Lecture 15.
Enhanced Distillation and Supercritical Extraction (1)
[Ch. 11]

- Enhanced Distillation
- Use of Triangular Graphs
  - Zeotropic mixture
  - Mixture forming one minimum-boiling azeotrope
  - Mixture forming two minimum-boiling azeotropes
- Residue-Curve Maps
- Distillation-Curve Maps
- Product-Composition Regions at Total Reflux

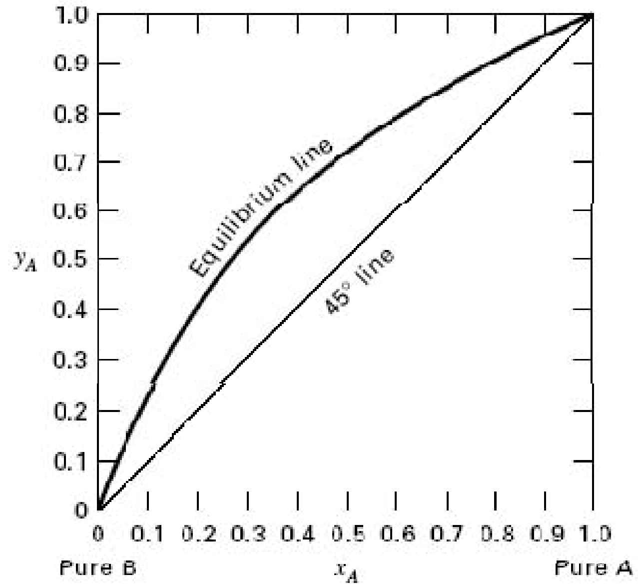
Enhanced Distillation

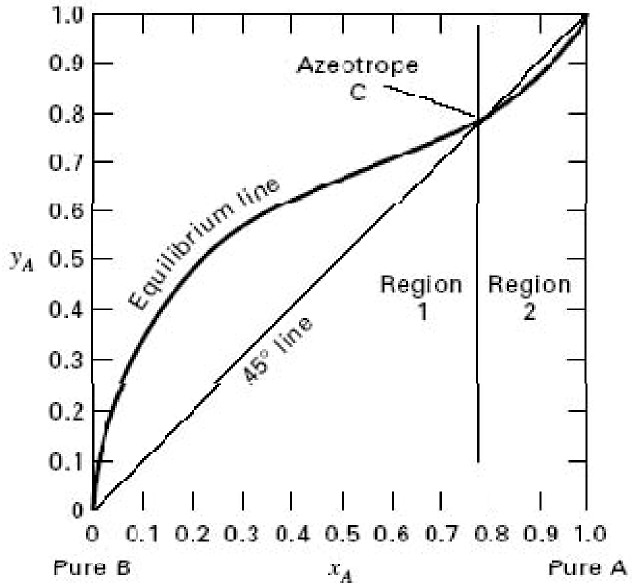
- Cases when ordinary distillation is not economical
  - Boiling point difference between components is less than 50℃
  - Relative volatility is less than 1.10
  - Mixture forms an azeotrope

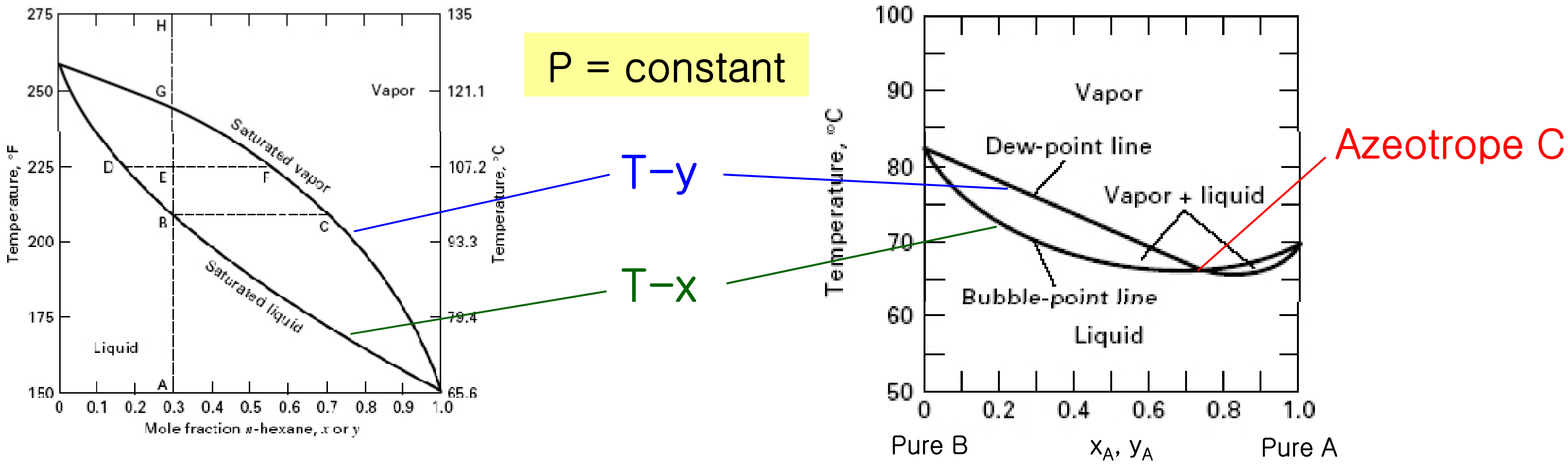
- Enhanced distillation
  - Extractive distillation : adding a large amount of solvent
  - Salt distillation : adding a soluble, ionic salt
  - Pressure-swing distillation : operating at two different pressures
  - Homogeneous azeotropic distillation : adding an entrainer
  - Heterogeneous azeotropic distillation : adding an entrainer
  - Reactive distillation : adding a separating agent to react selectively and reversibly with feed component(s)

Zeotropic *vs*. Azeotropic Systems

Binary zeotropic system | **Binary azeotropic system**







Use of Triangular Graphs

- Triangular vapor–liquid diagram for ternary mixture
  - Too complex to understand
- Plot with only equilibrium liquid composition for a ternary mixture
  - Easy to understand
  - Convenient to use
  - Provide useful information in distillation of ternary components
    - Residue curve
    - Distillation curve

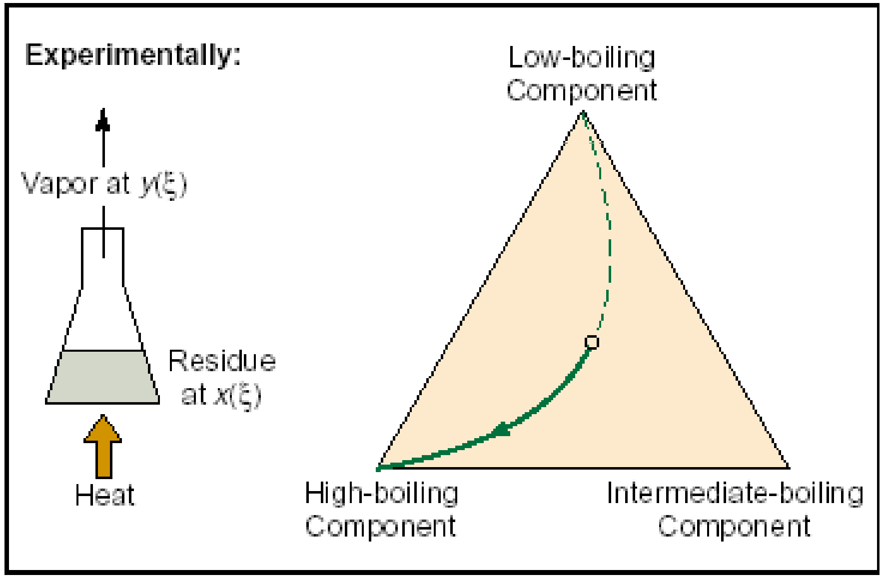
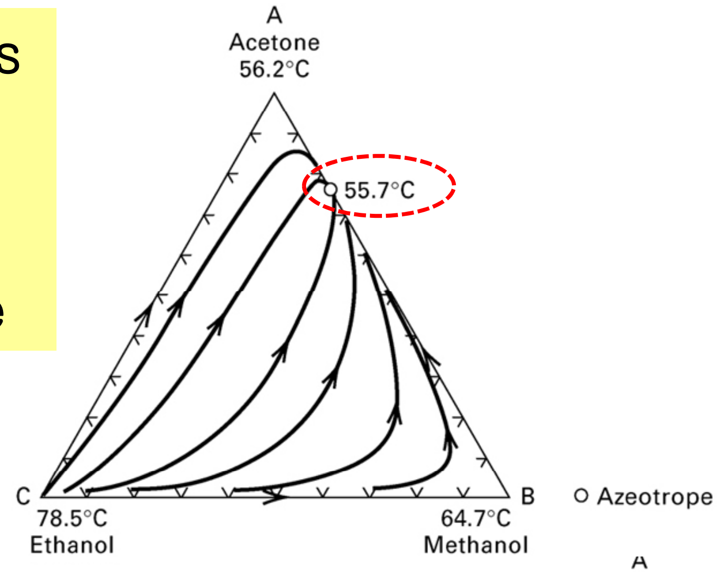


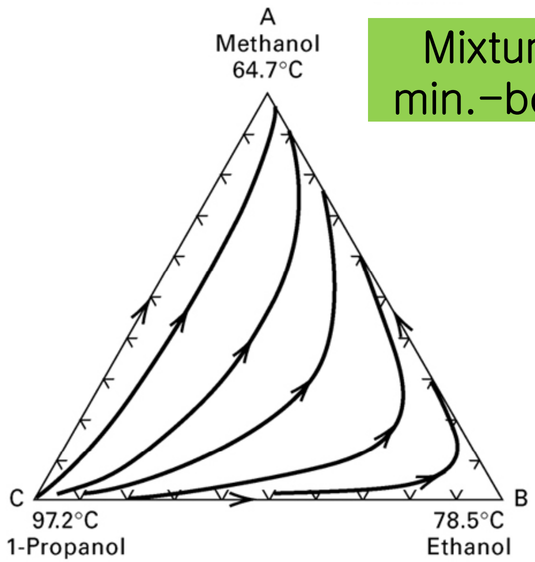
Figure 1. RCMs, using experimental or generated data, show the composition of the residue of a simple batch distillation over time.

Distillation Curves for Ternary Systems

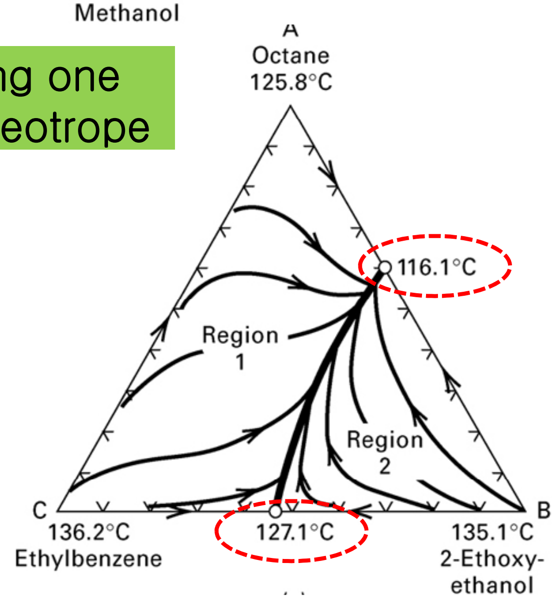
Each curve in each diagram is the locus of possible equilibrium liquid-phase compositions that occur during distillation of a mixture



Mixture forming one min.-boiling azeotrope



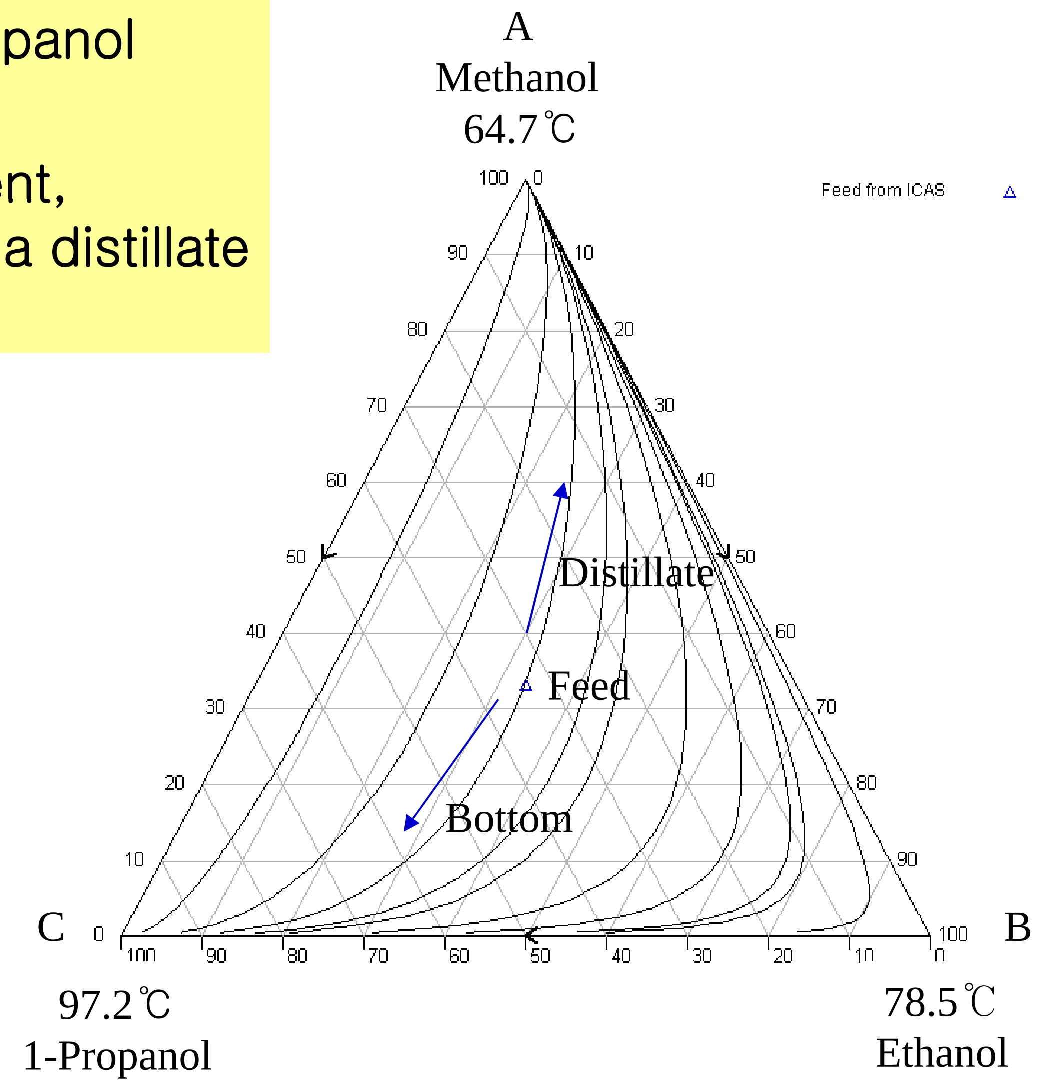
Mixture not forming an azeotrope



Mixture forming two min.-boiling azeotropes

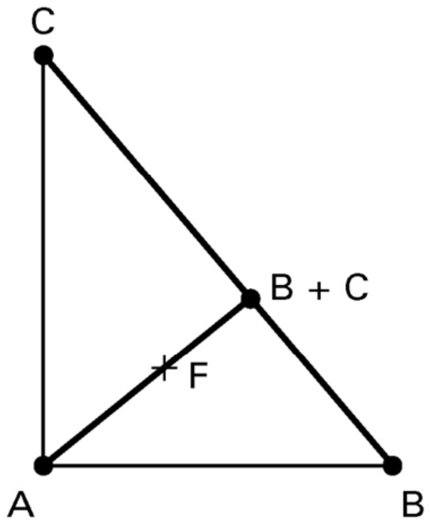
Zeotropic Mixture

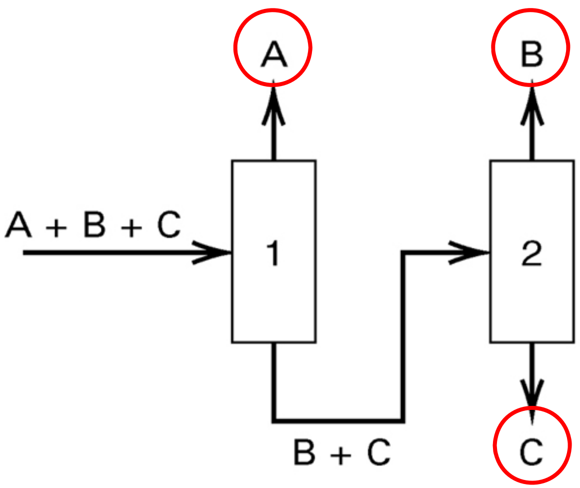
- Product can be either nearly pure methanol or nearly pure 1-propanol
- Nearly pure ethanol (B), the intermediate-boiling component, cannot be produced either as a distillate or bottoms



Distillation Sequences for Ternary Zeotropic Mixtures

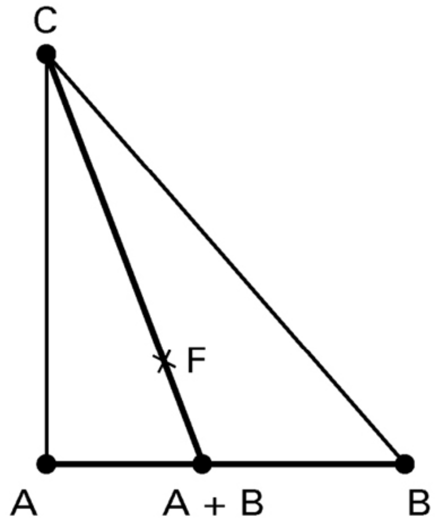
Direct sequence

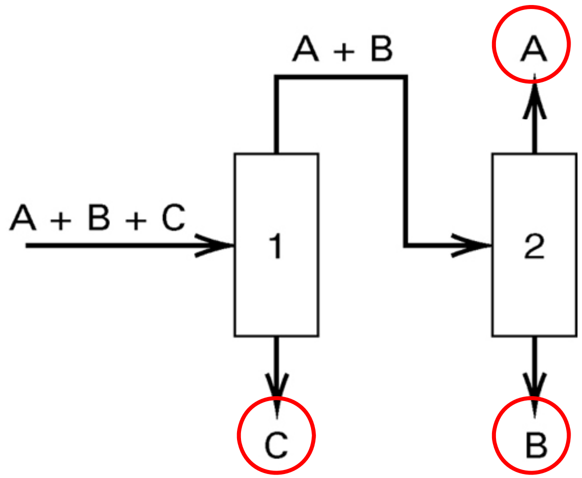




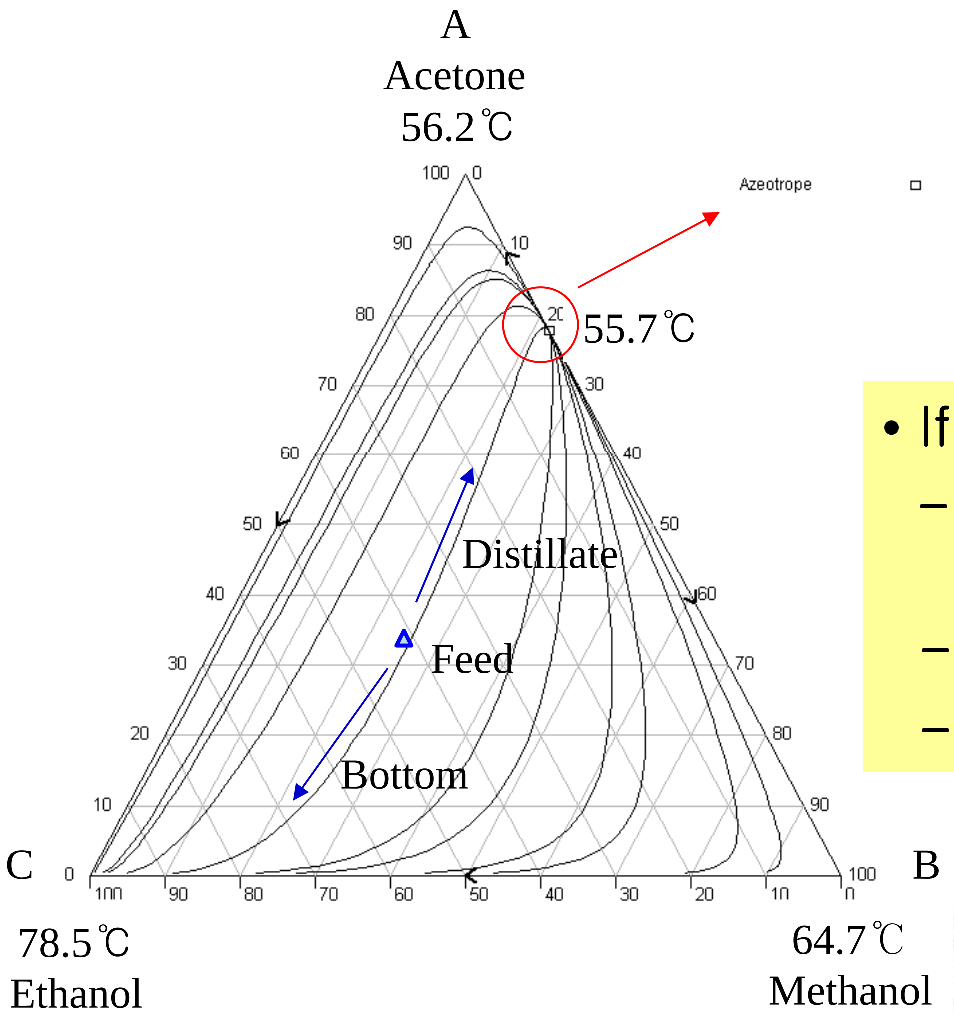
Feed, distillate, and bottoms product compositions lie on a straight, total-material-balance line

Indirect sequence





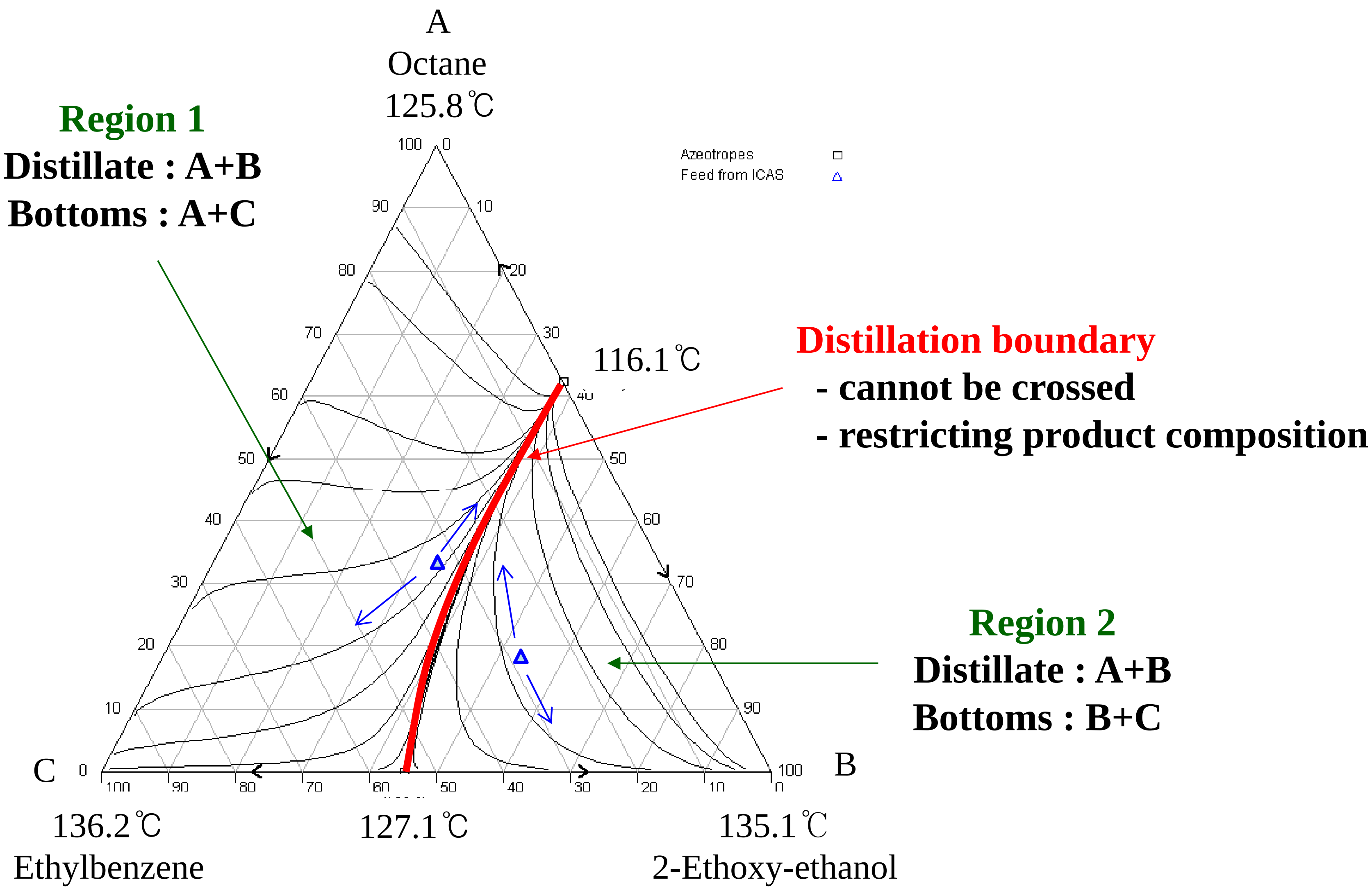
Mixture Forming One Minimum–Boiling Azeotrope



- If the column split is properly selected
  - Ternary distillate or bottoms products can be avoided
  - Little or no ethanol in the distillate
  - Little or no acetone in the bottoms

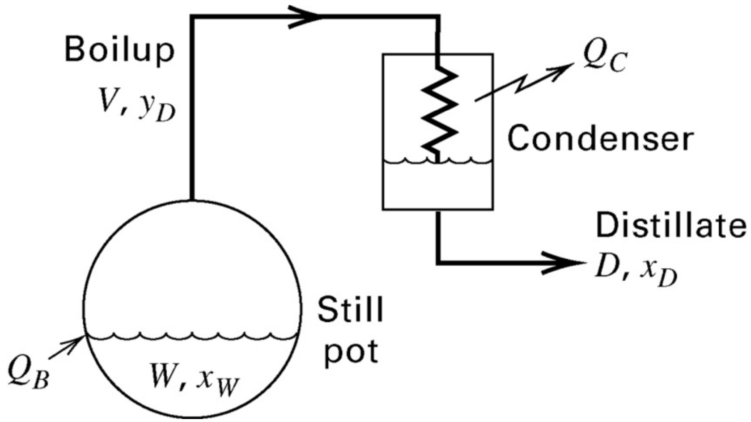
Case	Feed:		Distillate:		Bottoms:	
	$x_{acetone}$	$x_{methanol}$	$x_{acetone}$	$x_{methanol}$	$x_{acetone}$	$x_{methanol}$
1	0.1667	0.1667	0.7842	0.2158	0.0000	0.1534
2	0.1250	0.3750	0.7837	0.2163	0.0000	0.4051
3	0.2500	0.2500	0.7837	0.2163	0.0000	0.2658
4	0.3750	0.1250	0.7837	0.2163	0.0000	0.0412
5	0.3333	0.3333	0.7837	0.2163	0.0000	0.4200

Mixture Forming Two Minimum–Boiling Azeotropes



Residue–Curve Maps (1)

- Rayleigh batch (differential) distillation
  - no trays, no packing, no reflux



D : instantaneous–distillate rate, mol/h

W : moles of liquid left in still

Rate of output : Dy_D

Rate of depletion :

$$-\frac{d}{dt}(Wx_W) = -W\frac{dx_W}{dt} - x_W\frac{dW}{dt}$$

$$W\frac{dx_W}{dt} + x_W\frac{dW}{dt} = -Dy_D$$

$$-Ddt = dW$$

$$\Rightarrow \quad \frac{dx_i}{dt} = (y_i - x_i)\frac{dW}{Wdt}$$

Residue–Curve Maps (2)

- Because W changes with time, it is possible to combine W and t into a single variable, ξ

$$\frac{dx_i}{dt} = (y_i - x_i)\frac{dW}{Wdt} \quad + \quad \frac{dx_i}{d\xi} = x_i - y_i$$

$$\frac{d\xi}{dt} = -\frac{1}{W}\frac{dW}{dt} \quad \rightarrow \quad \xi\{t\} = \ln\left[\frac{W_0}{W(t)}\right]$$

$$\frac{dx_i}{d\xi} = x_i - y_i, \quad i = 1, 2$$

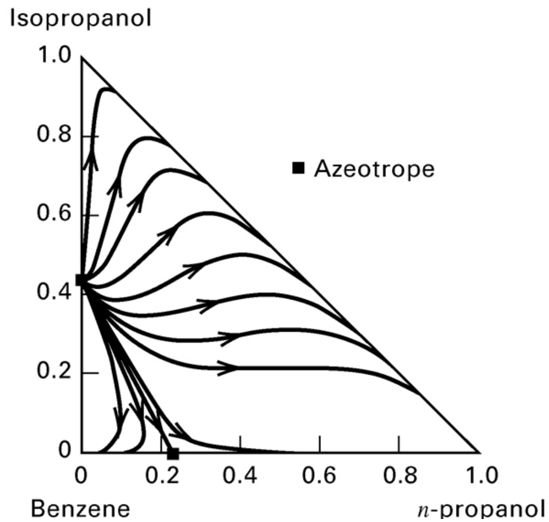
$$\sum_i^3 x_i = 1$$

$$y_i = K_i x_i, \quad i = 1, 2, 3$$

$$\sum_i^3 K_i x_i = 1$$

Bubble-point-temperature equation

Nine variables:
P, T, x_1, x_2, x_3, y_1, y_2, y_3, ξ



- Residue curve: a plot of liquid-residue composition with time (from a lower-boiling state to a higher-boiling state)
- Residue-curve map: a collection of residue curves for a given ternary system

Distillation−Curve Maps

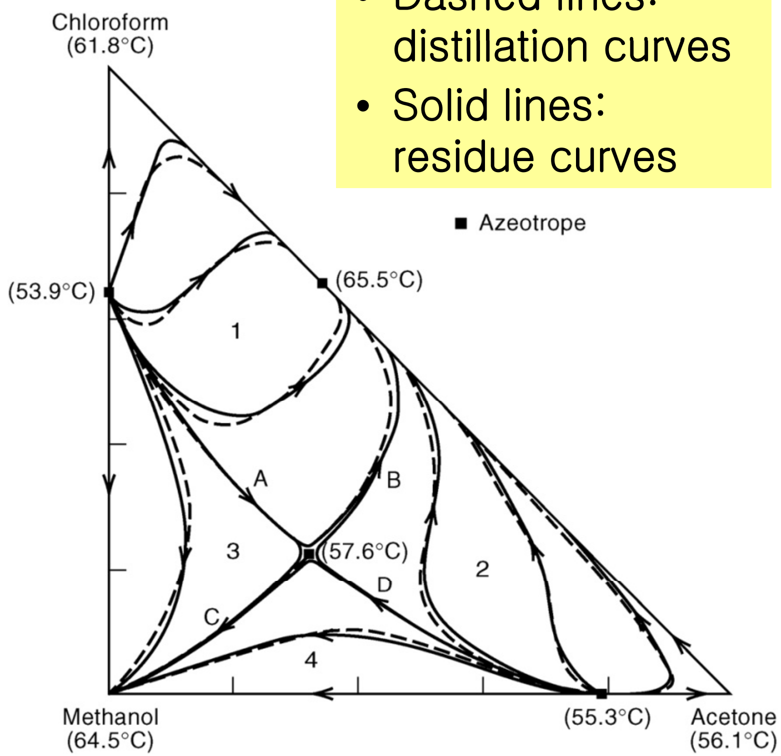
- Distillation curve
  : ternary diagram determined for total reflux (infinite reflux ratio) at a constant pressure, usually 1 atm

$$x_{i,j+1} = y_{i,j}$$

$$y_{i,j} = K_{i,j} x_{i,j}$$

- Distillation−curve map
  : a collection of distillation curves, including distillation boundaries
- Residue curve *vs*. distillation curve
  - Residue curves: continuous curves
  - Distillation curves: discrete points

- Dashed lines: distillation curves
- Solid lines: residue curves

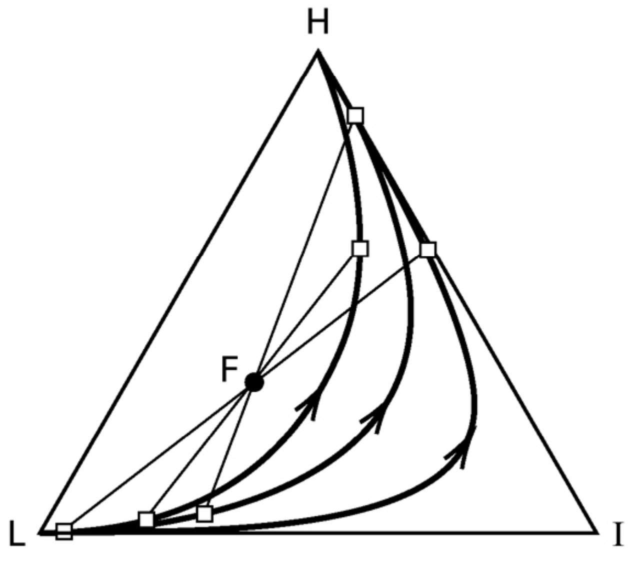


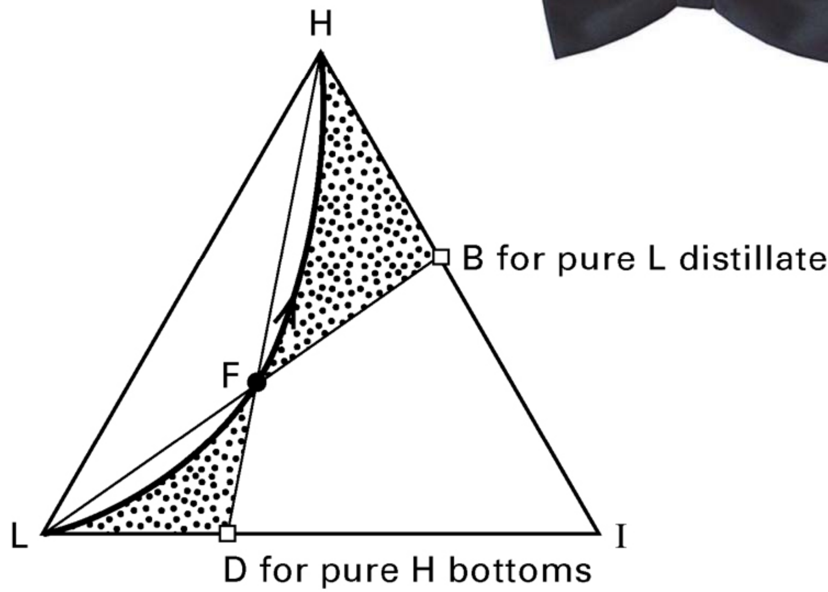
Product-Composition Regions at Total Reflux (1)

- Material balance line

  : a straight line connecting distillate and bottoms compositions must pass through the feed composition

- Feasible-product-composition region
  - two lines limit the possible product range
  - bow-tie region

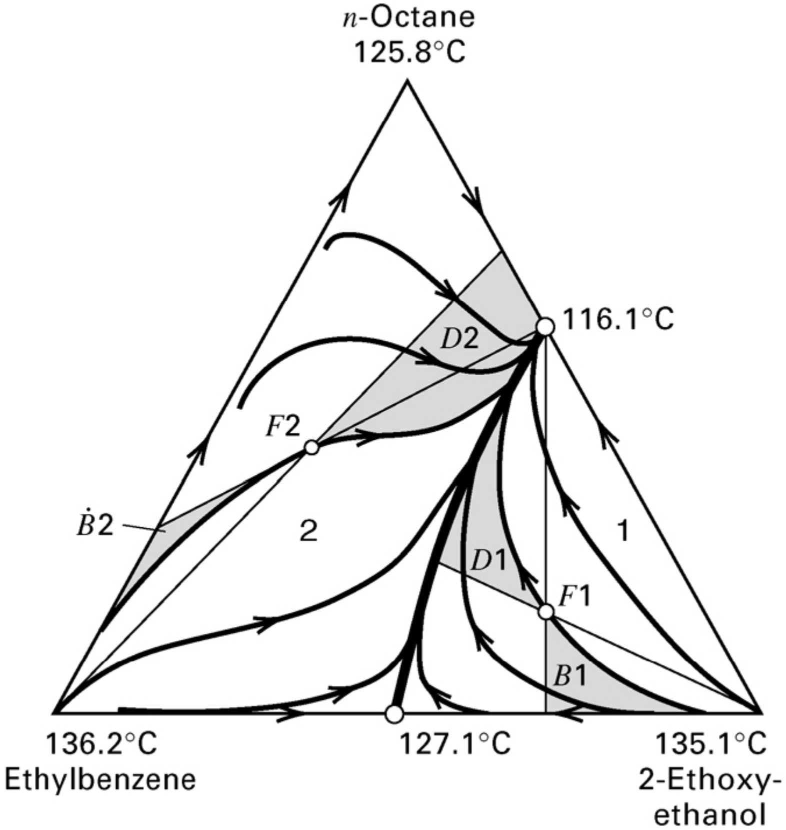




Product–Composition Regions at Total Reflux (2)

- For an azeotropic system, a feasible-product-composition region can be found for each distillation region

Ternary mixture with two minimum-boiling binary azeotropes



Ternary mixture with three binary azeotropes and one ternary azeotrope