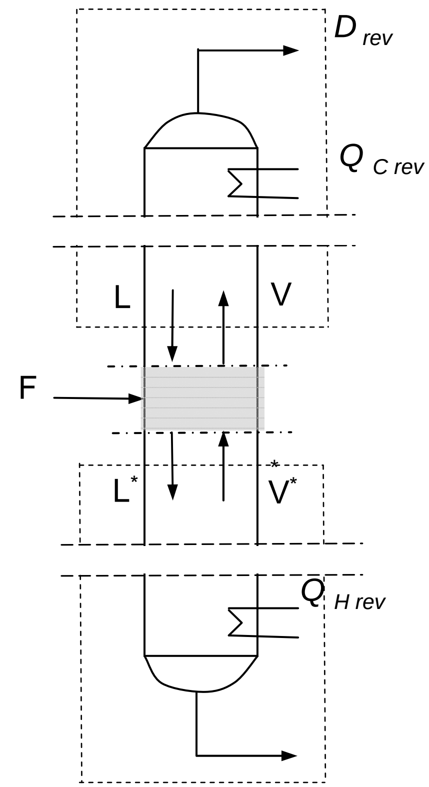
Reversible path for a bottom (B): azeotropic system.

Points computed with newton homotopy.

3.- Reversible distillation columns and sequences.

Specifying:
1) Feed composition,
2) product compositions B and D satisfying total mass balance,
2) reboil and reflux ratios satisfying total energy balance,
3) equilibrium between L* and V* and between L and V,

liquid composition profiles can be computed.



PINCH CURVES, PINCH PATHS, REVERSIBLE PROFILES, REVERSIBLE PATHS, ETC.

NO ASSUMPTION ON V-L EQUILIBRIUM AND ON ENTHALPY MODELS

3.- Reversible distillation columns and sequences.

PINCH EQUATIONS

$$y_{i,s} = K_{i,s} x_{i,s}$$ Equilibrium

Mass balances

$$L_s \; x_{i,s} + D \; x_{i,D} = V_s \; y_{i,s}$$

$$L_s + D = V_s$$

Energy balance

$$L_s \; h_{L,s} + D \; h_D + Q_D = V_s \; h_{V,s}$$

Given:
X_D, Y_D, P, T_D and Q_D
at least one liquid composition can be computed: $\underline{X}_{,s}$
$s \in S$: set of different kinds of pinches.

NO ASSUMPTION ON V-L EQUILIBRIUM AND ON ENTHALPY MODELS

$$K_i = K_i \,(x_{i,s}, y_{i,s}, T_s, p_s)$$

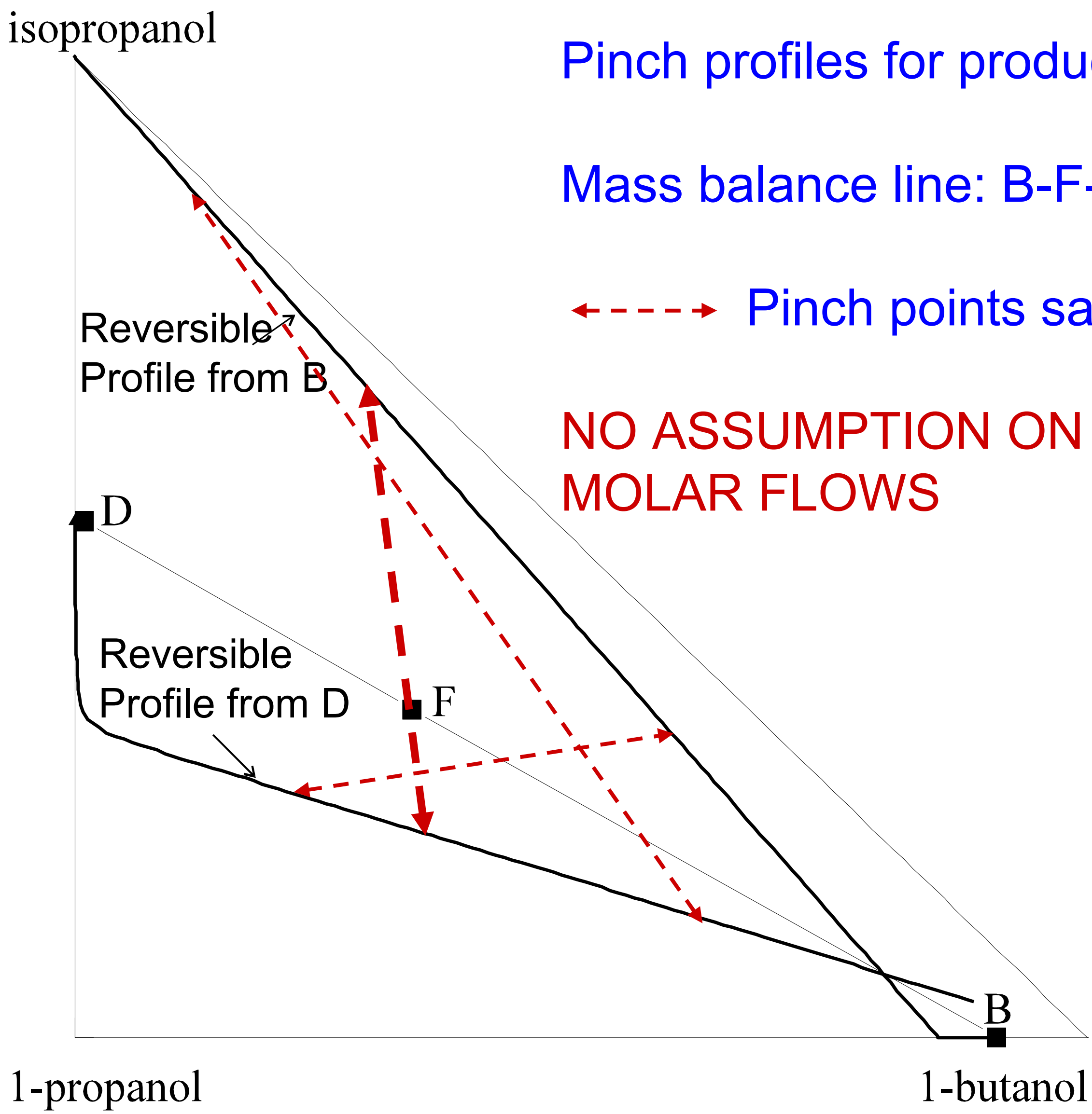
$$h_{L,s} = h_{L,s} \,(x_{i,s}, T_s, p_s)$$

$$h_V = h_V \,(y_{i,s}, T_s, p_s)$$

$$p_s = p_C$$ Constant pressure

Thermodynamic Properties

3.- Reversible distillation columns and sequences.



Pinch profiles for products B and D.

Mass balance line: B-F-D

Pinch points satisfying total energy balance.

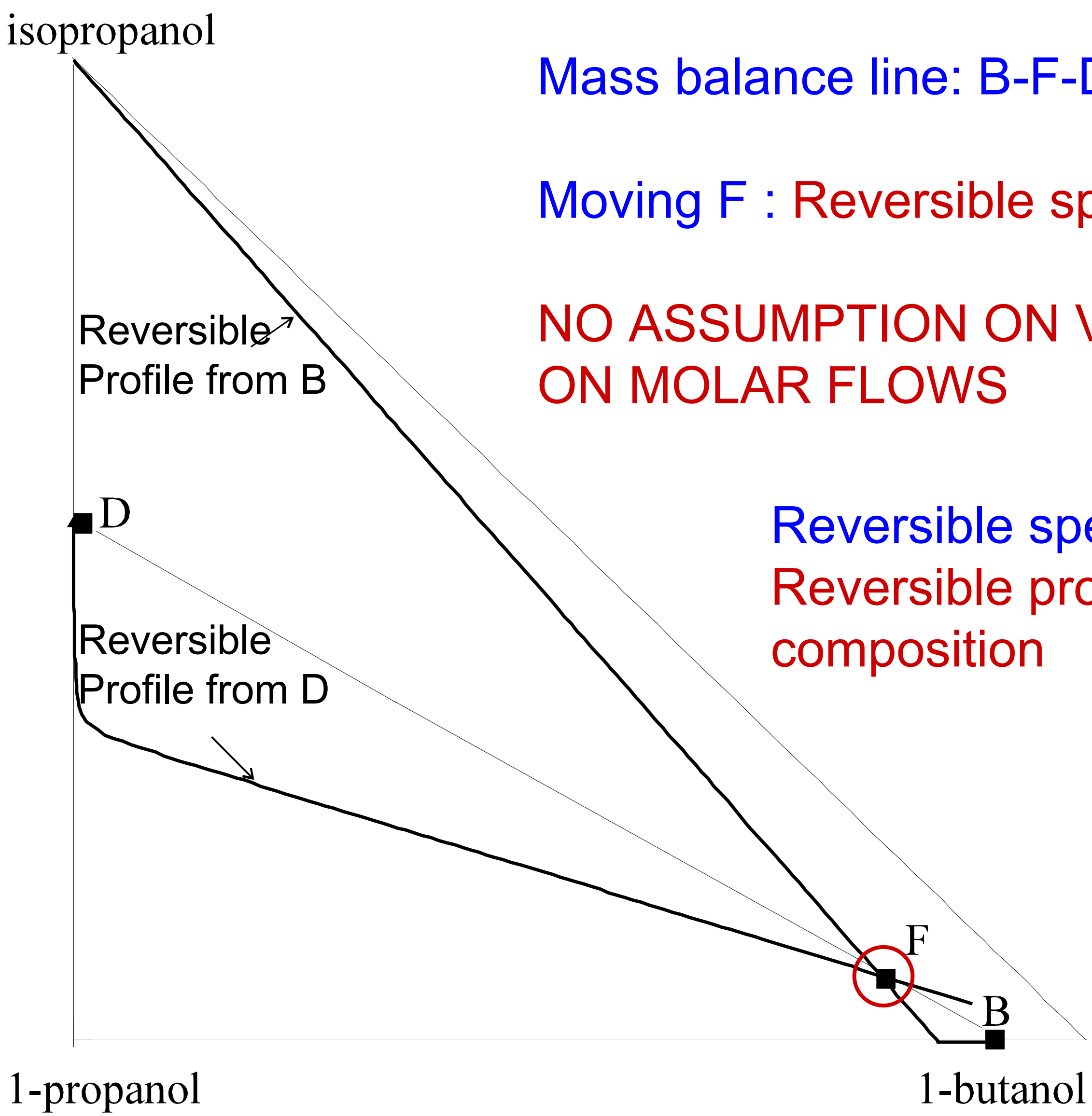
NO ASSUMPTION ON V-L EQUILIBRIUM AND ON MOLAR FLOWS

Pinch profiles for products B and D.

Mass balance line: B-F-D

Moving F : Reversible specification

NO ASSUMPTION ON V-L EQUILIBRIUM AND ON MOLAR FLOWS



Reversible specification
Reversible profiles intersect at feed composition

Pinch profiles for products B and D.
Sharp splits.
Adiabatic profiles and pinch profiles.

Pinch points → critical points for the adiabatic profiles

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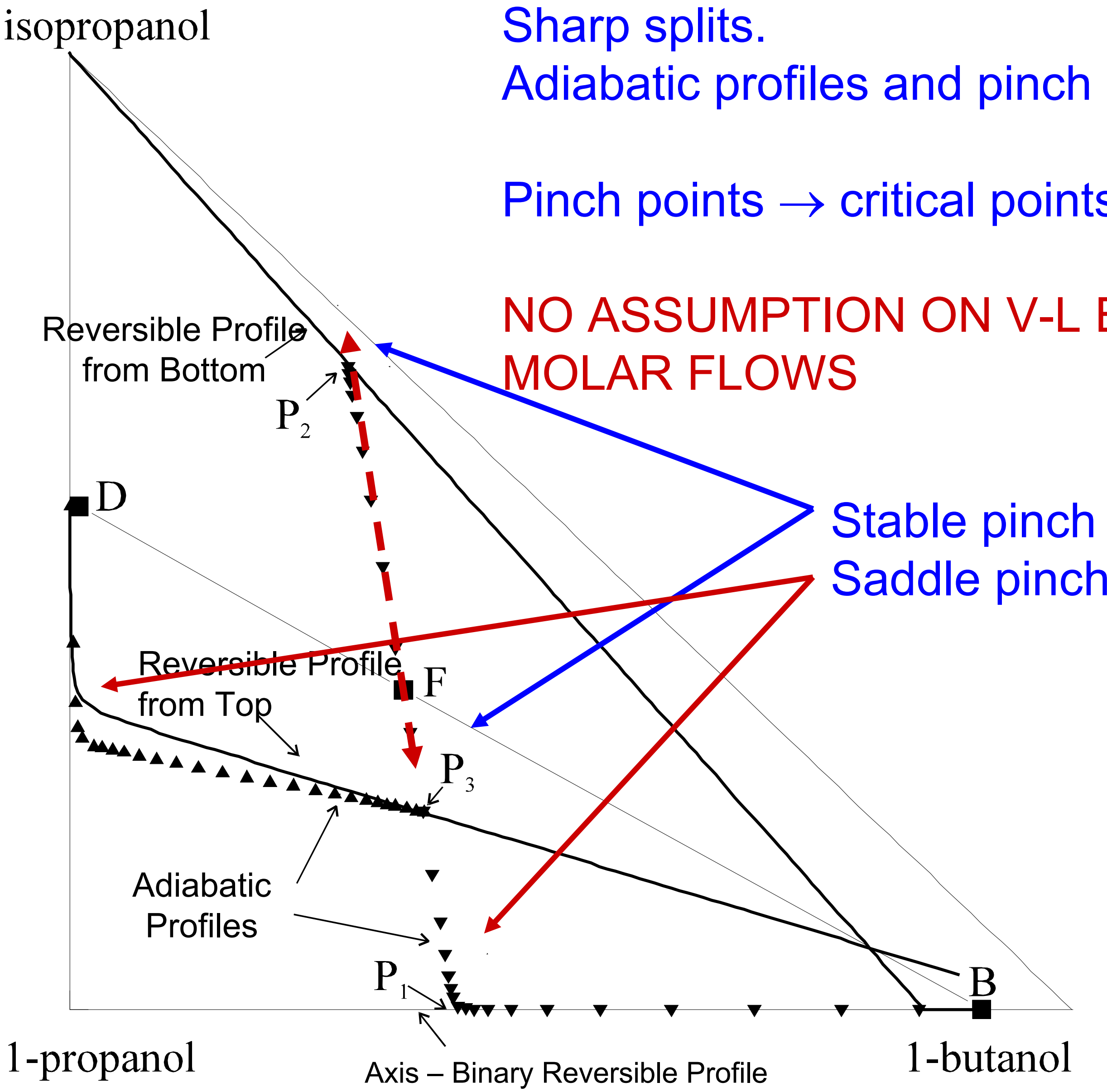

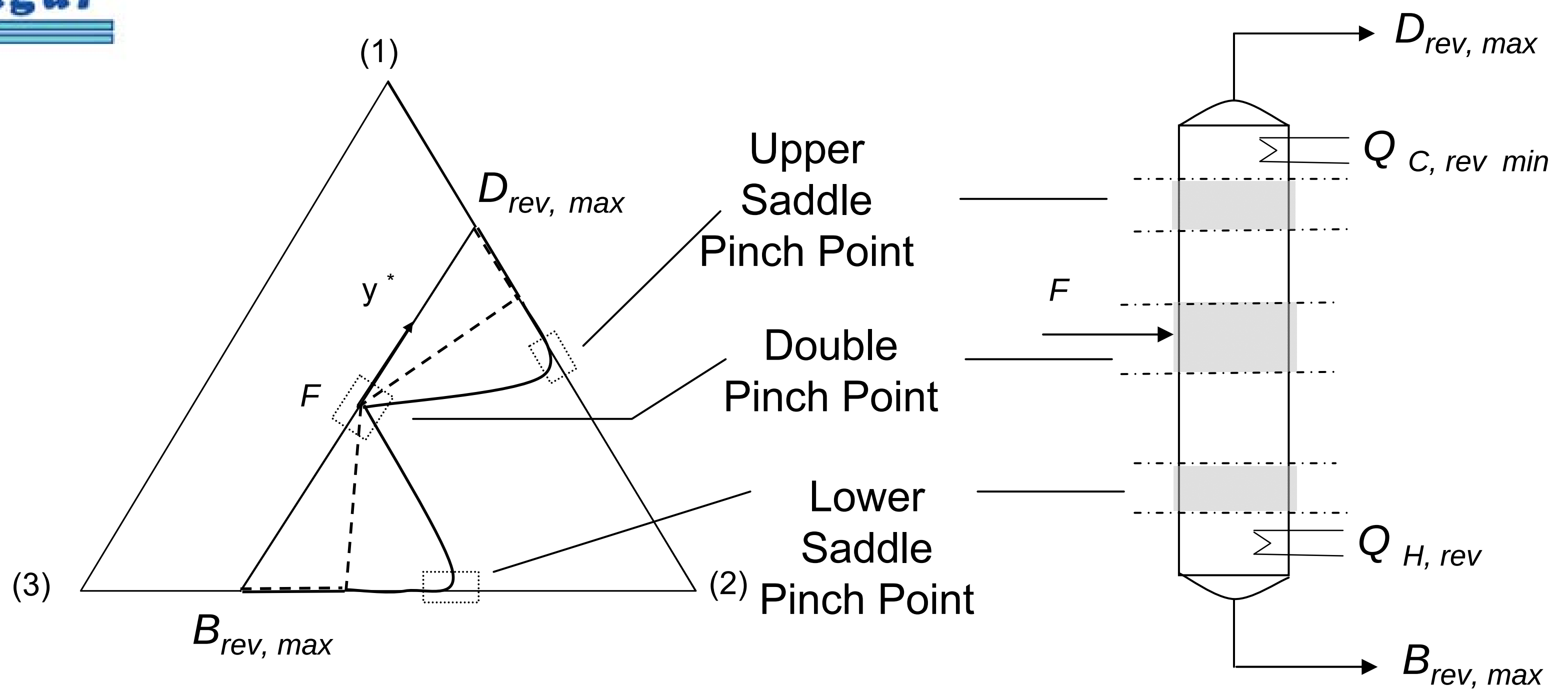

Reversible Distillation. (Sharp).

For each feed composition, there exists a special, “preferred” specification.

V-L equilibrium vector (Y*-X*) belongs to Mass balance line: D-F-B.

NO ASSUMPTION ON V-L EQUILIBRIUM AND ON MOLAR FLOWS

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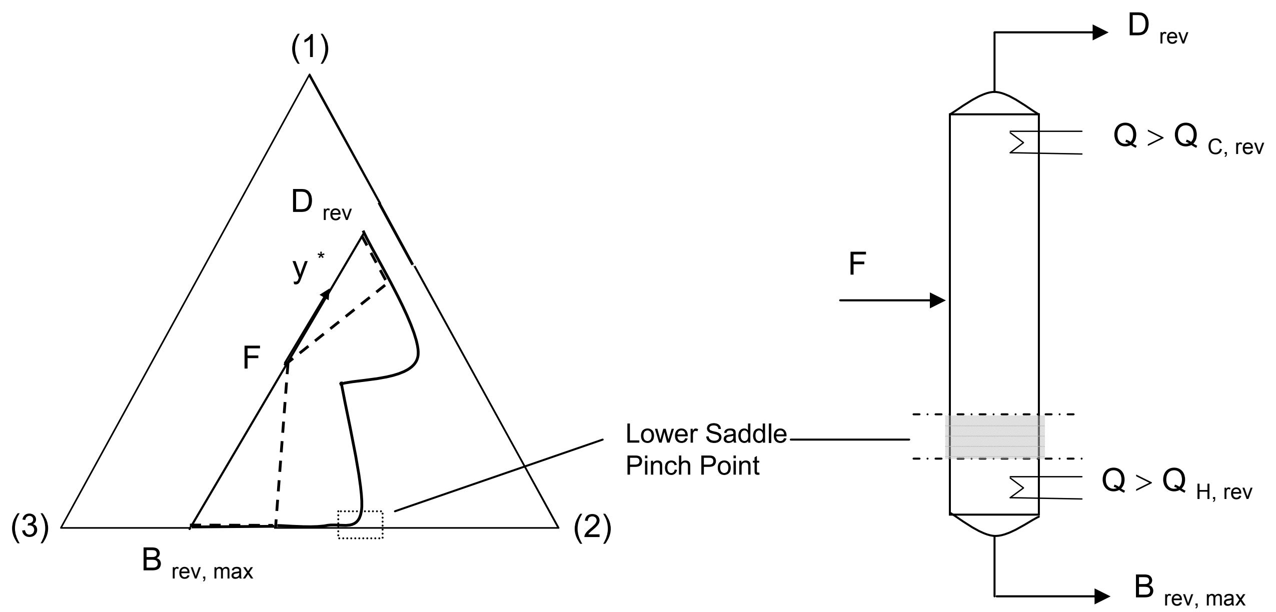
Reversible distillation.

For each feed composition, there exists a special “preferred” product specification set.

Other product specifications ⇒ Non reversible distillation (1 col.)

Are pinch points always “observable” in adiabatic columns profiles?

It depends on feed and product specification and on RR. Non sharp in this figure.



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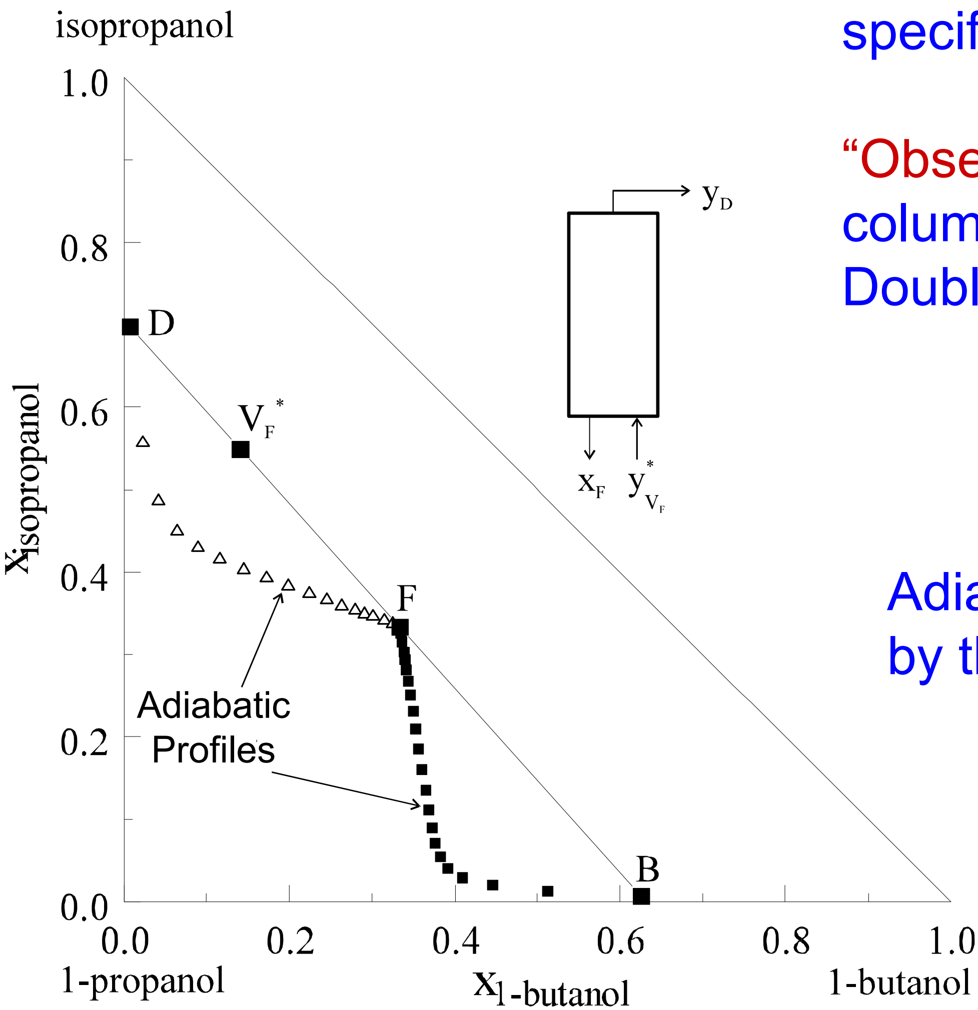
Reversible distillation.

(Y* - X*) □ B-F-D ⇒ Reversible specification

"Observable" pinch in adiabatic column.

Double feed pinch.



Adiabatic profile shape is determined by the pinch point.

Non Reversible distillation.

(X* - Y*) ⊄ B-F-D

Pinch topology.

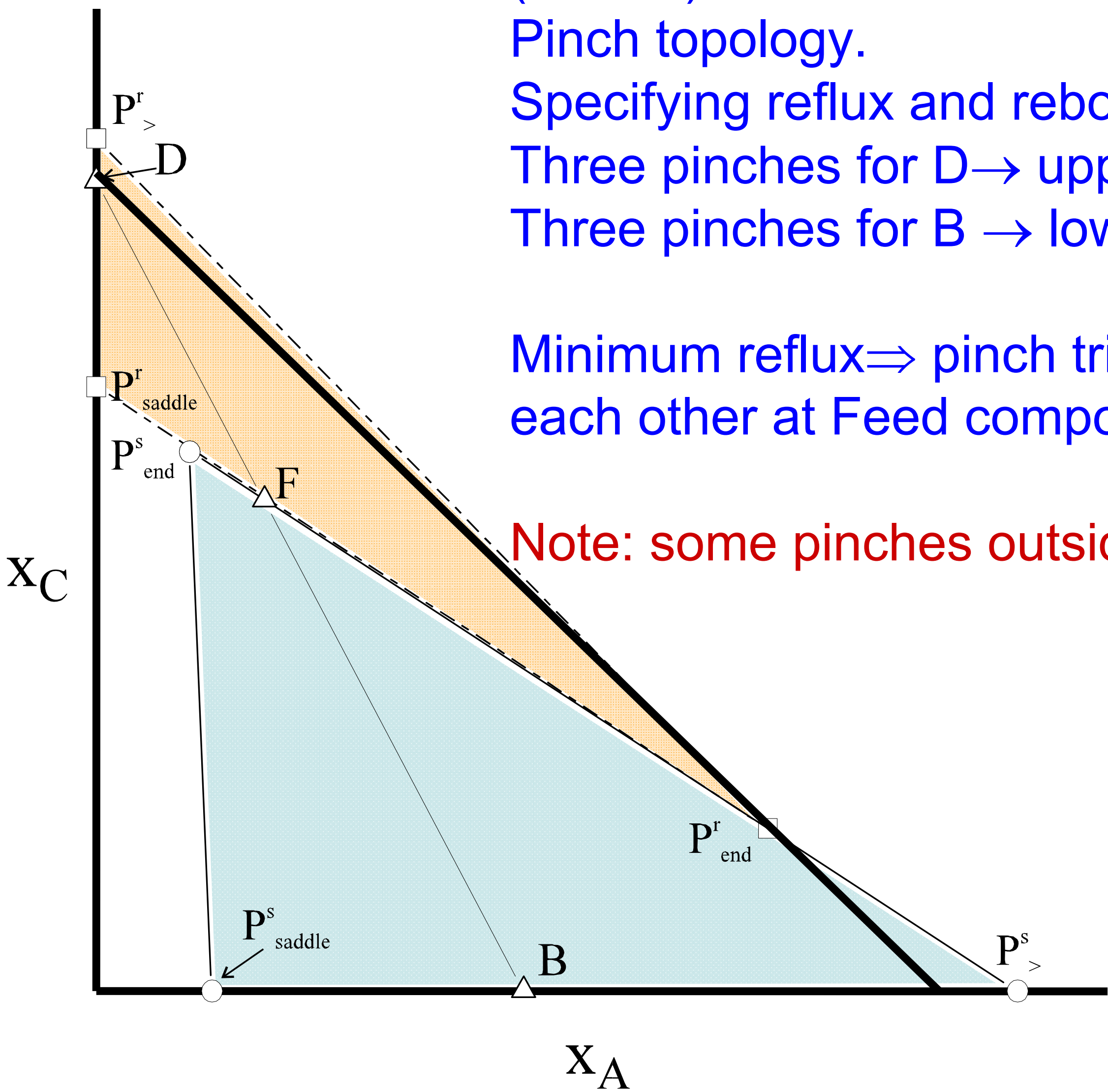
Specifying reflux and reboil ratios

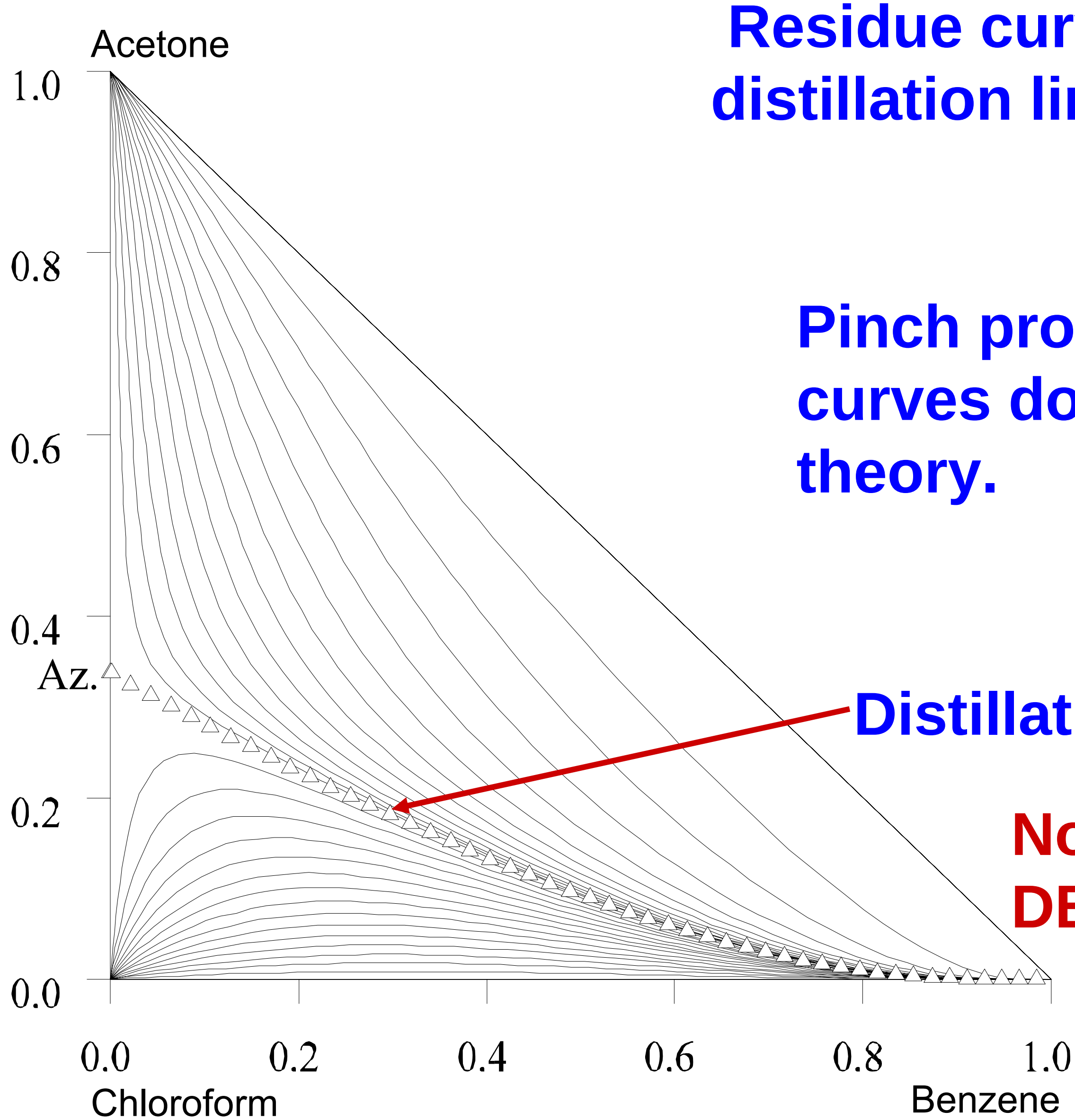
Three pinches for D→ upper triangle

Three pinches for B → lower triangle

Minimum reflux⇒ pinch triangles touch each other at Feed composition

Note: some pinches outside: x_b<0





Residue curves distillation lines

Pinch profiles and Residue curves dominate distillation theory.

Distillation boundary (DB)

Not possible to cross DB at total reflux

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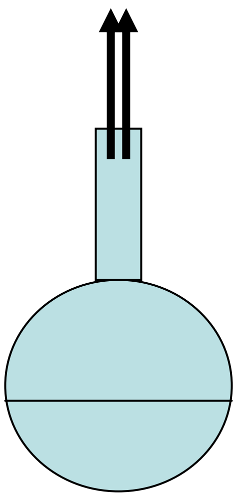
Residue curves

$$\frac{d(V\,x_i)}{dt} = -F_{Vap}\,y_i$$

$$\frac{dV}{dt} = -F_{Vap}$$

$$K_i\,x_i = y_i$$

F_{vap}; $\underline{Y}$; T; P



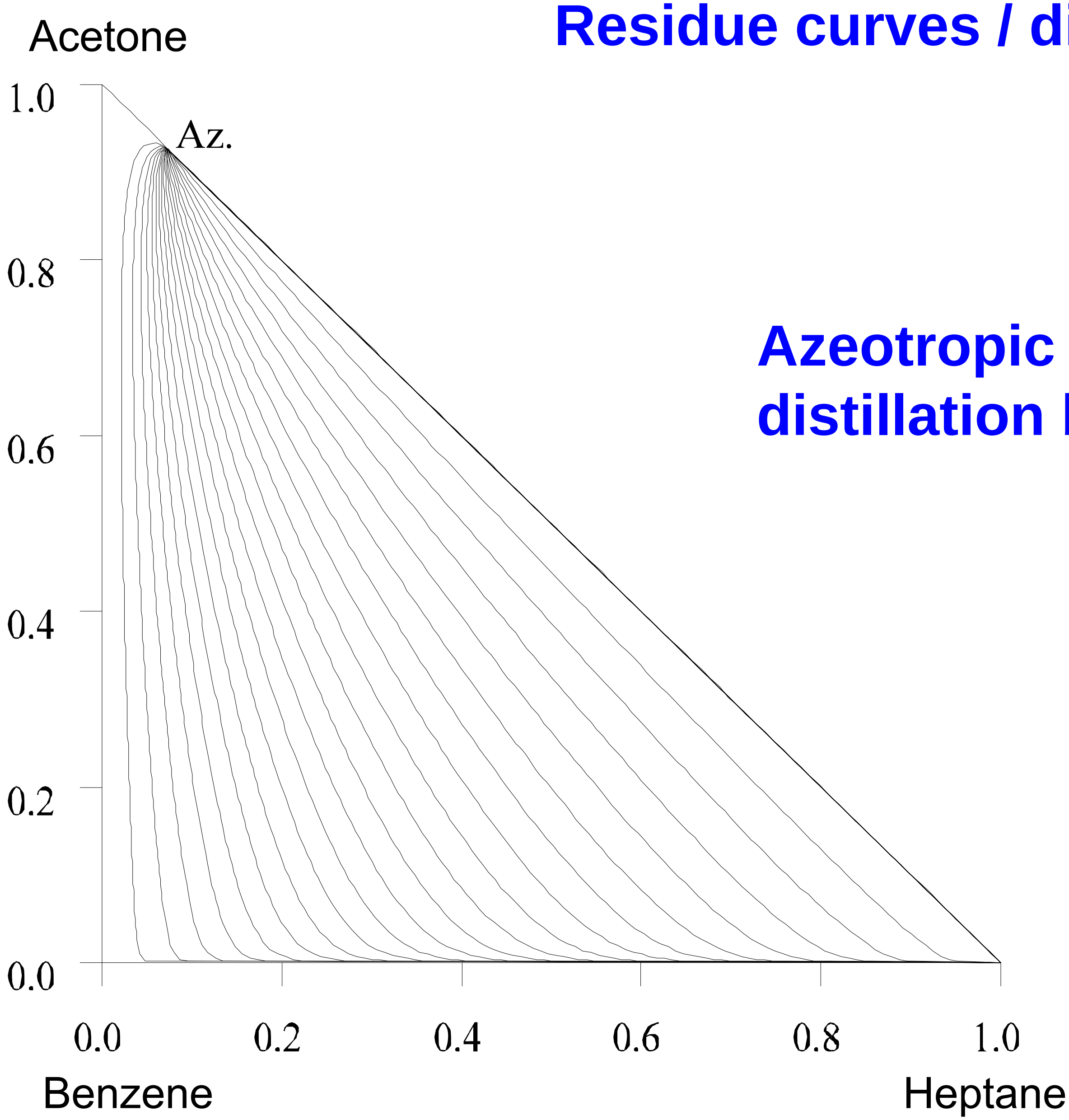
V; $\underline{X}$; T; P

$$V\frac{d\,x_i}{dt} = -F_{Vap}(y_i - x_i)$$

$$\frac{dV}{dt} = -F_{Vap}$$

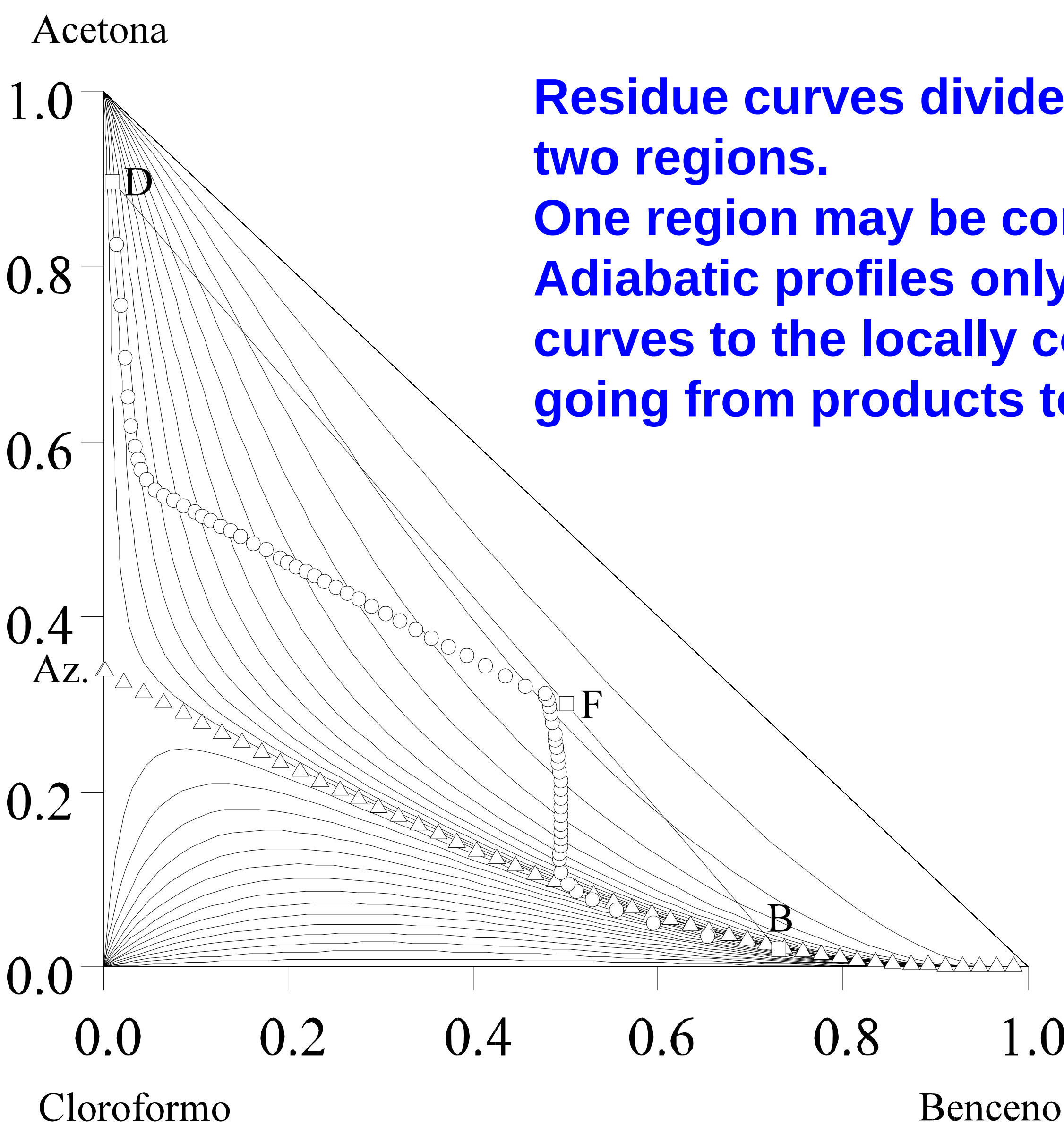
$$K_i\,x_i = y_i$$

Residue curves / distillation lines



Azeotropic system with no distillation boundary

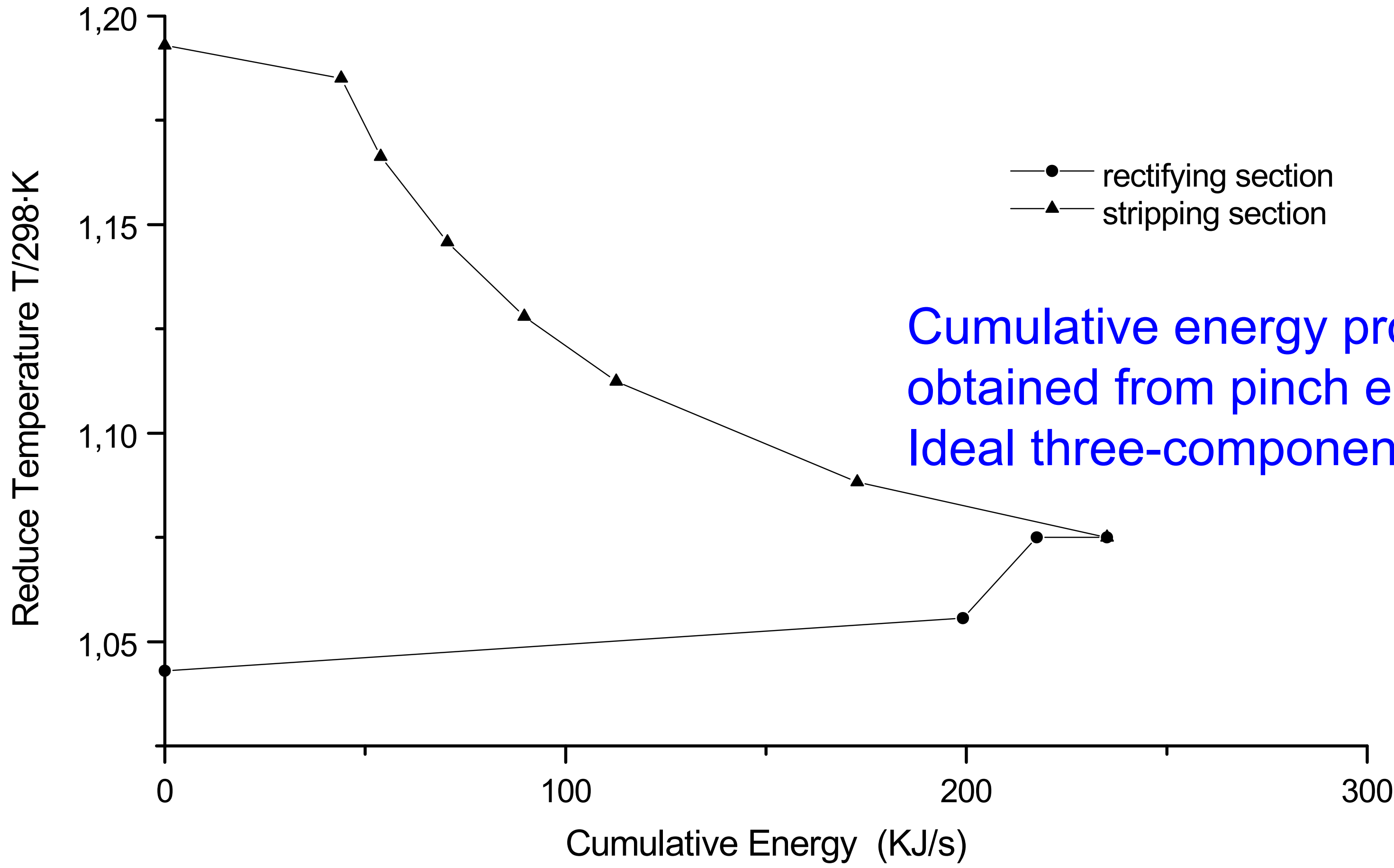
Ternary systems



Residue curves divide the simplex in two regions.
One region may be convex.
Adiabatic profiles only cross residue curves to the locally convex side when going from products to feed.

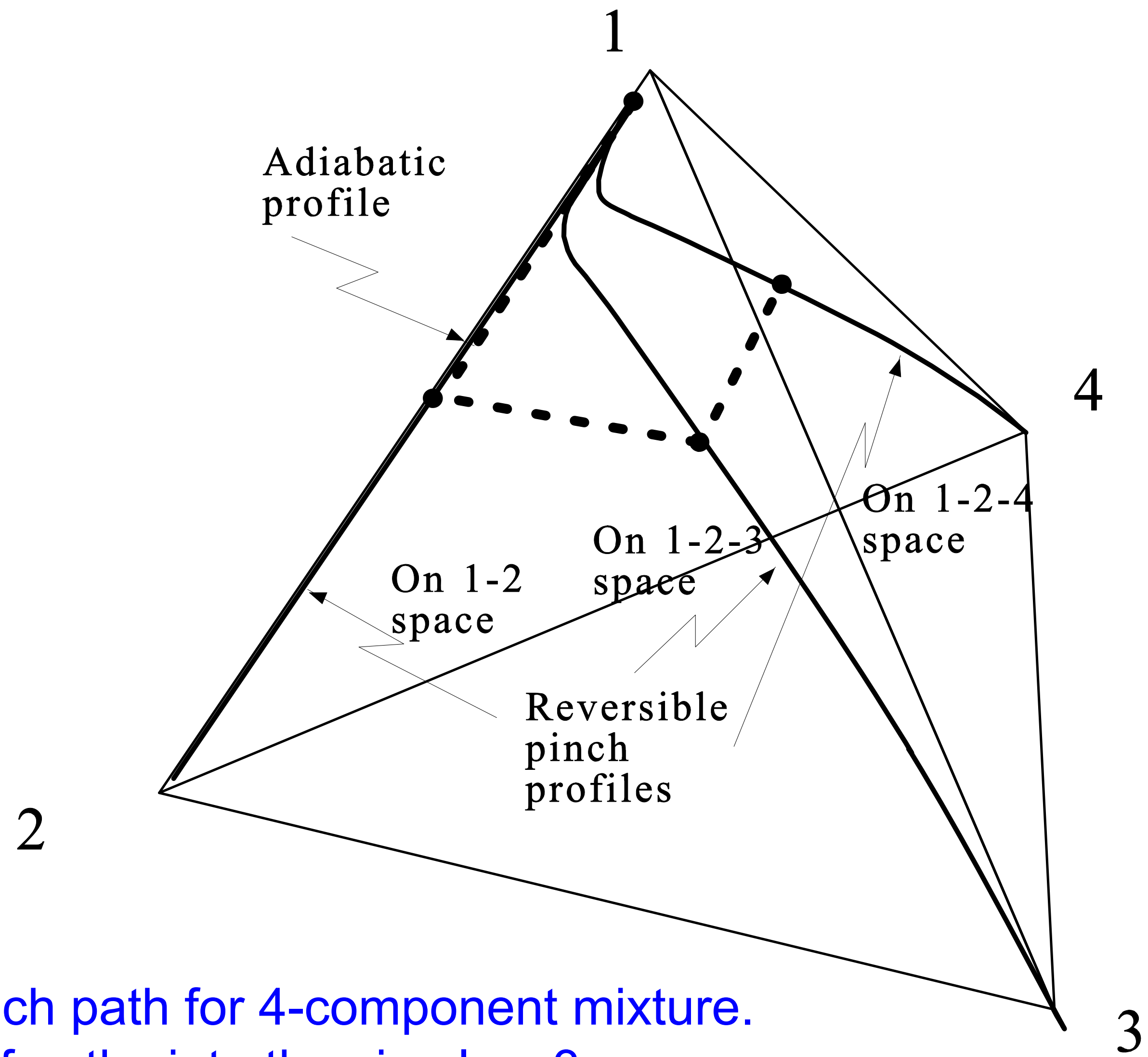
Improving energy distribution in Simple columns.

Temperature – Energy Pinch profiles



Cumulative energy profiles obtained from pinch equations. Ideal three-component mixture

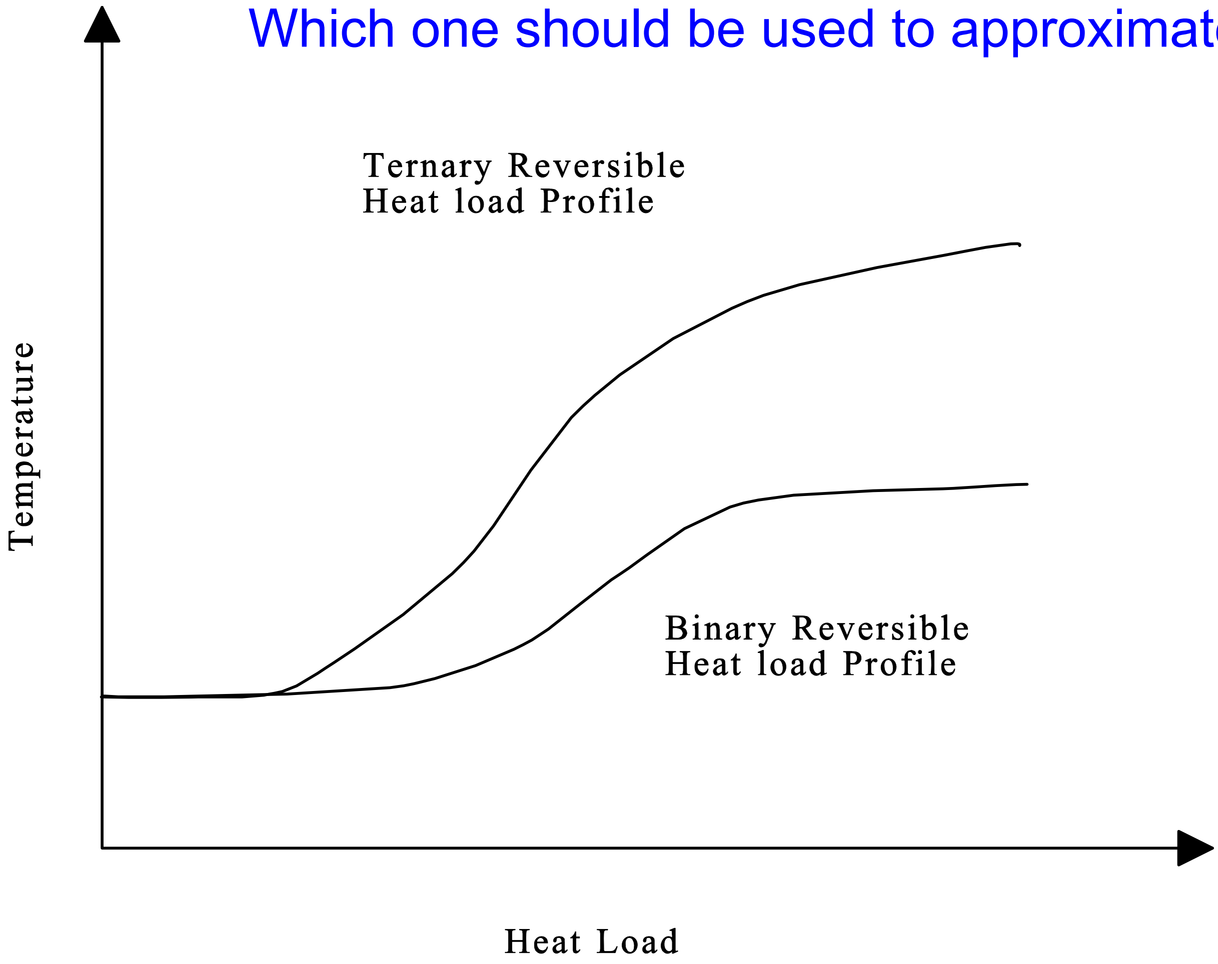
Improving energy distribution in simple columns.



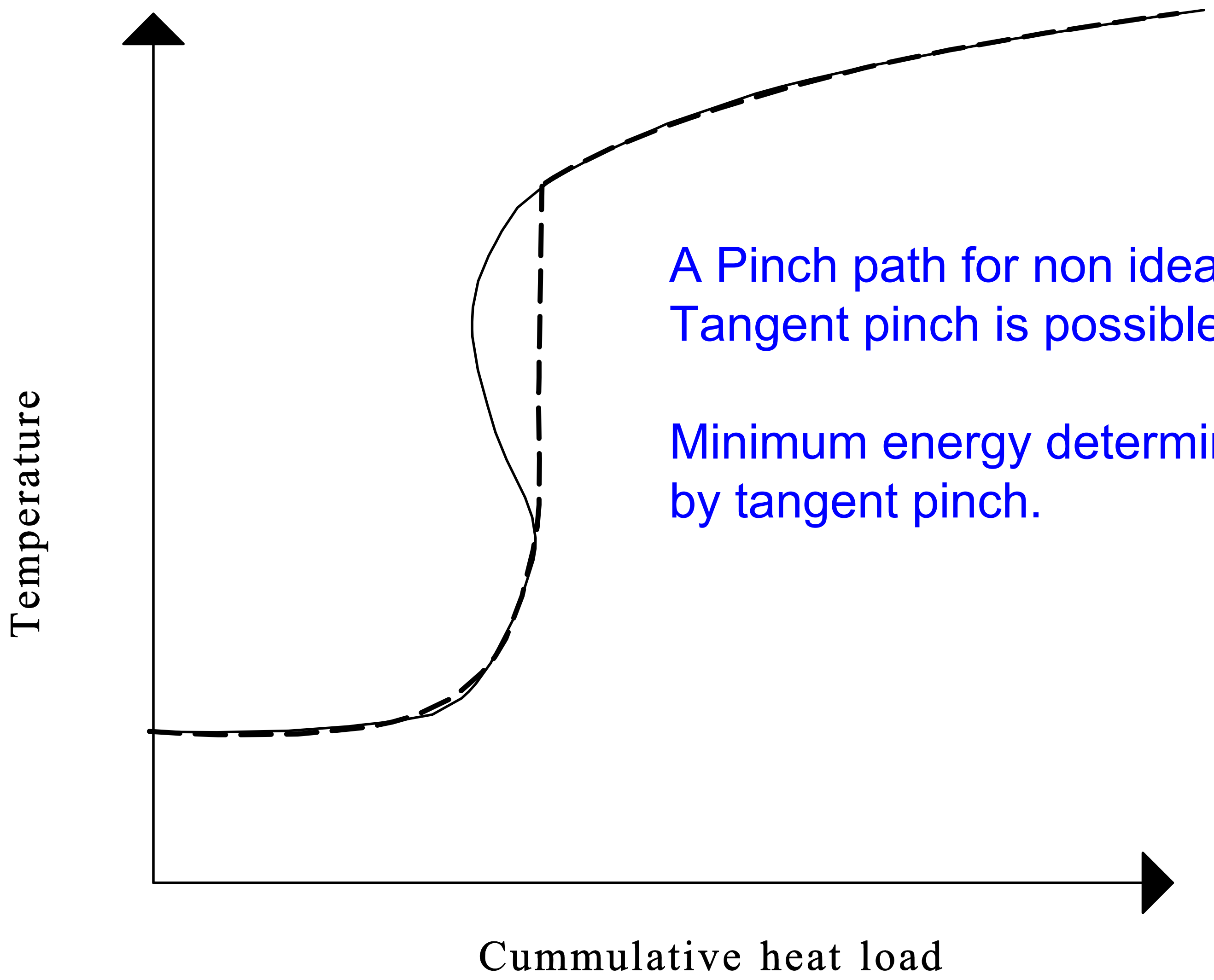
Pinch path for 4-component mixture.
# of paths into the simplex: 3

Improving energy distribution in simple columns.

Pinch path for 3-component mixture.
# of paths into the simplex: 2
Which one should be used to approximate reversible profiles?



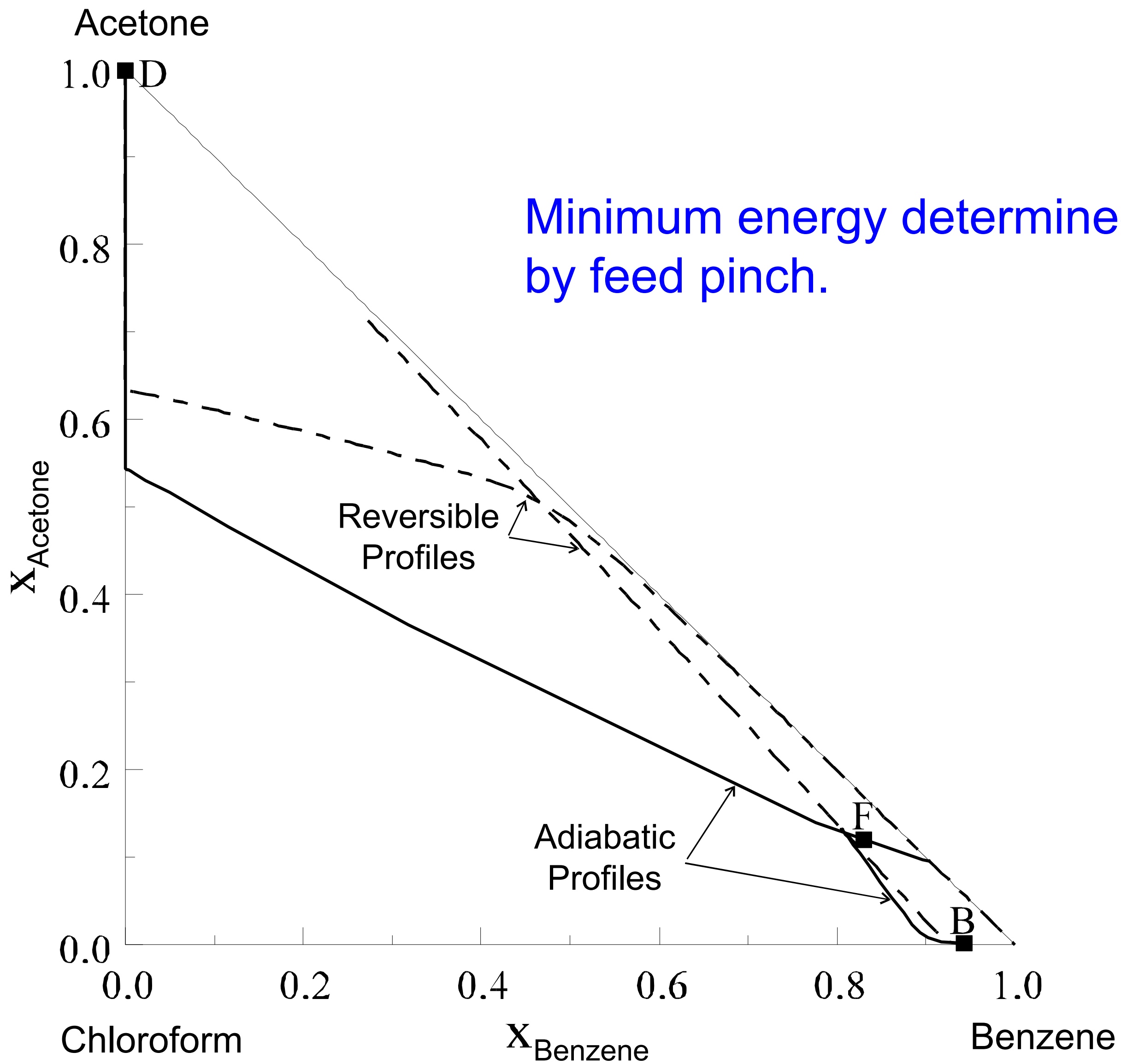
Improving energy distribution in simple columns.



A Pinch path for non ideal mixture.
Tangent pinch is possible.

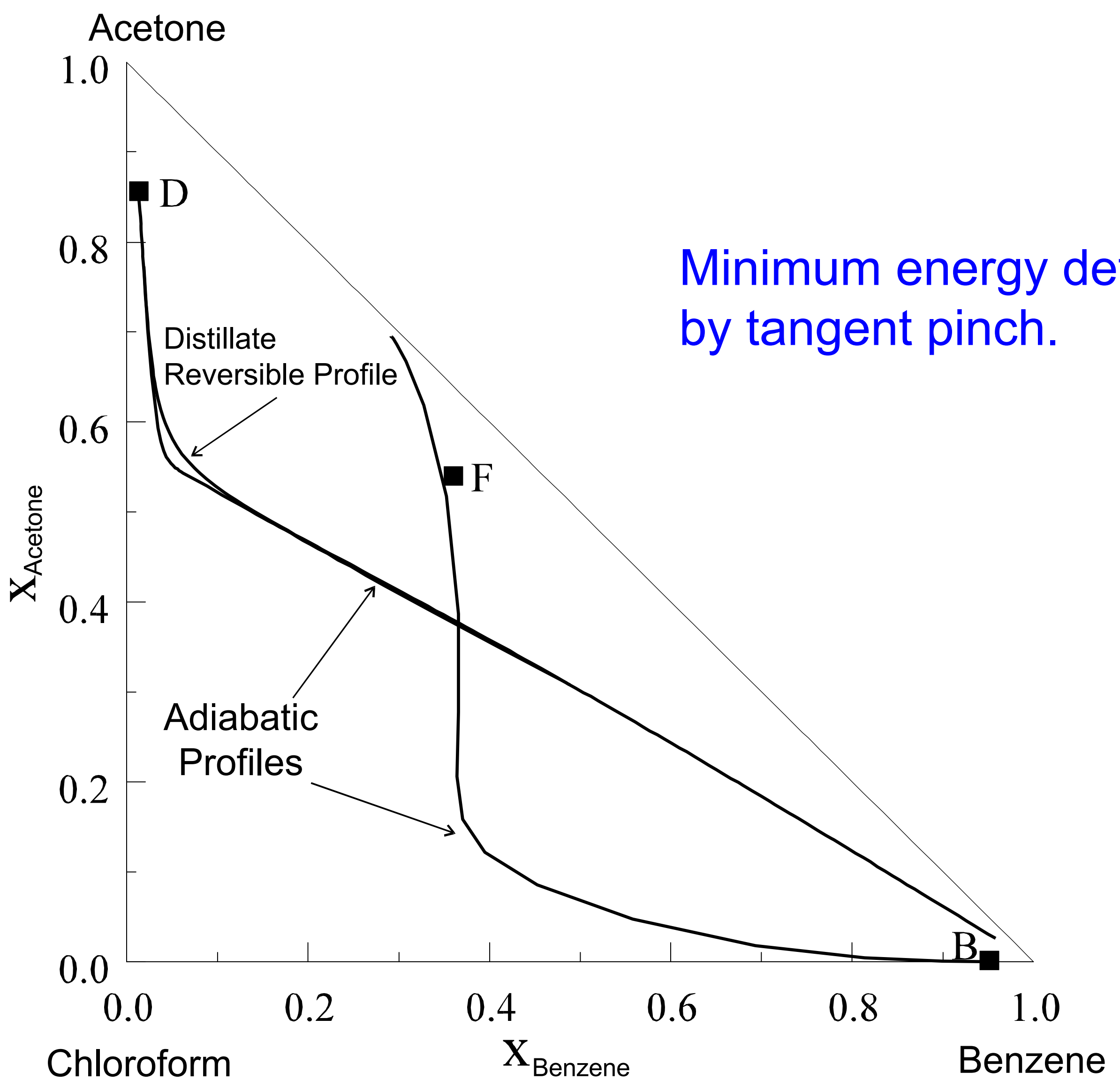
Minimum energy determined
by tangent pinch.

Improving energy distribution in simple columns.



Minimum energy determined by feed pinch.

Improving energy distribution in simple columns.

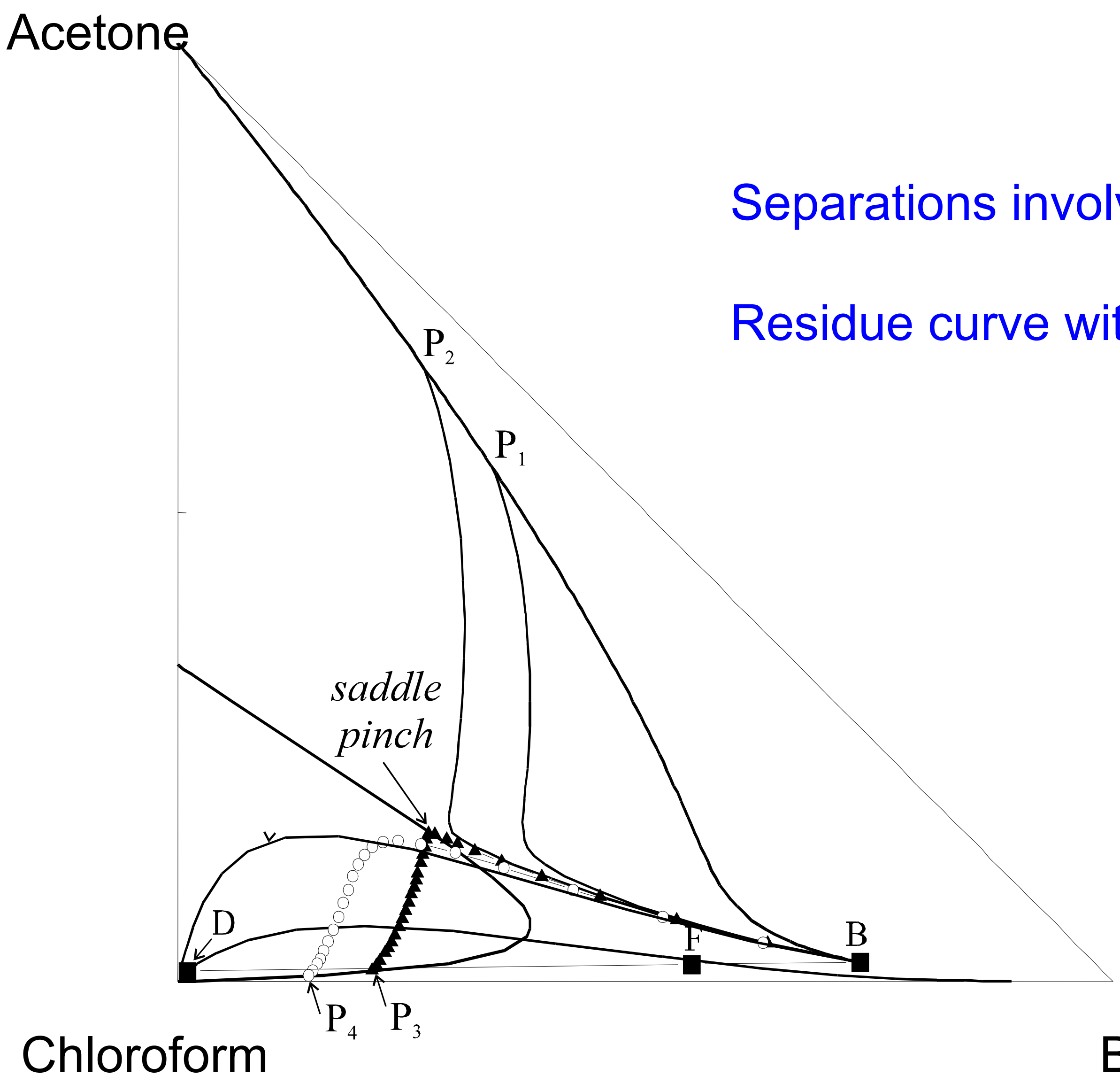


Minimum energy determined by tangent pinch.

Improving energy distribution in simple columns.

Separations involving tangent pinch.

Residue curve with inflexion points.



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Reversible Distillation Sequence Model (RDSM)

What is the **superstructure** that most closely approximates the Reversible Distillation of Multicomponent Mixtures like?

Which is the optimal **energy distribution** in the RDSM-based sequence?

A Reversible Column

Theoretical model.

Infinite number of stages.

Continuous heat distribution along column length.

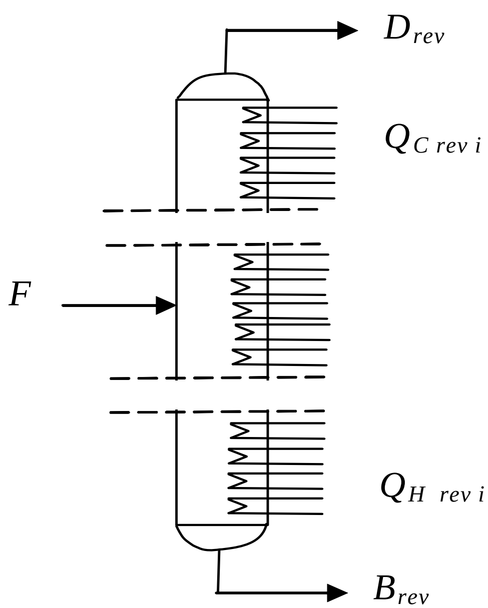
Heat to and from the column is transferred at zero temperature difference.

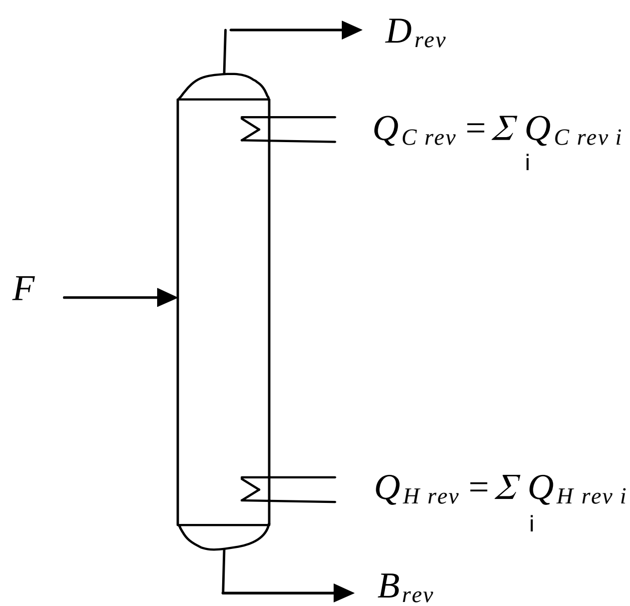
No contact of non-equilibrium streams take place in any point of the column.

Only one separation task can be performed: **the reversible separation**.

RDC Adiabatic Approach

A sufficiently high number of stages must be employed.
The same energy is involved in the separation with a different distribution.
The same products are achieved but different composition profiles develop within each unit.





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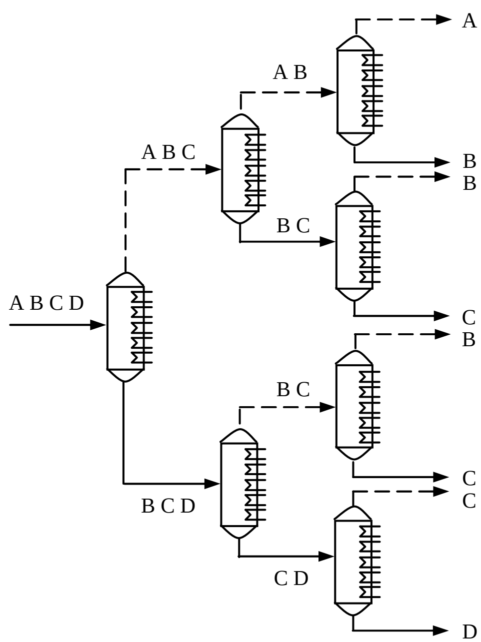
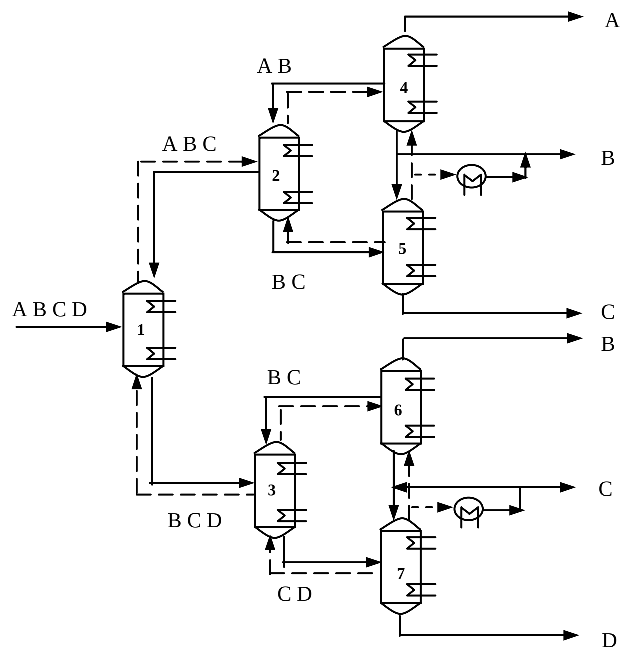
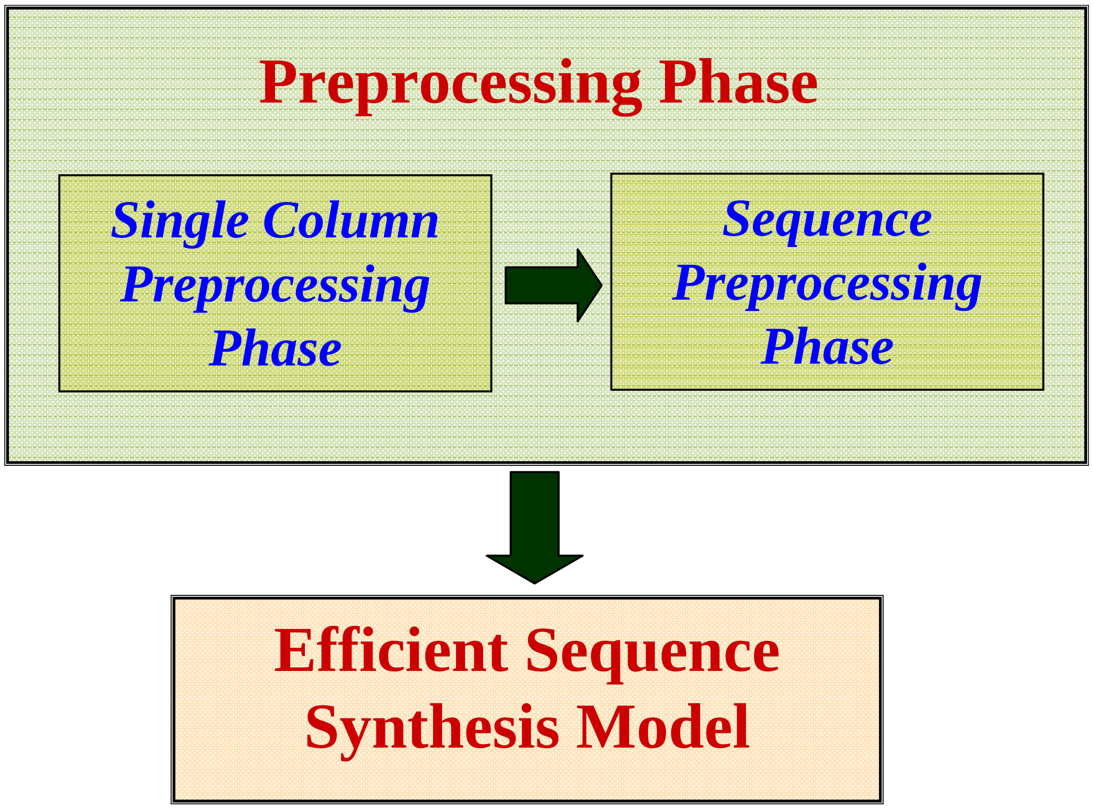
RDSM Sequence



RDSM-based Sequence



RDSM-based Synthesis Model



Preprocessing Phase

Single Column Preprocessing

Adiabatic Approximation to the Reversible Separation

- ✓ Values to **initializate** variables.
- ✓ Values to **bound** critical variables related to unit interconnection and heat loads.
- ✓ Parameters to **formulate** objective functions.

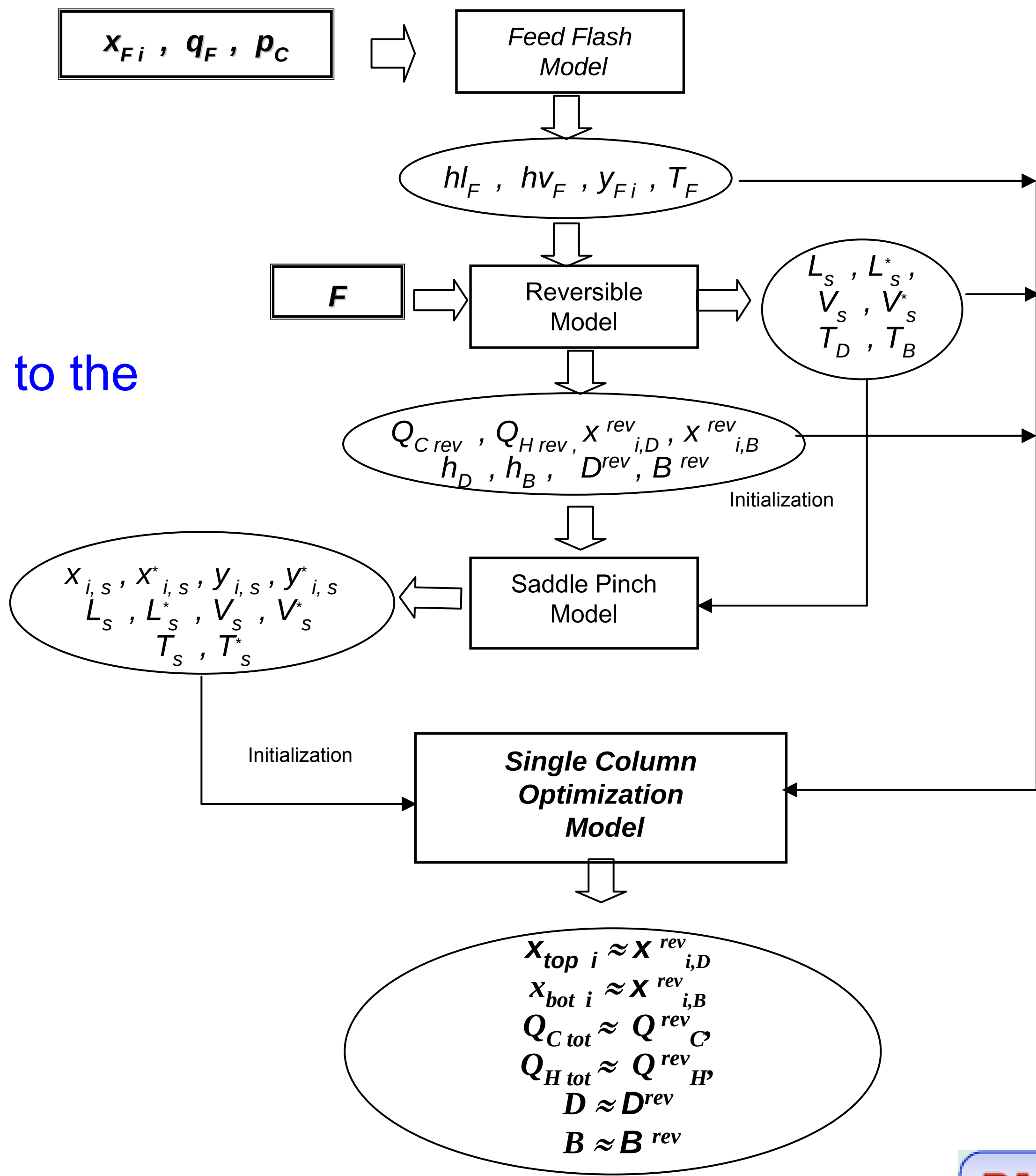
Sequence Preprocessing

Reversible Products, Saddle Pinch Points and Reversible Exhausting Pinch Points Calculations

- ✓ Optimal Energy Distribution for each single unit.
- ✓ **Number of stages** for each single column of the sequence.
- ✓ Objective functions and constraints to approach the reversible separation task.

Single Column Preprocessing

Adiabatic Approximation to the Reversible Separation



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(RM):

$$\min \quad z = x^{rev}_{c,D} + x^{rev}_{a,B}$$

$$L + (1 - q_F) F = L^*$$

$$V + q_F F = V^*$$

Known values from flash calculations at Feed

$$L + D^{rev} = V$$

$$L^* = V^* + B^{rev}$$

$$L x_i + D^{rev} x^{rev}_{i,D} = V y_i$$

$$L^* x_i = V^* y_i + B^{rev} x^{rev}_{i,B}$$

$$L h_L + D^{rev} h_D + Q^{rev}_C = V h_V$$

$$L^* h_L + Q^{rev}_H = V^* h_V + B^{rev} h_B$$

Single Column Preprocessing

$$K_i = K_i (x_i, y_i, T, p) \quad i = 1, \ldots NC$$

$$h_L = h_L'(x_i, T, p)$$

$$h_V = h_V(y_i, T, p)$$

Adiabatic Approximation to the Reversible Separation

(SPM):

Known values from
flash calculations at Feed

$$x_{NC,s} = 0 \qquad y_{NC,s} = 0$$

$$L_s + D^{rev} = V_s$$

$$L_s \; x_{i,s} + D^{rev} \; x^{rev}_{i,D} = V_s \; y_{i,s}$$

$$L_s \; h_{L,s} + D^{rev} \; h_D + Q_C^{rev} = V_s \; h_{i,s}$$

$$x^*_{1,s} = 0 \qquad y^*_{1,s} = 0$$

$$L_s^* = V_s^* + B^{rev}$$

$$L_s^* \, x_{i,s} = V_s^* \, y_{i,s} + B^{rev} \; x^{rev}_{i,B}$$

$$L_s^* \, h^*_{L,s} + Q_H^{rev} = V_s^* \, h^*_{V,s} + B^{rev} \; h_B$$

Single Column Preprocessing

Adiabatic Approximation to the Reversible Separation

$$K_i = K_i \; (x_i, y_i, T, p) \quad i = 1, \ldots NC$$

$$h_L = h_L'(x_i, T, p)$$

$$h_V = h_V(y_i, T, p)$$

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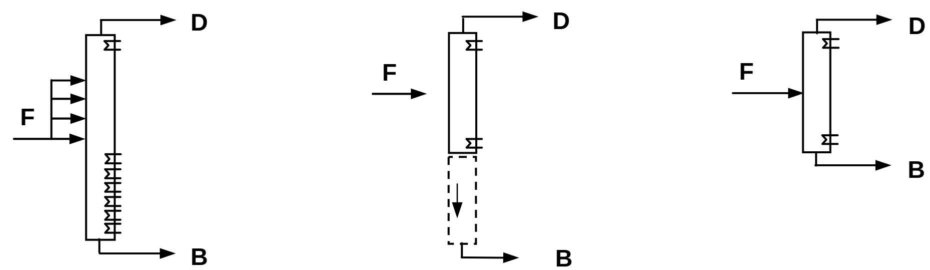
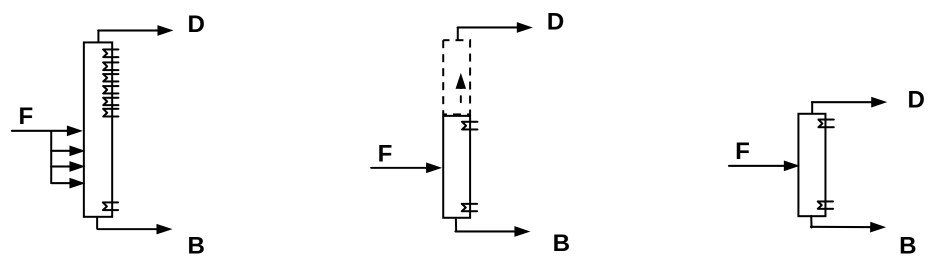
The number of trays is selected by optimizing the condenser, reboiler and/or feed stream locations.

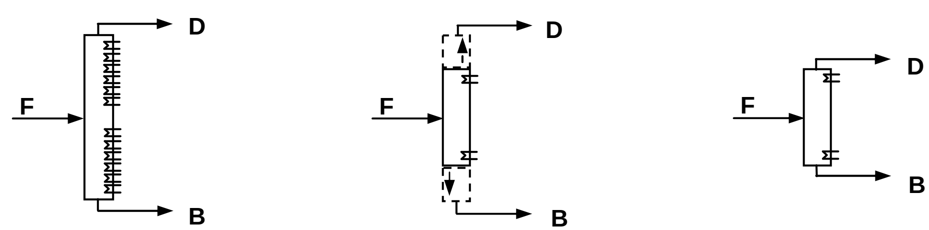
Variable feed and reboiler location



Variable feed and condenser location

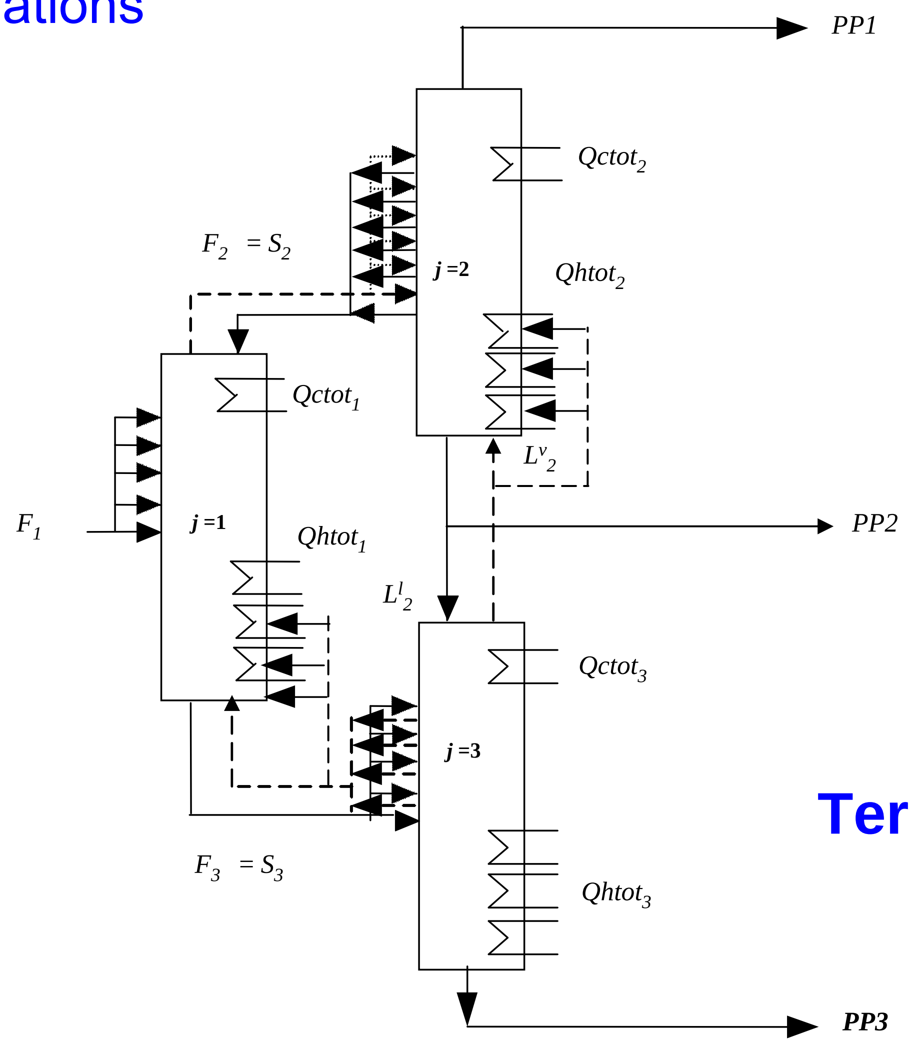


Variable condenser and reboiler location

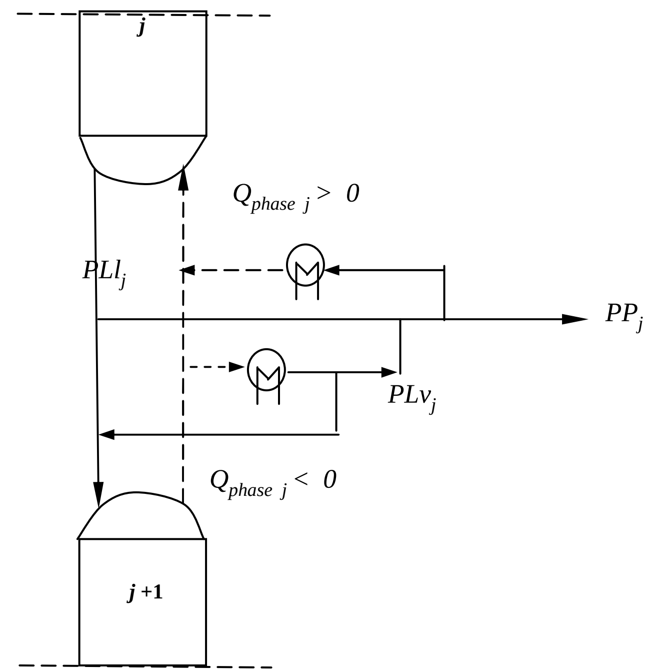


Sequence Preprocessing

Reversible Products, Saddle Pinch Points and Reversible Exhausting Pinch Points Calculations

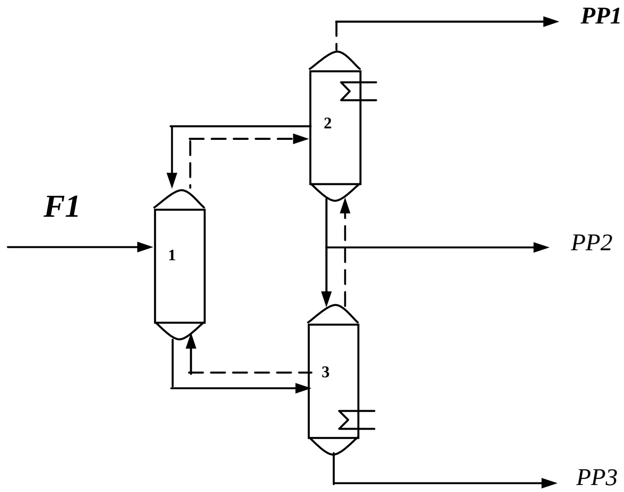


Heat Integration Superstructure

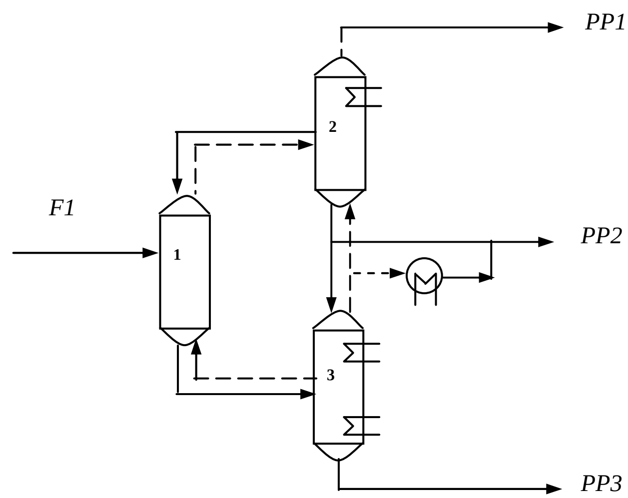


Ternary mixture.

Less efficient RDSM-based superstructures:

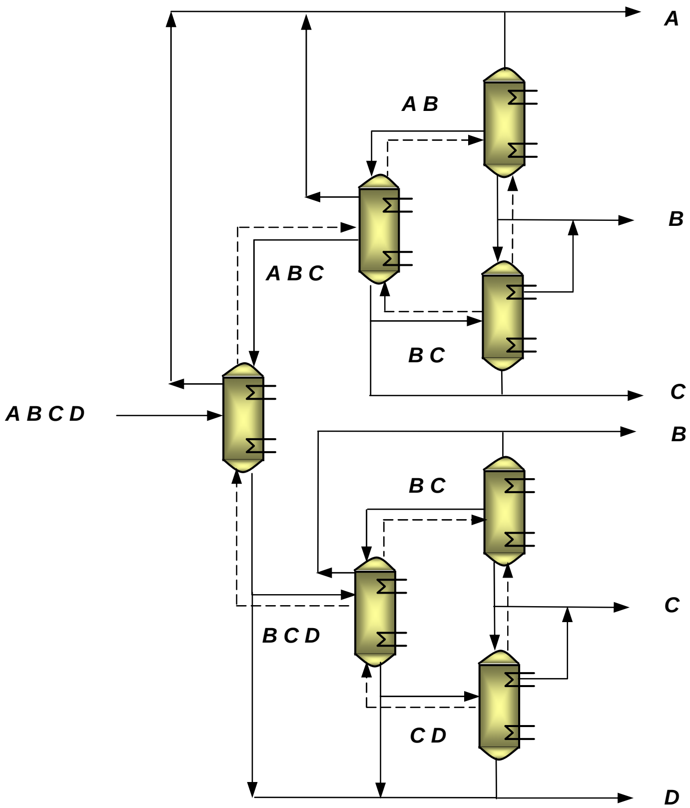


Fully Thermally Coupled Scheme (Petlyuk Column)

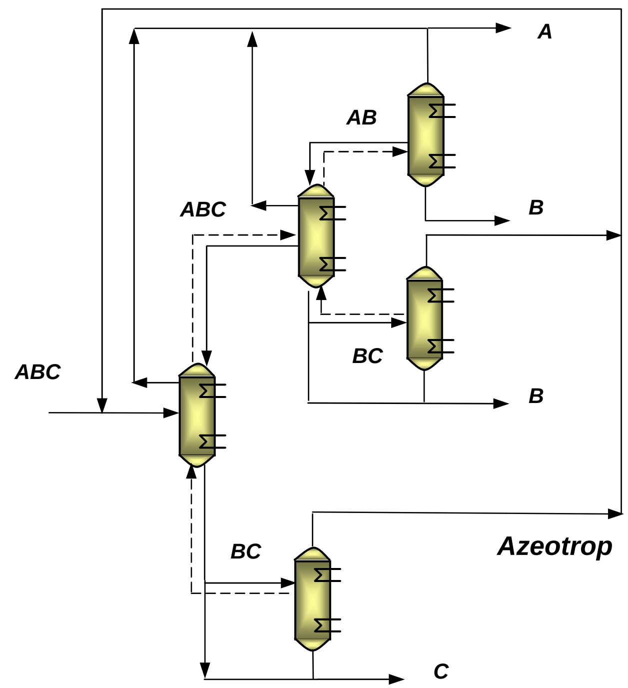


Fully Thermally Coupled Scheme with Heat Integration

3.- Reversible distillation columns and sequences.



Zeotropic Mixture

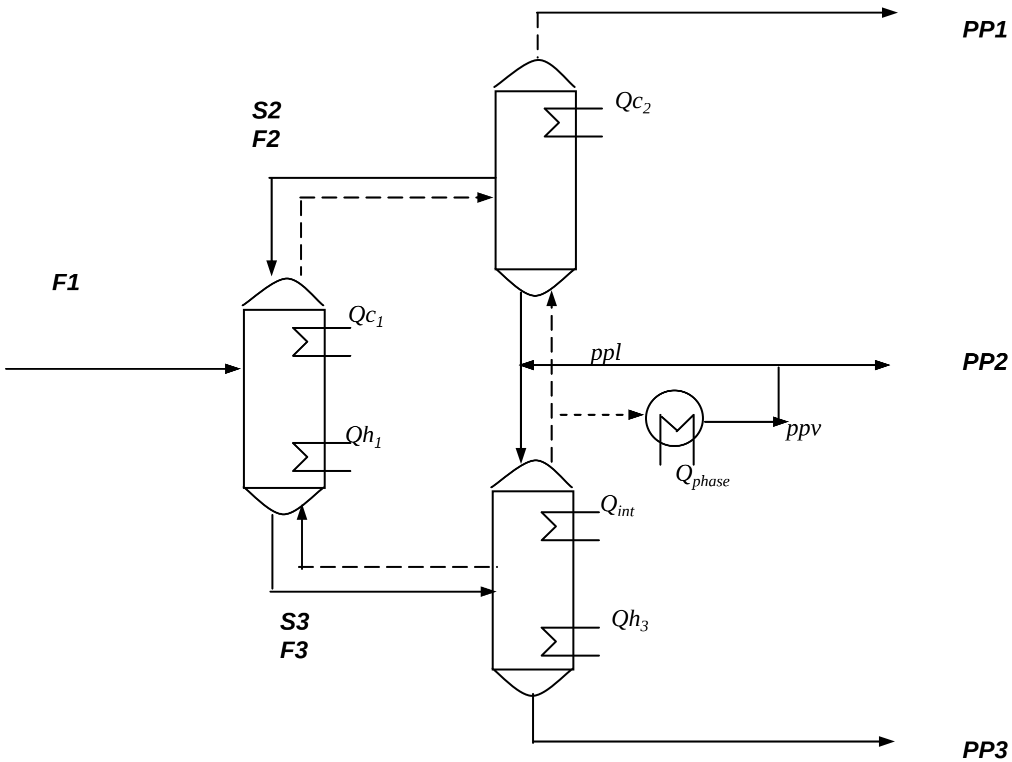


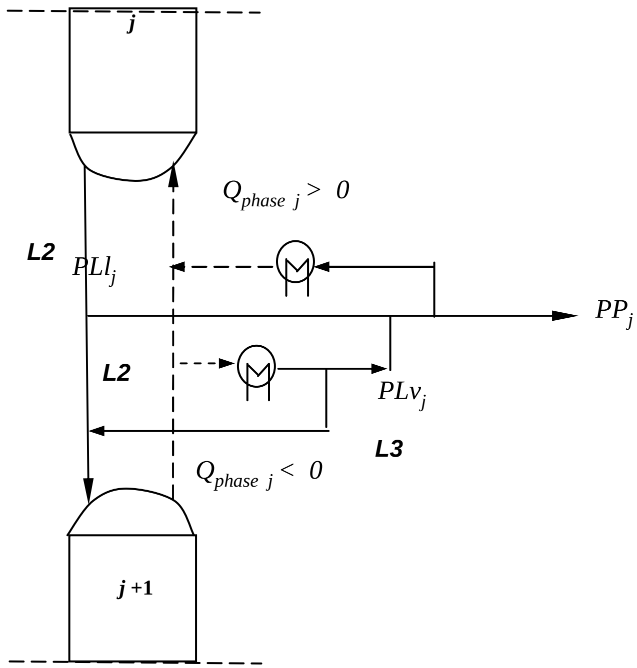
Azeotropic Mixture

3.- Reversible distillation columns and sequences.

Numerical Examples

Models implemented and solved in **GAMS** employing **DICOPT CONOPT**.





3.- Reversible distillation columns and sequences.

Stream	Flow rate (mol/sec) Theoretical	Flow rate (mol/sec) Our Model	Composition Theoretical	Composition Our Model	Entering stage number for
	Feed: n-pentane, n-hexane, n-heptane 0.3/0.5/0.2 Stages: col1 30, col2 80, col3 50				
F2	5.34	**5.36**	0.6355/0.364/0	**0.634/0.3652/6e-4**	40
F3	8.16	**8.08**	0/0.714/0.286	**4e-3/0.71/0.2856**	26
S2	1.05	**1.15**	0.375/0.625/0	**0.373/0.6257/9e-4**	1
S3	2.45	**2.29**	0/0.864/0.1356	**1e-3/0.863/0.1356**	30
$L2^v$	1.88	**1.77**	0/1/0	**2e-3/0.997/7e-4**	80
$L2^l$	2.49	**2.4**	0/1/0	**2e-3/0.997/7e-4**	1
ppl	0.67	**0.60**	0/1/0	**2e-3/0.997/7e-4**	-
ppv	4.33	**4.42**	0/1/0	**2e-3/0.997/7e-4**	-

3.- Reversible distillation columns and sequences.

Product	Flow rate (mol/sec)	Composition
PP1	2.974	0.99/6e-5/0
PP2	5.03	5e-3/0.994/3e-4
PP3	1.998	0/1e-4/0.999

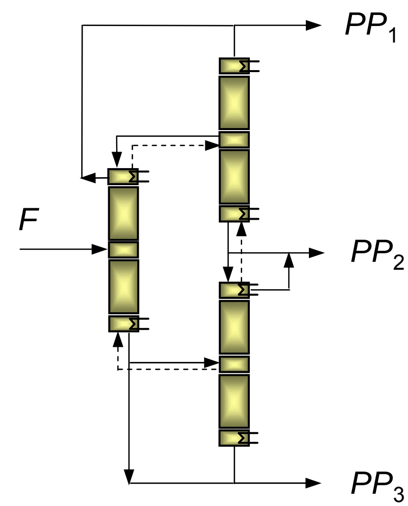
	Energy (KJ/sec)	
Heat Duty	Theoretical	Our Model
Qctot1	-16.63	**-18.29**
Qhtot1	107.21	**114.57**
Qctot2	-204.3	**-203**
Qhtot2	-	**1**
Qctot3	-50.27	**-57.81**
Qhtot3	293.4	**313.78**

4.- Optimal synthesis distillation columns sequences.

Problem specs

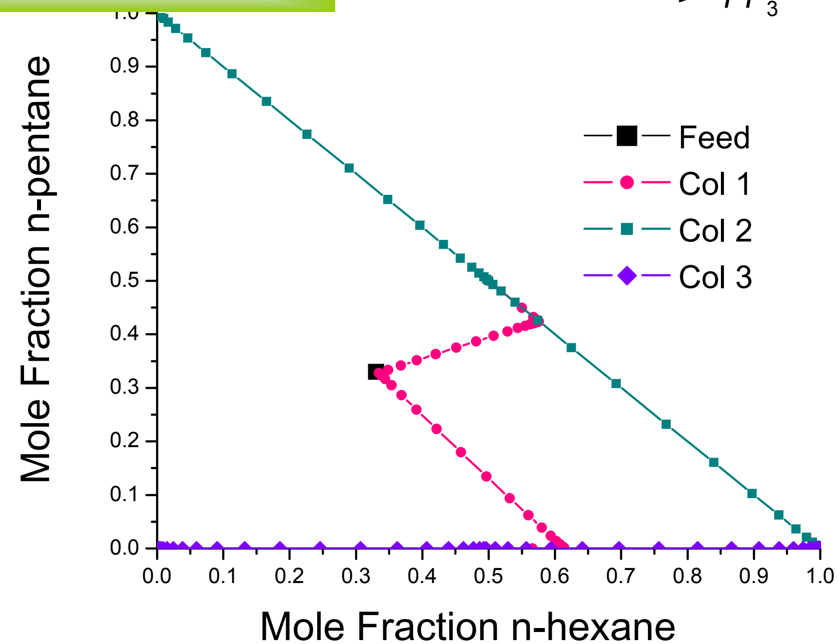
Mixture: **N-pentane/ N-hexane/ N-heptane**
Feed composition: 0.33/ 0.33/ 0.34
Feed: 10 moles/s
Pressure: 1 atm
Max no trays: 15 (each section)
Min purity: 98%
Ideal thermodynamics

Superestructure



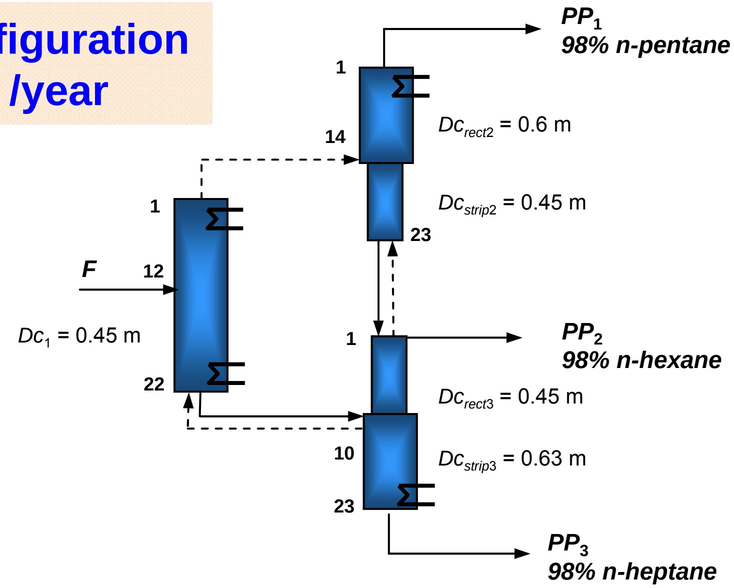
NLP Model	
Continuous Variables	**3301**
Constraints	**3230**
MILP Model	
Continuous Variables	**15000**
Discrete Variables	**96**
Constraints	**8000**

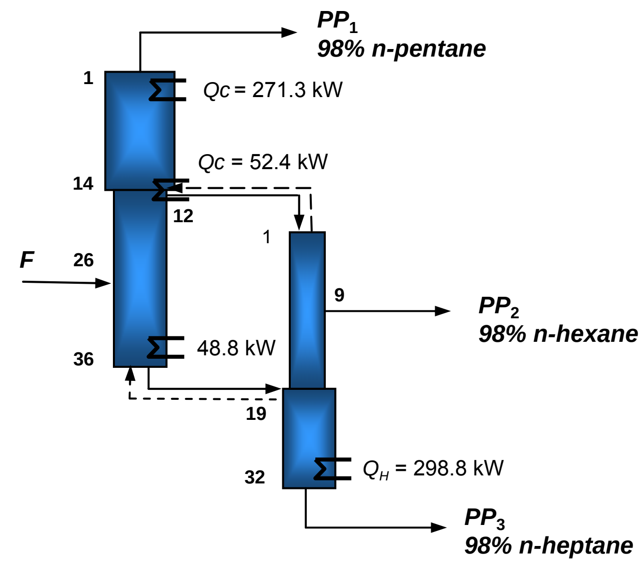
Initialization

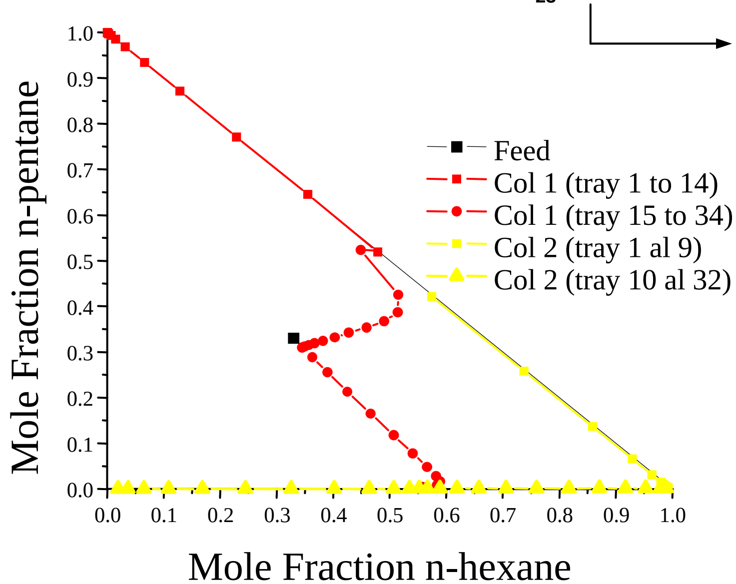


4.- Optimal synthesis distillation columns sequences.

Optimal Configuration
$140,880 /year



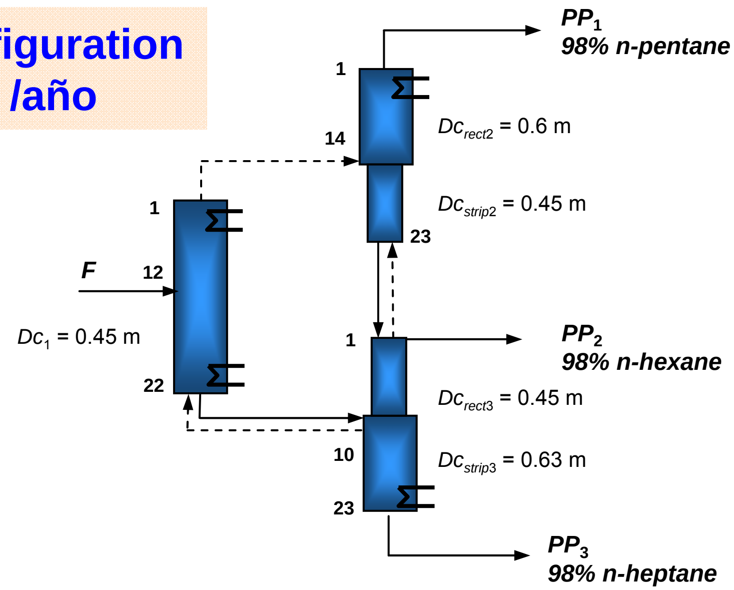


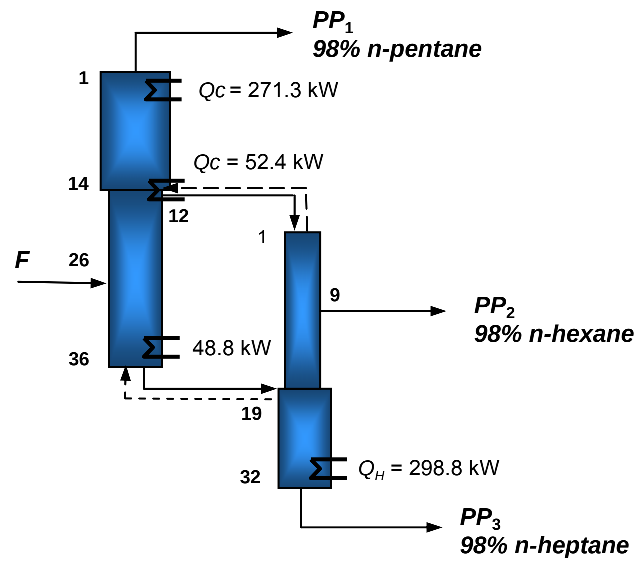


Optimal Design	
Annual cost ($/year)	**140,880**
Preprocessing(min)	**2.20**
Subproblems NLP (min)	**6.97**
Subproblems MILP (min)	**2.29**
Iterations	**5**
Total solution time (min)	**11.46**

4.- Optimal synthesis distillation columns sequences.

Optimal Configuration
$140,880 /año





Optimal Design	
Annual cost ($/year)	**140,880**
Preprocessing(min)	**2.20**
Subproblems NLP (min)	**6.97**
Subproblems MILP (min)	**2.29**
Iterations	**5**
Total solution time (min)	**11.46**

Side-Rectifier $143,440 /year

Direct Sequence $145,040 /year

4.- Optimal synthesis distillation columns sequences.

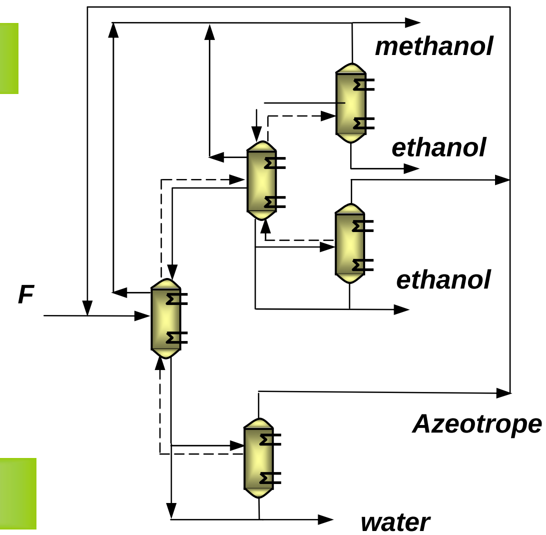
Problem specifications
(Yeomans y Grossmann, 2000)

Mixture: **Methanol/ Ethanol/ Water**
Feed composition: 0.5/ 0.3/ 0.2
Feed flowrate: 10 moles/s
Pressure: 1 atm
Initial trays: 20 (per section)
Purity specification: 90%

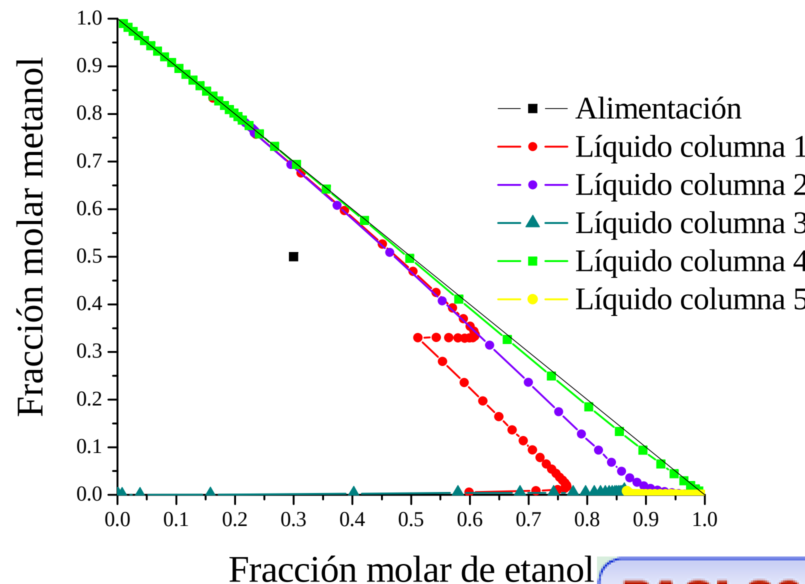
NLP Model	
Continuous Variables	**9025**
Constraints	**8996**
Nonlinear non-zeroes	**18230**

MILP Model	
Continuous Variables	**12850**
Discrete Variables	**96**
Constraints	**18000**

Superstructure



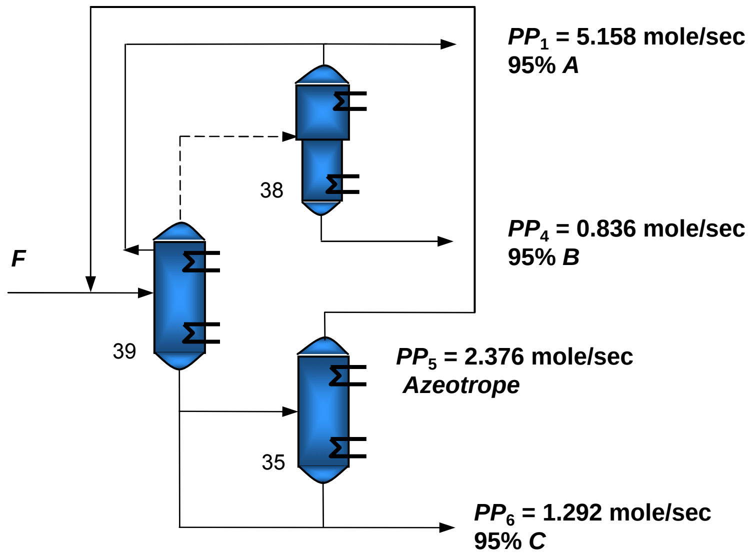
Initialization



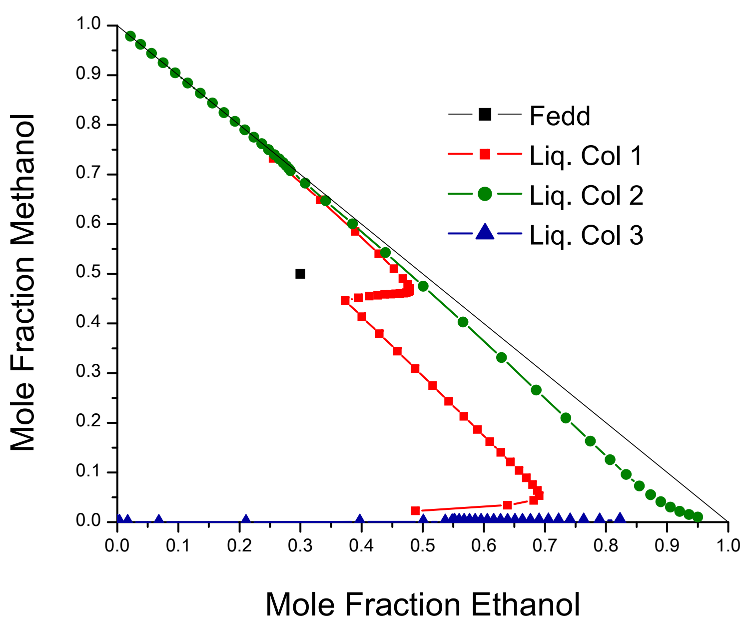
4.- Optimal synthesis distillation columns sequences.

Product Specifications 95%

Optimal Configuration
$318,400 /año



Profiles Optimal Configuration



Optimal Solution

Annual Cost ($/year)	**318,400**
Preprocessing (min)	**6.05**
Subproblems NLP (min)	**36.3**
Subproblems MILP (min)	**3.70**
Iteraciones	**3**
Total Solution Time (min)	**46.01**

Conclusions

Distillation optimization with rigorous models remains major computational challenge

Optimal feed tray and number of trays problems are solvable

Keys: Initialization, MINLP/GDP models

Synthesis of complex columns remains non-trivial
Progress with initialization, GDP, decomposition

Improvements potential in distillation processes