Distillation

Processos de Separação

LEQB

2023/2024

Summary

- Distillation of azeotropic mixtures
- Batch Distillation

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Distillation of azeotropic mixtures

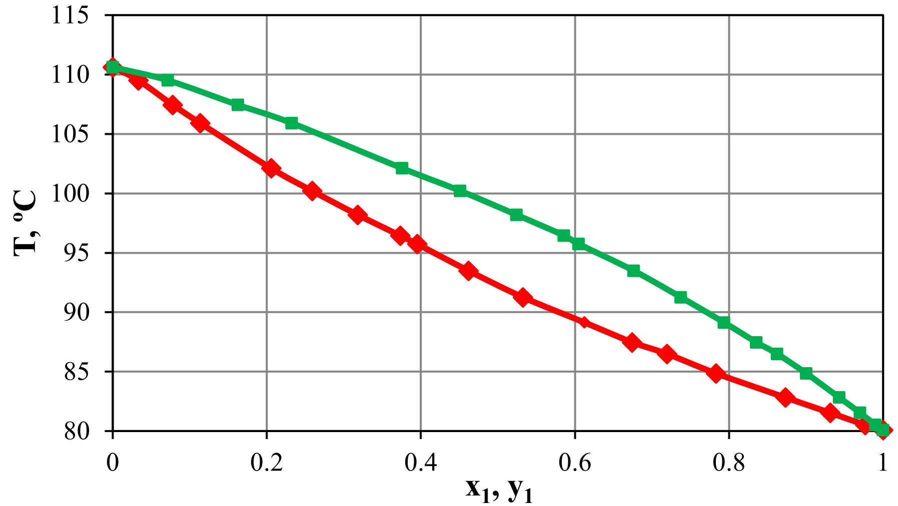
Azeotropic mixtures are mixtures that do not vary in composition when distilled, i.e. the composition of the liquid and vapor phases are the same!

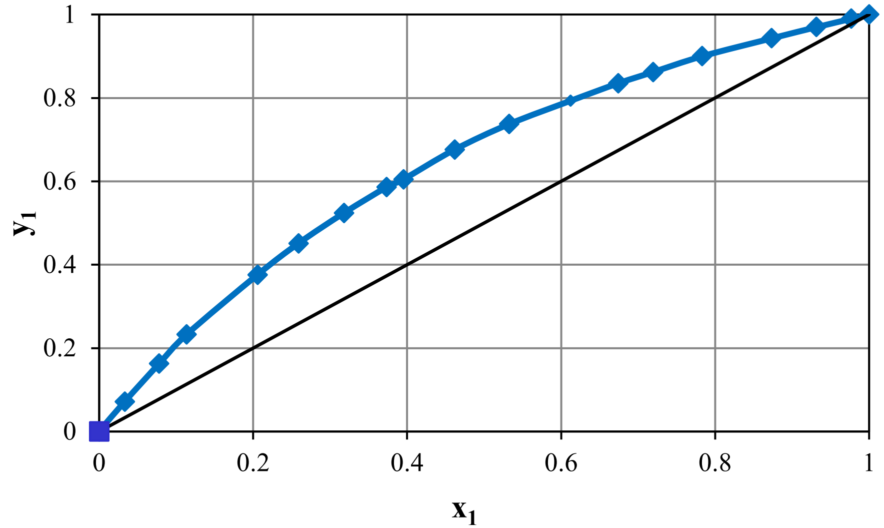
- Homogeneous Azeotropes
- Heterogeneous Azeotropes

"IDEAL" SYSTEM!

$$T_{boiling}|_{benzene} = 80.1°C$$

$$T_{boiling}|_{toluene} = 110.6\ °C$$



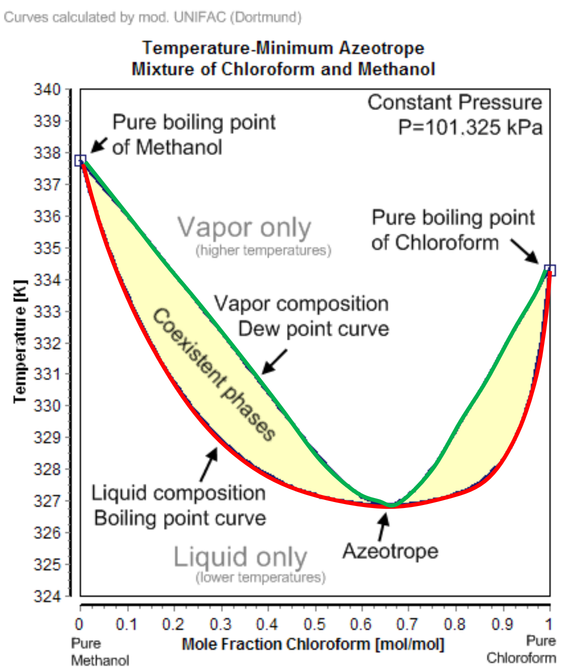


Binary mixture Benzene (1) + Toluene (2) at 1 bar

- All the mixtures vaporize at a temperature between the normal boiling points of the pure compounds
- K_i ($=y_i/x_i$) $\neq 1$, always

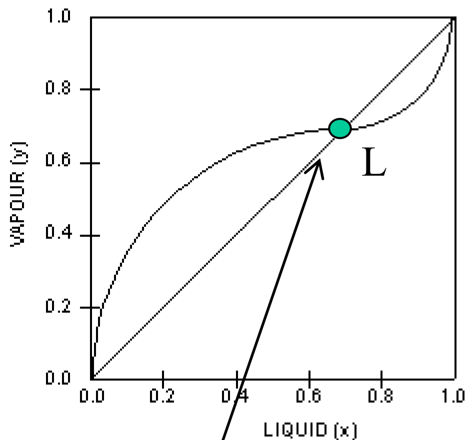
Homogeneous azeotrope: Minimum-boiling azeotrope

Chloroform + Methanol



A and C repel each other!

=> Minimum of temperature!

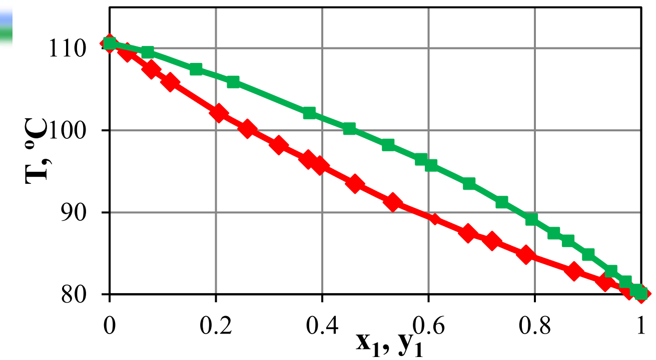


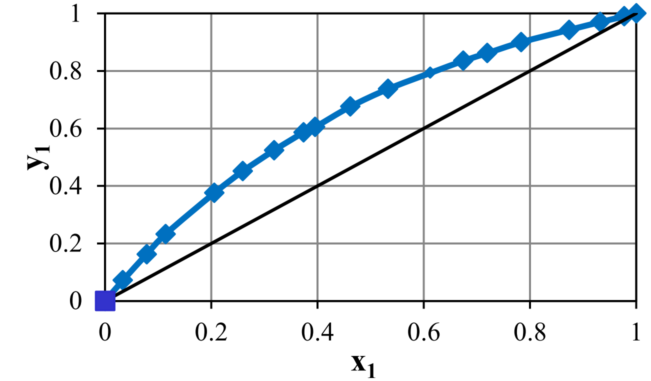
Inversion of selectivity!

"L": $y_{az} = x_{az}$

↓

Azeotrope



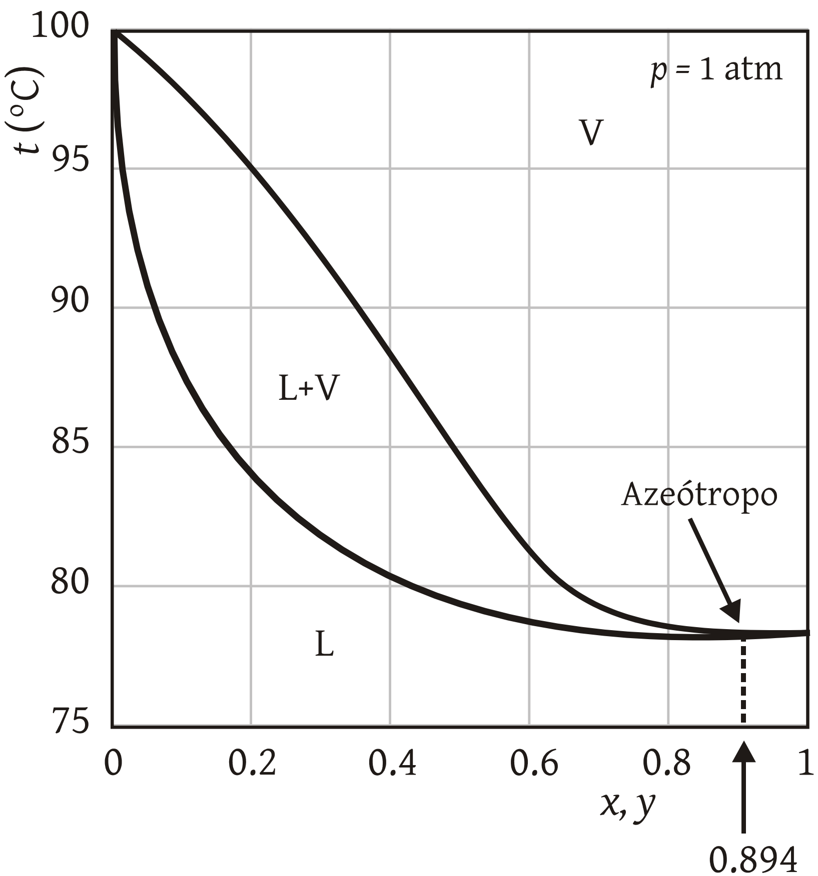


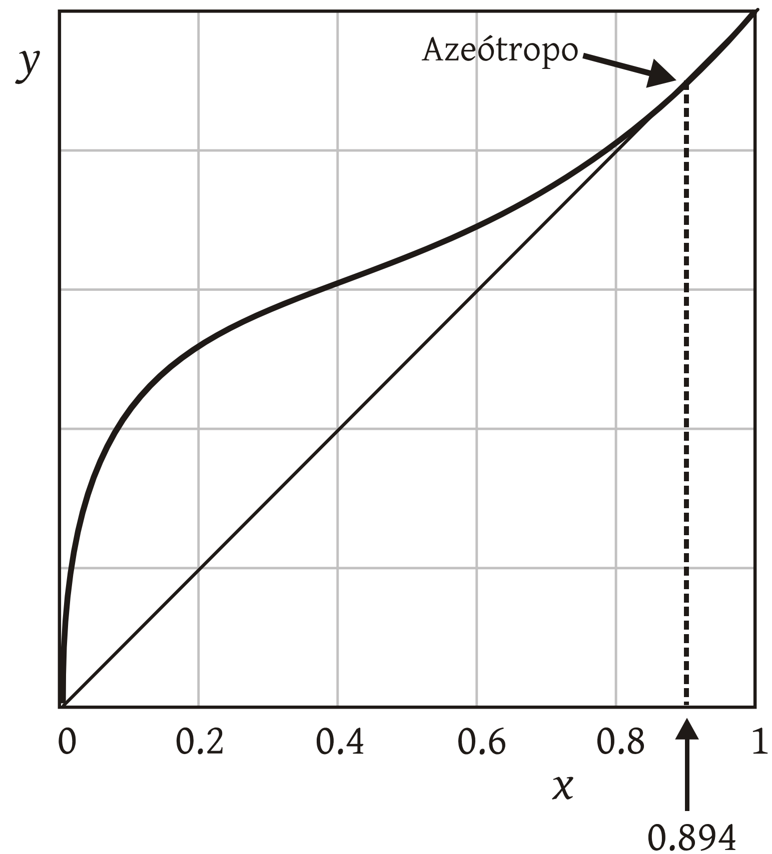
$$T_b|_{methanol} = 338\ K$$

$$T_b|_{chloroform} = 334\ K$$

$$T_b|_{azeotrope} = 327\ K$$

Ethanol/water system at 1 atm





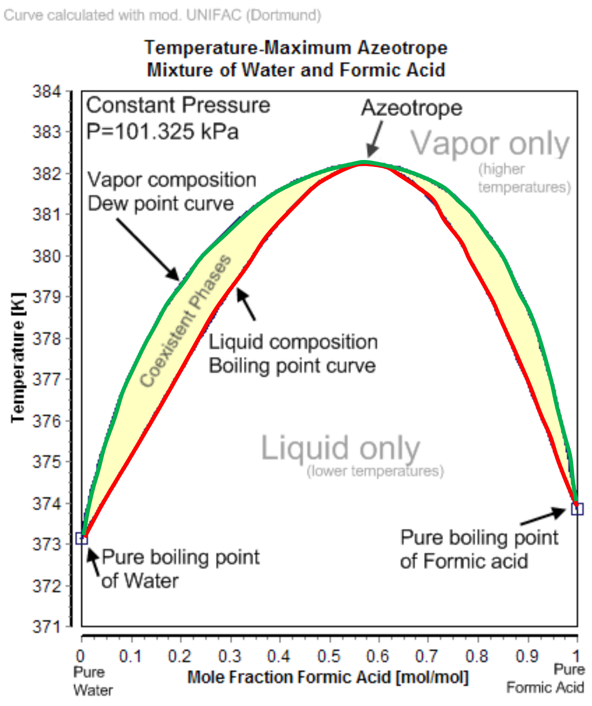
<u>Azeotropic point</u>: 78.2°C, 89.4 mol% EtOH

$T_b|_{ethanol} = 78.4\ °C$ (95.6% v/v)

Below 70 mm Hg no azeotrope exists for ethanol/water

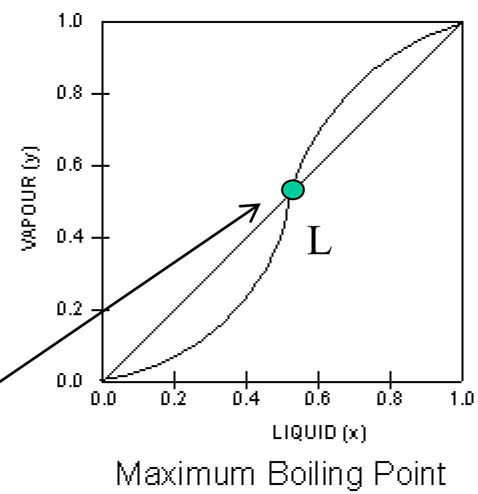
Homogeneous azeotrope: Maximum-boiling azeotrope

Formic acid + Water



A and C attract each other!

=> Maximum of temperature!



"L": $y_{az} = x_{az}$

↓

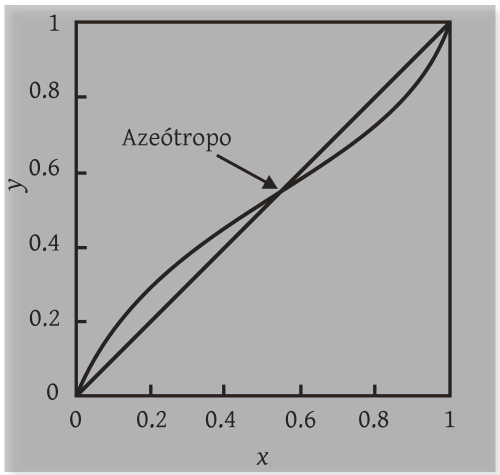
Azeotrope

Inversion of selectivity!

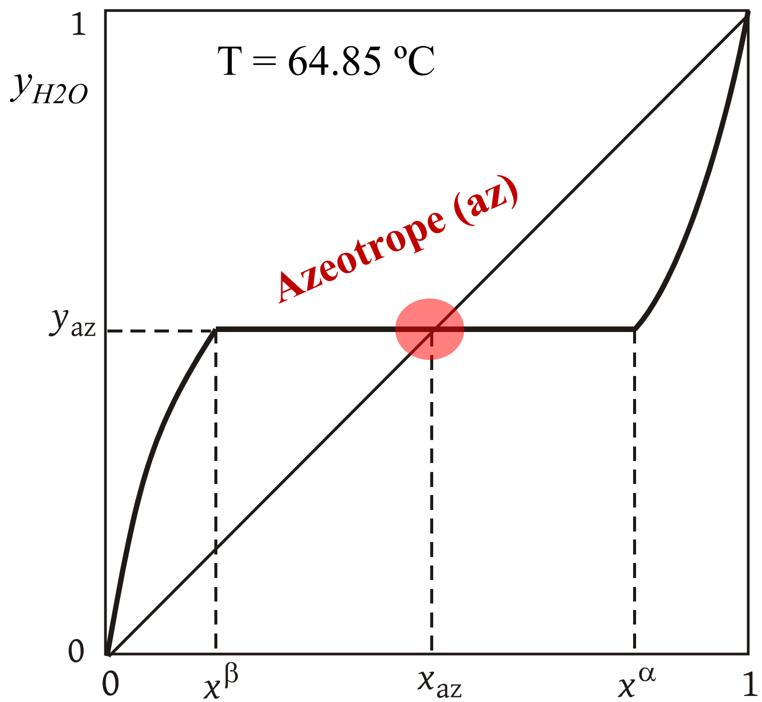
Heterogeneous azeotrope

the vapor from the azeotrope will condense to form two immiscible liquid phases

Example: system benzene + water + ethanol



Homogeneous azeotrope



18.5% ethanol
74.1% benzene
7.4% water

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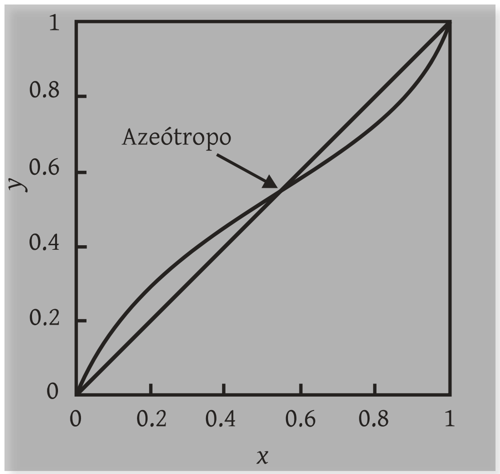
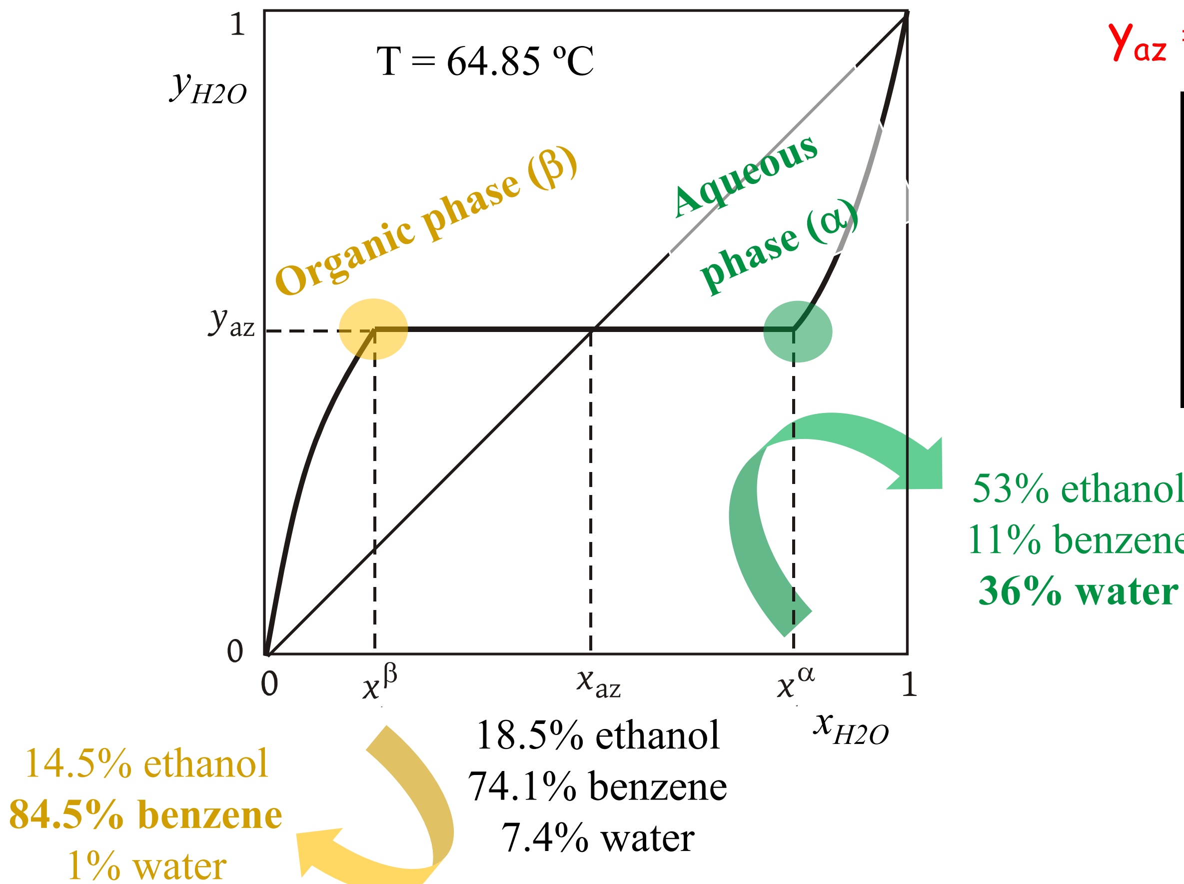
Example: system benzene + water + ethanol

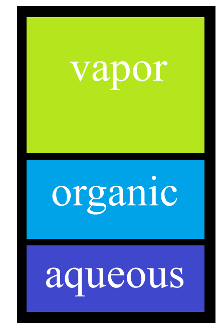


Homogeneous azeotrope

$y_{az} = x_{az}$



$y_{az} \neq x^{\alpha} \neq x^{\beta}$



Fractionation of azeotropic mixtures

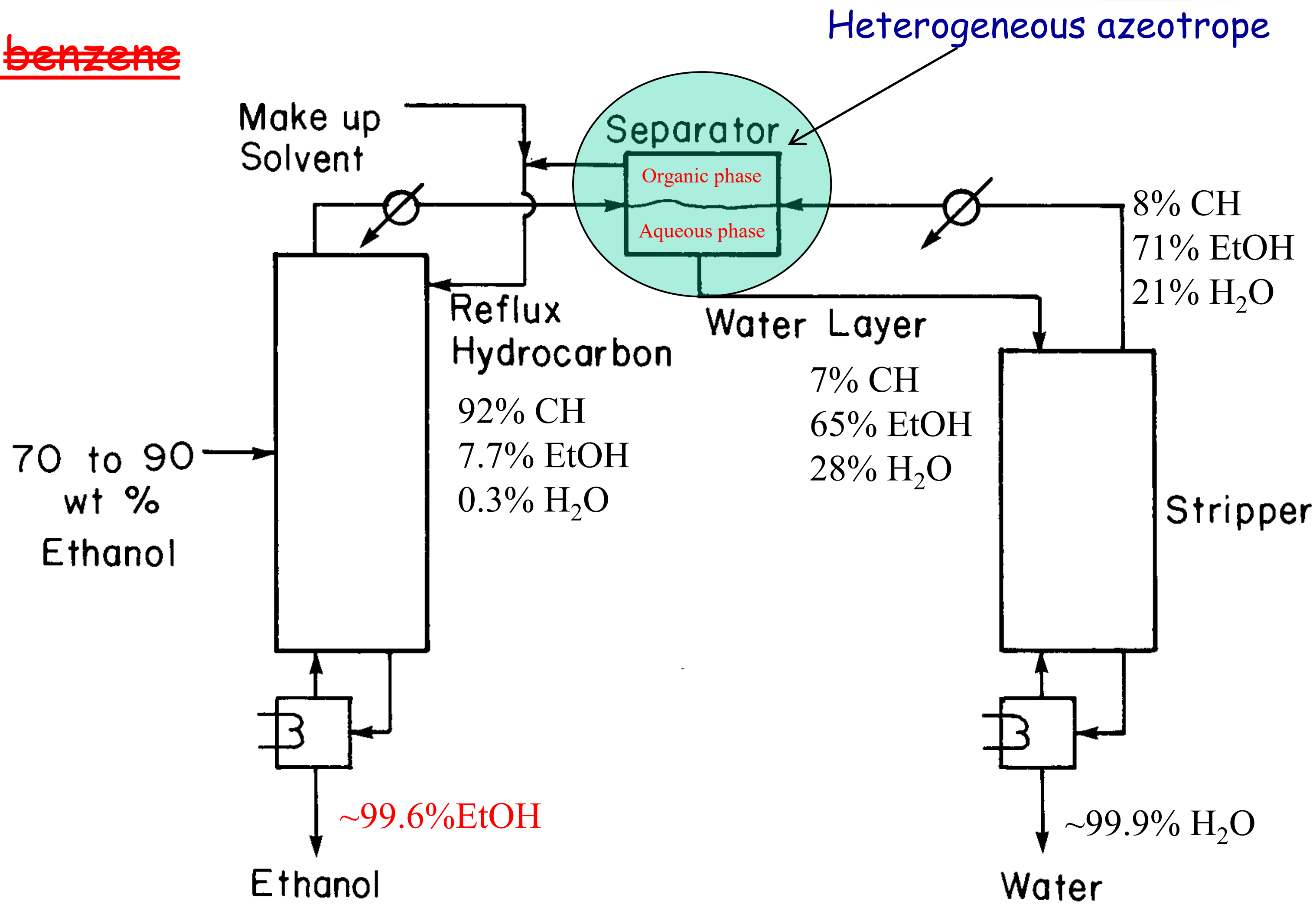
How do we do it?

- By changing the pressure where azeotropy occurs
- By adding a third compound which will form a new, **heterogenous**, azeotrope (**azeotropic distillation**)
- By adding a third compound that modifies the thermodynamic equilibrium (**extractive distillation**)

Azeotropic distillation

Solvents: Cyclohexane, ~~benzene~~

A third component ("entrainer") is added to the initial mixture forming a new azeotrope



Extractive distillation

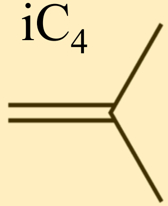
A third compound (a solvent with high boiling point) is added to modify the relative volatility of the components of the original mixture

A process used to:

- Fractionate the azeotropic mixture
- Fractionate mixtures that have components with very similar boiling points (α ~1)

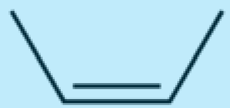
Separating the isobutene from the butene's isomers

iC_4



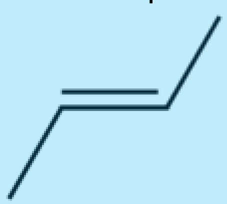
Isobutylene
(T_{eb} -6.9 ºC)

1-Butene (α-butylene)
(T_{eb} -6.5 ºC)

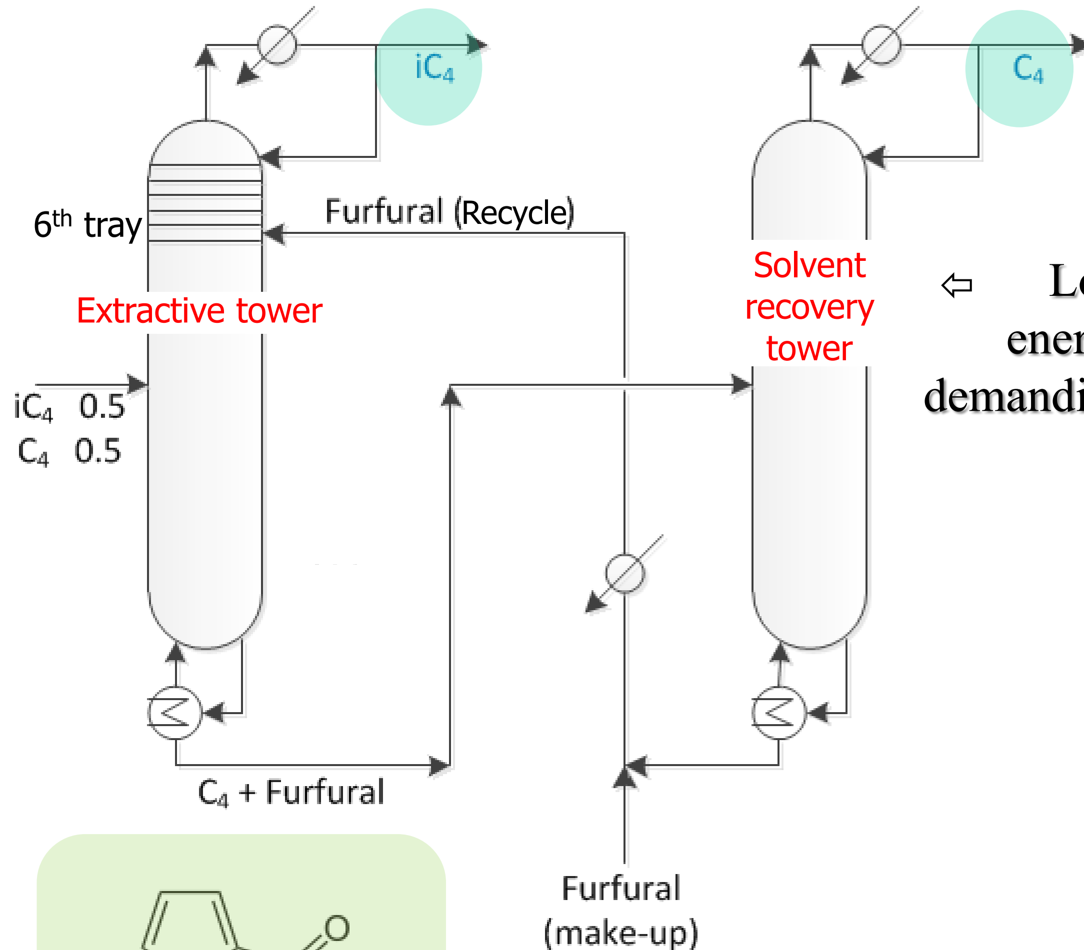


(2Z)-but-2-ene (cis-β-butylene)
(T_{eb} 1 ºC)

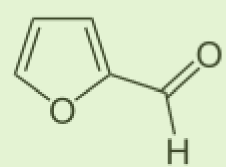
C_4



(2E)-but-2-ene (trans-β-butylene)
(T_{eb} 4 ºC)



⇦ Low energy demanding



Furfural (T_{eb} 162 ºC)

Furfural ⇨ p_V butenes (C_4) ↘

- Batch distillation

Batch distillation

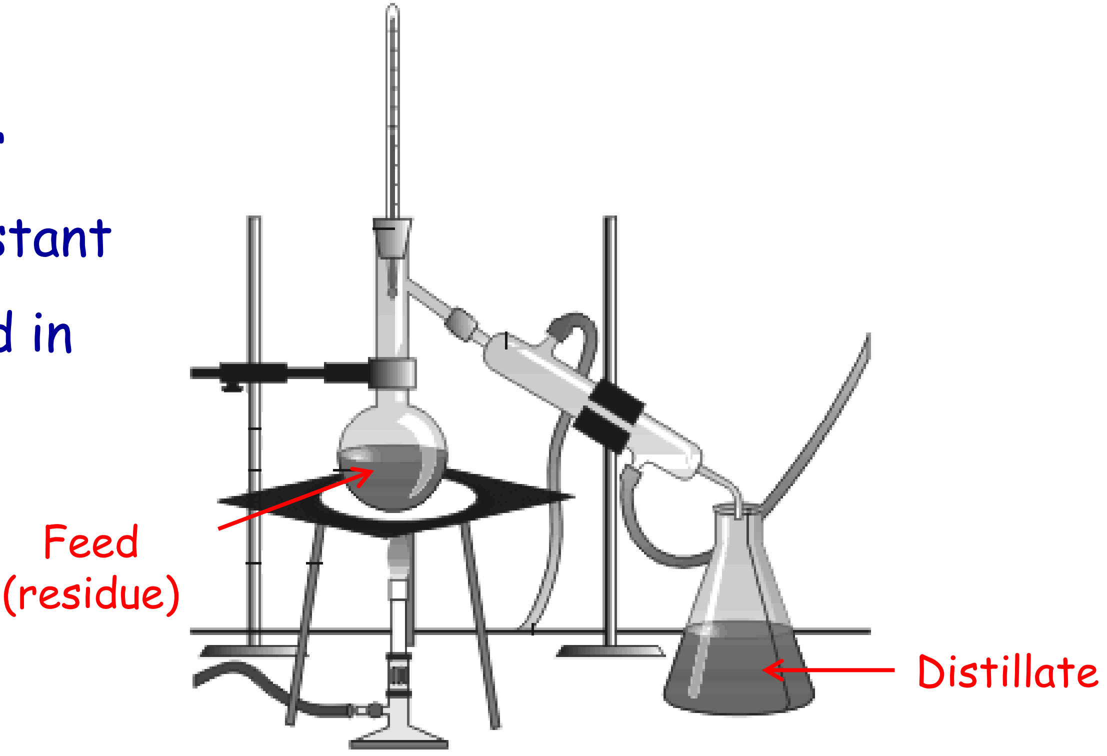
When should be used?

- ✓ small quantities of feed to process
- ✓ feed is produced at irregular periods (seasonal)
- ✓ Large fluctuations in feed composition

Batch distillation

Transient process!

The compositions of the liquid and vapor phases change with time, but at each instant the vapor is in equilibrium with the liquid in the flask!



Continuous removal of the vapor that is formed during the process

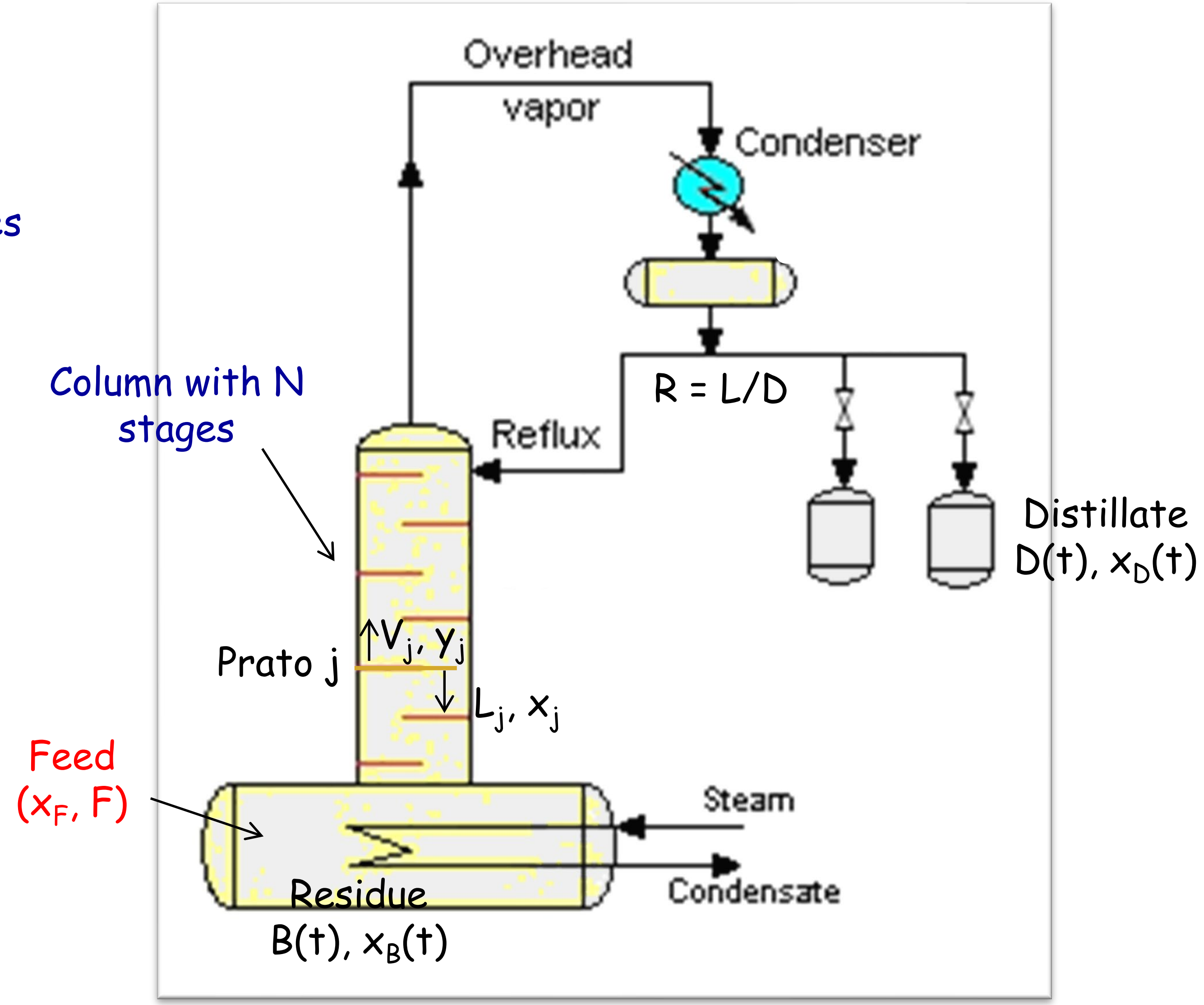
Multistage batch distillation

Two modes of operation:

- **constant** reflux ratio
(composition of the distillate varies between x_{Di} and x_{Df})

- **variable** reflux ratio
(x_D is constant!)

The composition in the boiler varies between x_F and x_{Bfinal} (and the flowrate between F and B_{final})



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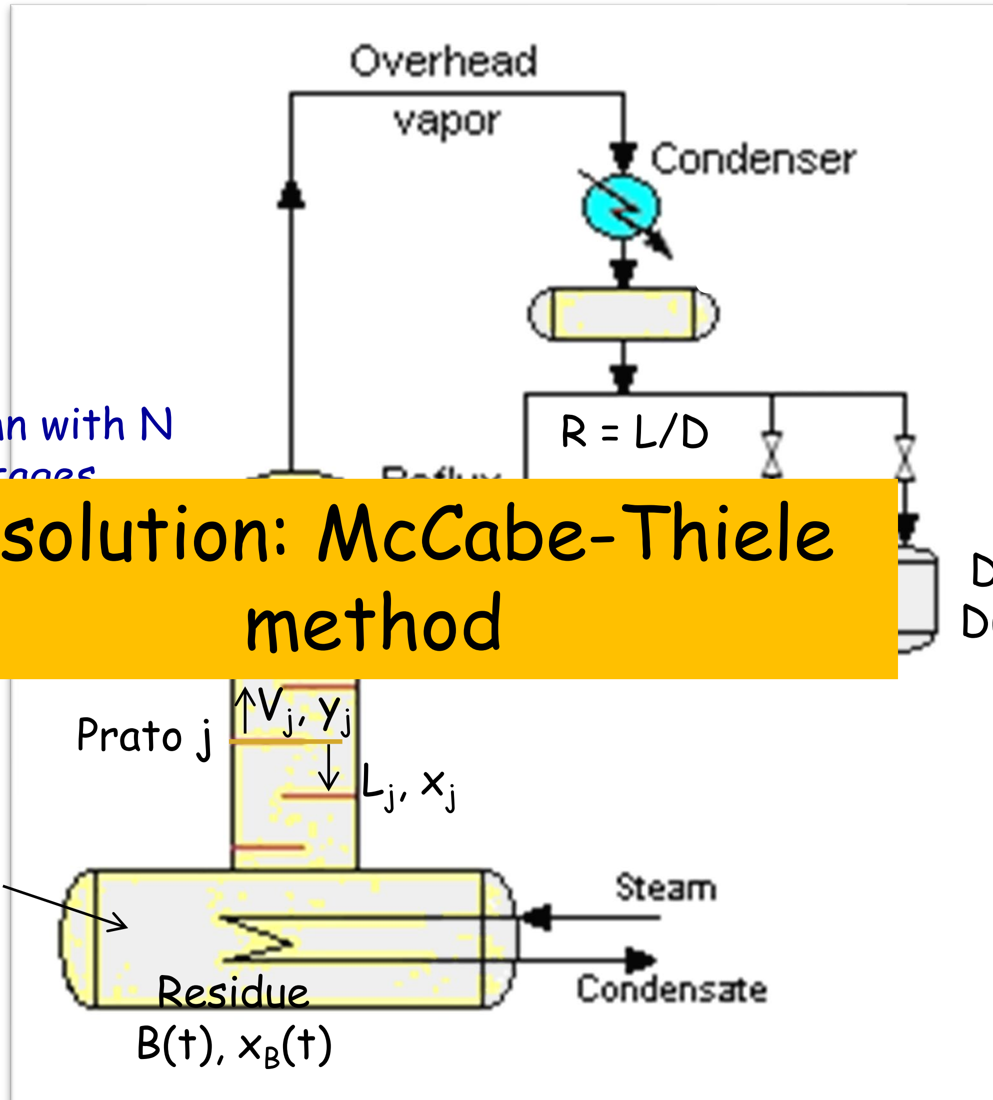

Resolution: McCabe-Thiele method

Problem 4

It is intended to distillate a batch of a methanol / water mixture having a molar percentage of methanol equal to 49%. The boiler is charged with 200 moles of the mixture and the distillation column has 3 theoretical plates and a total condenser. The system is operated with a constant reflux ratio equal to 0.64. At the end of the process, it remains in the boiler 106.6 moles of residue with a composition of 18 mol% in methanol. Calculate:

(a) the composition of the distillate obtained at the beginning

b) The composition of the distillate at the end of the process

Multistage batch distillation; photograph of packaged batch distillation/solvent recovery system of approximately 400-gallon capacity.

Courtesy of APV Equipment, Inc., Tonowanda, New York

1 US gallon = 3.8 liters