Effect of Pressure and Third Component on Azeotropic Composition

December 23, 2009

PreFEED Corporation

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Introduction

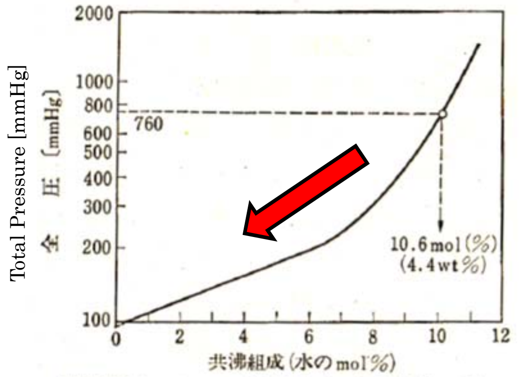
One of the factors that complicate handling distillation separation processes is the azeotropic phenomenon. A system which forms an azeotropic mixture cannot be separated into pure components by ordinary distillation.

Therefore, various measures such as chemical absorption, the addition of a third component, pressure changes, reactive distillation and the like have been devised since long ago to deal with this issue.

Here, we will discuss the effect of pressure and of adding a third component on the azeotropic composition.

Effect of Pressure on Azeotropic Point

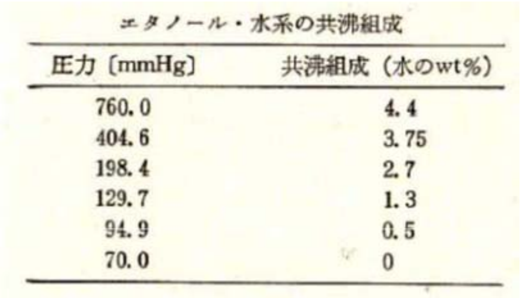
- It is generally known that azeotropic composition varies with external pressure.
- In the ethanol - water system, as the pressure is lowered, the azeotropic composition moves to the pure ethanol side, and when it reaches 70 mmHg, the azeotropic point disappears.
- However, there is little merit in applying this process industrially because when performing distillation separation at 70 mmHg, a large-scale depressurization operation would be required and the top column temperature would be low.



共沸組成：エタノール濃度 89.4 mol% (95.6 wt%)
最低沸点：78.15°C

Azeotropic Composition (Water mol%)
Azeotropic Composition: Ethanol Concentration
89.4 mol%(95.6 wt%)
Minimum Boiling Point: 78.15 C

Azeotropic Composition of Ethanol - Water System
Pressure [mmHg] Azeotropic Composition (Water wt%)



エタノール・水系の共沸組成

圧力〔mmHg〕	共沸組成（水のwt%）
760.0	4.4
404.6	3.75
198.4	2.7
129.7	1.3
94.9	0.5
70.0	0

"Jyouryu Riron to Keisan" (*in Japanese*: Distillation Theory and Calculation), P.276-227, Kogaku-tosho

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Effect of Pressure on Azeotropic Point

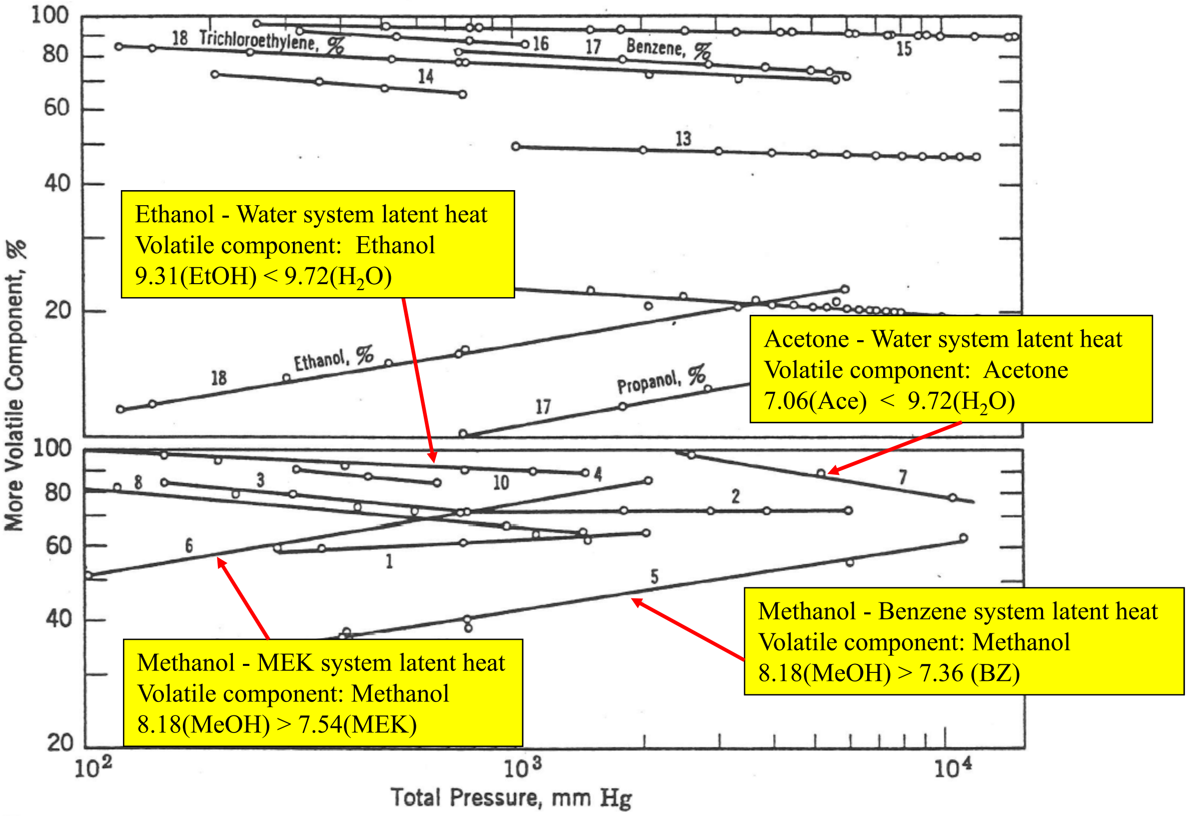
- Based on experimental results, Vrevskii summarizes the effect of pressure on a binary azeotropic mixture as follows.
- In a minimum azeotropic mixture, the proportion of the composition with a large latent heat of vaporization increases with increasing pressure.

In 1940 Vrevskii examined many measured values of binary systems, and as a result, stated the following regarding the influence of pressure.

"When the solution with the highest value of the total pressure curve of the system (the system with the minimum azeotropic mixture) boils without forming two liquid phases, as the temperature rises (naturally the pressure also increases), the relative content in the azeotropic composition of the component with the larger latent heat of vaporization increases. When the solution with the lowest value of the total pressure curve of the system (the maximum azeotropic mixture) boils without forming two liquid phases, as the temperature rises (as the pressure rises), the relative content in the azeotropic composition of the component with the smaller latent heat of vaporization increases."

"Saishin Jyouryuu Kogaku" (*in Japanese*: Latest Distillation Engineering) Hirata Mitsuho, P. 51, Nikkan Kogyo Shimbunsha

Pressure versus Volatile Component Ratio at Azeotropic Point



Ethanol - Water system latent heat
Volatile component: Ethanol
9.31(EtOH) < 9.72(H_2O)

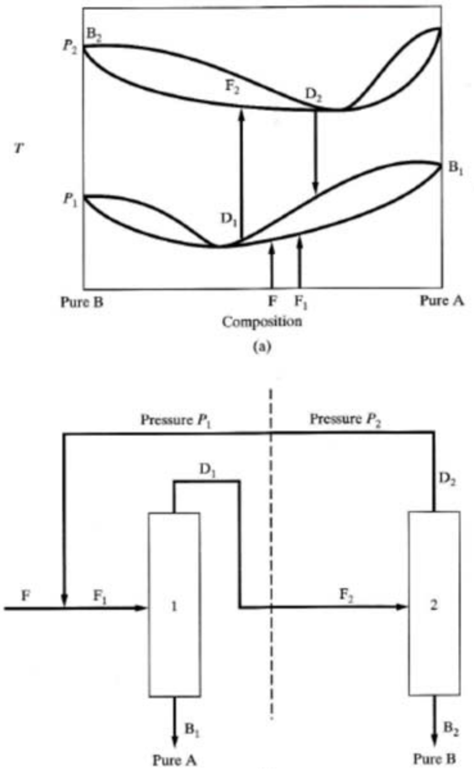
Acetone - Water system latent heat
Volatile component: Acetone
7.06(Ace) < 9.72(H_2O)

Methanol - MEK system latent heat
Volatile component: Methanol
8.18(MeOH) > 7.54(MEK)

Methanol - Benzene system latent heat
Volatile component: Methanol
8.18(MeOH) > 7.36 (BZ)

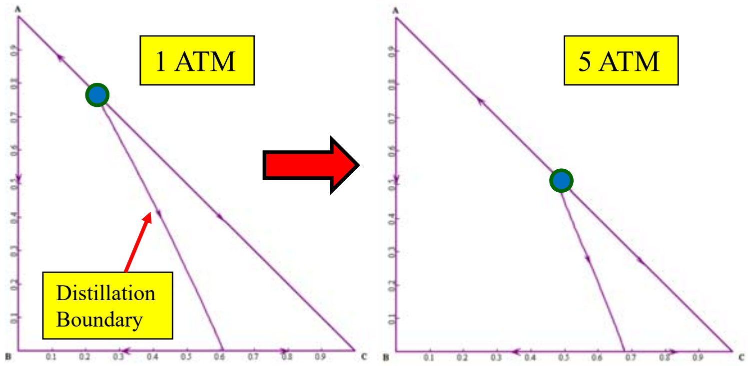
“Azeotropic Distillation I”, D.F. Othmer (verfahrenstechnik, 8 1974, Nr 3)

Pressure Swing Distillation



“Process Design Principles”, P.187, Wiley

Van Winkle (1967) showed that the separation of a binary minimum azeotropic mixture can be performed by pressure-swing (left figure).



1 ATM

5 ATM

Distillation Boundary

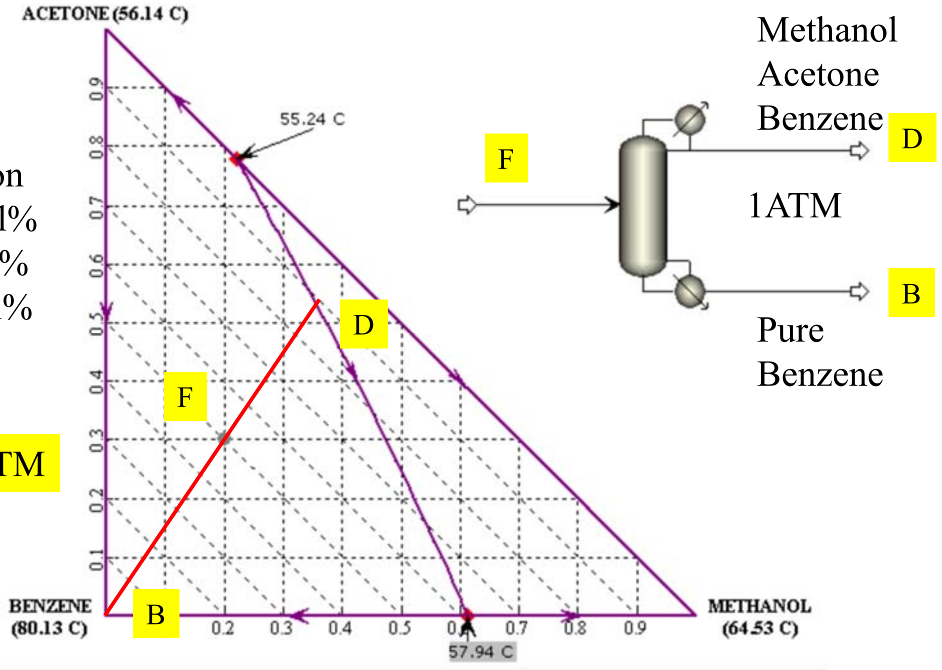
Separation studies in which the distillation boundary moves due to pressure have also been carried out for ternary systems (upper figure).

Pressure Swing : Application Example

- Consider an application for the ternary Methanol-Benzene-Acetone system. We would like to recover a high yield of benzene and methanol, but under normal pressure benzene is contained in the top composition (about 10 mol%).

Feed Composition
Methanol: 20mol%
Acetone: 30 mol%
Benzene: 50 mol%

1ATM

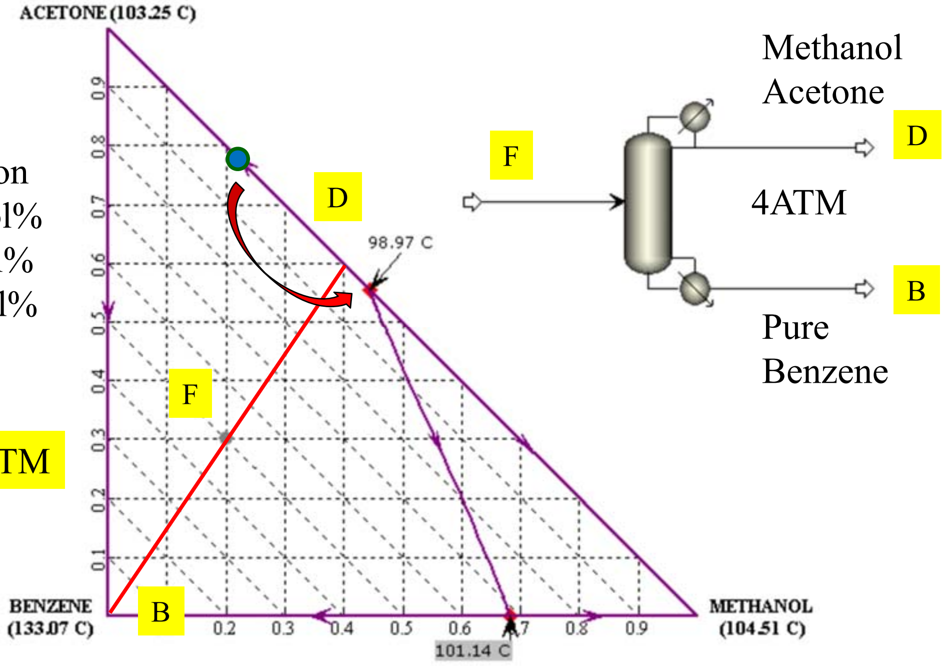


Movement of Distillation Boundary: Distillation Boundary under Pressurization

- By raising the pressure, the distillation boundary moves, and benzene can be recovered without loss.
  However, methanol cannot be recovered under this condition.

Feed Composition
Methanol: 20mol%
Acetone: 30 mol%
Benzene: 50 mol%

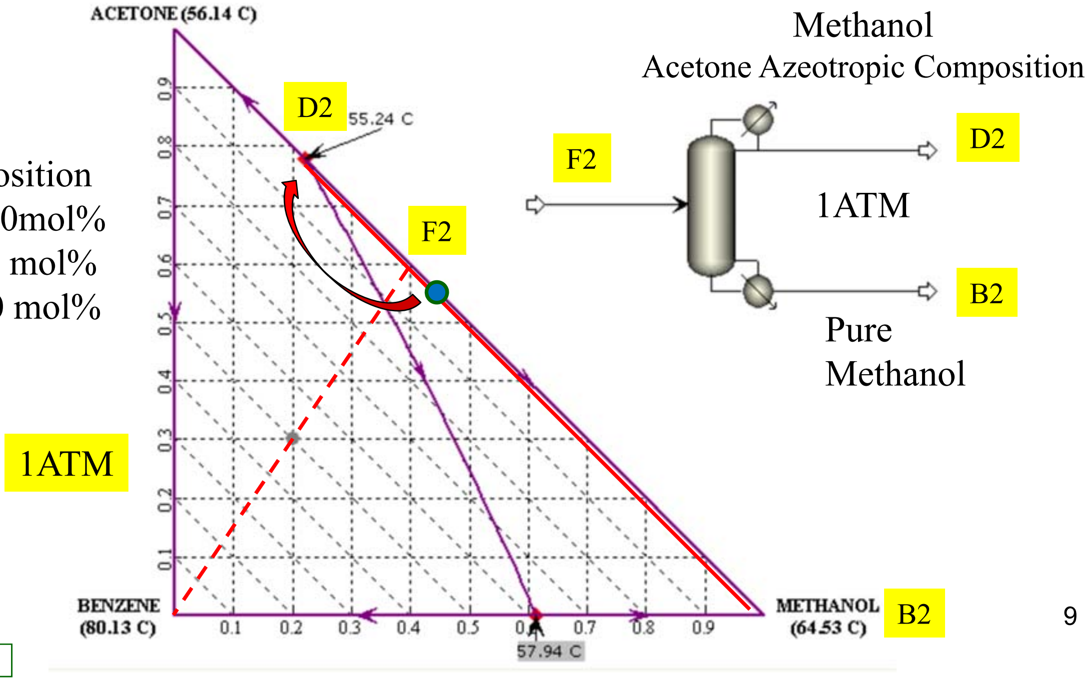
4ATM



Movement of Distillation Boundary:
Distillation Boundary under Normal Pressure

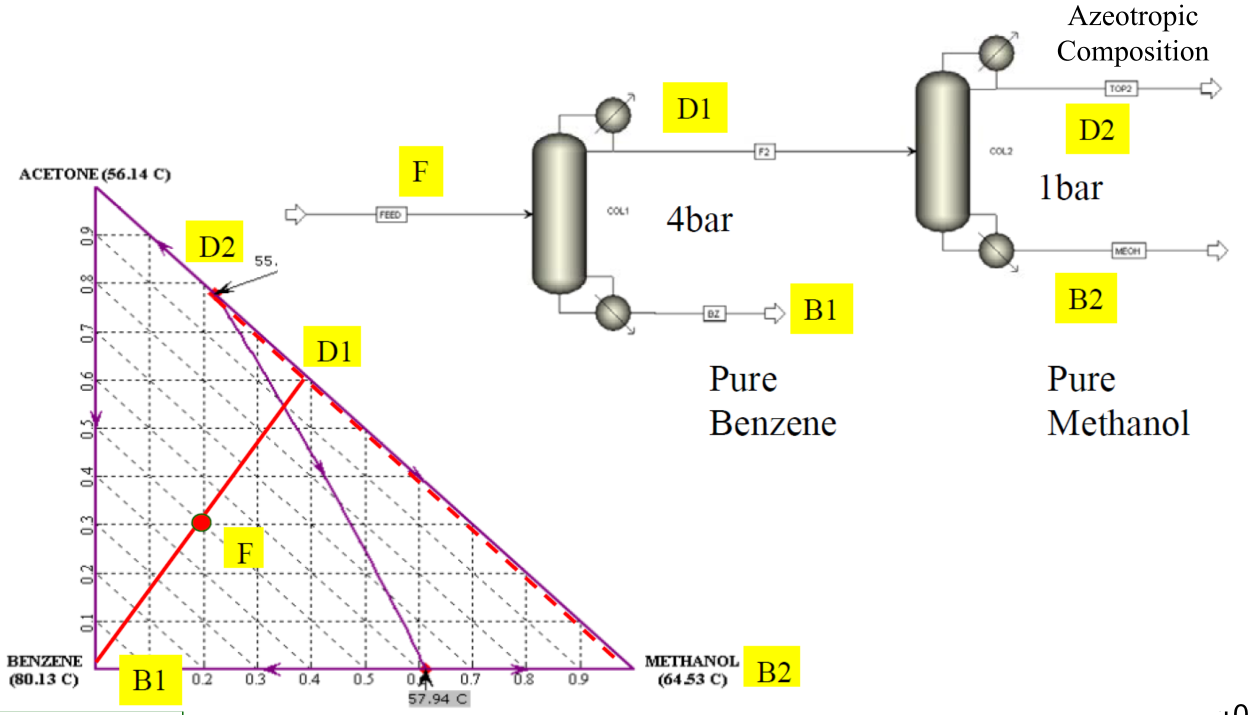
- Next, consider restoring the pressure to the normal pressure. The overhead composition (F2) of the first column becomes the feed of the second column, and in this region it is possible to separate the pure methanol at the BTM. In other words this means that the distillation boundary can be crossed by pressure swing.

Feed Composition
Methanol: 20mol%
Acetone: 30 mol%
Benzene: 50 mol%



Final Flowsheet

- It is possible to obtain both benzene and methanol products with high purity. However, methanol separation entails a loss of azeotropic components.



Effect of Addition of Third Component

- Consider distillation by adding a third component C to an A-B binary azeotropic mixture. When the boiling point of component C is high and it has affinity with component B, component B is captured by component C and becomes difficult to evaporate, and the relative volatility of components A and B increases.
- At this time, the relative volatility is as follows.

$$Py_i = x_i \gamma_i P^o{}_i$$

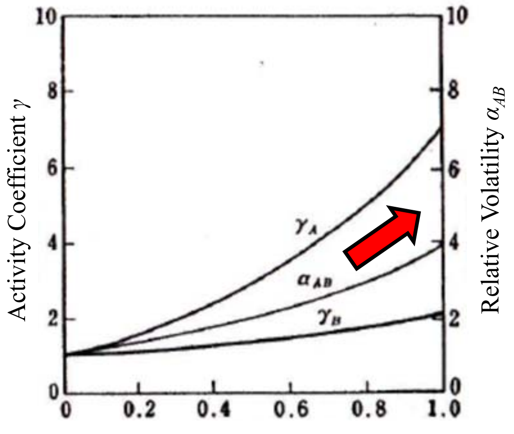
$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P^o{}_i}{P}$$

$$\alpha_{AB} = K_A / K_B = \left(\frac{y_A}{x_A}\right) / \left(\frac{y_B}{x_B}\right) = \left(\frac{\gamma_A}{\gamma_B}\right)\left(\frac{P^o{}_A}{P^o{}_B}\right)$$

P : System pressure

γ_i : Activity coefficient of component i

$P^o{}_i$: Vapor pressure of component i



x_B Solvent Concentration in Liquid Phase (Mole Fraction)

“Saishin Jyouryuu Kogaku” (in Japanese: Latest Distillation Engineering) Hirata Mitsuho, P. 107, Nikkan Kogyo Shimbunsha

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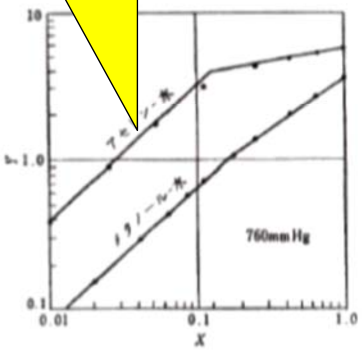
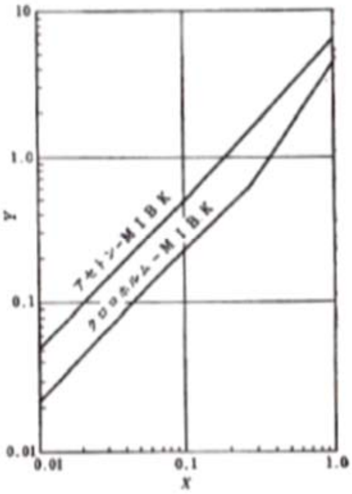
Effect of Addition of Third Component

Hirata *et al.* found that Y/X is constant in many systems between 0.01 <X <0.1 when the concentration of the third component is high (> 80 mol%) .
That is, in the region where the concentration of the third component is sufficiently high, it is expected that the relationship between A-B will be like that of an ideal solution.

Linear Relationship
$Y=\alpha X$



Acetone (1) - Water (3) System and Methanol (2) - Water (3) System X-Y Plots



Acetone (1) - Methyl Isobutyl Ketone (3) System and
Chloroform (2) - Methyl Isobutyl Ketone (3) System X-Y Plots

Assuming that $X = \frac{x_1}{x_2}$, $Y = \frac{y_1}{y_2}$

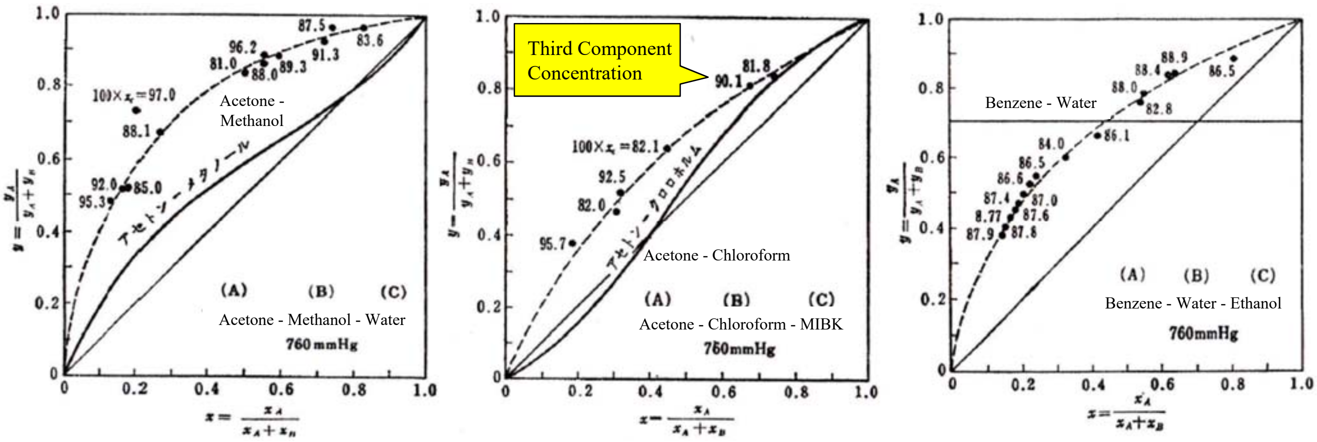
$$\alpha = \frac{y_1}{x_1} \Big/ \frac{y_2}{x_2} = \frac{y_1}{y_2} \Big/ \frac{x_1}{x_2} = \frac{Y}{X}$$

$$Y = \alpha X$$

“Saishin Jyouryuu Kogaku” (in Japanese: Latest Distillation Engineering) Hirata Mitsuho, P. 110, Nikkan Kogyo Shimbunsha

Behavior of Third Component in High Concentration Region

- For the acetone-methanol minimum azeotropic mixture, the acetone-chloroform maximum azeotropic mixture, and the benzene-water heterogeneous mixture, the azeotropic point of the pseudo binary system disappears by addition of a third component and the relative volatility greatly increases.



- When the concentration of the third component (C) is sufficiently high, it can be considered that C becomes dominant around components A and B, and that the interaction between A and B decreases.

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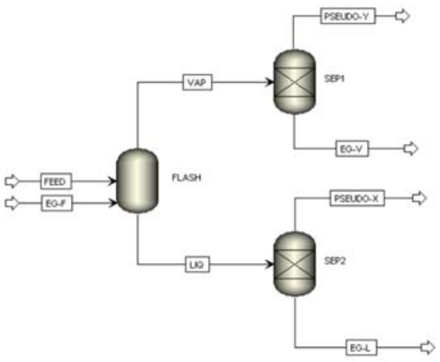
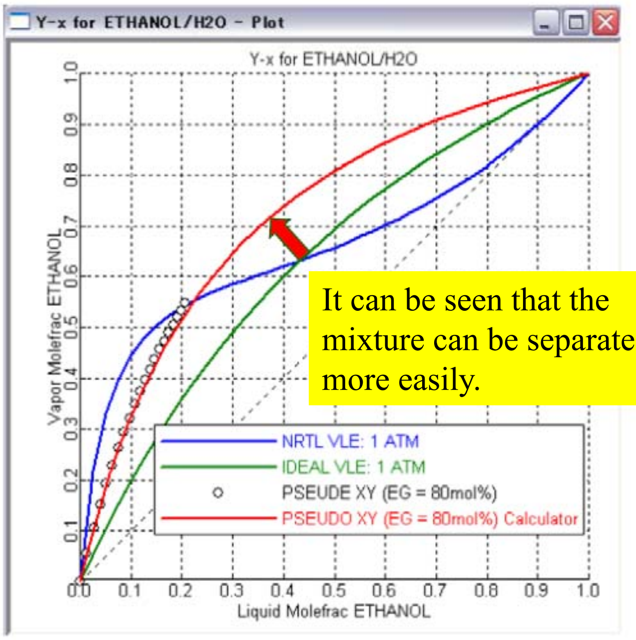
Behavior of Third Component in High Concentration Region

- Consider an example in which ethylene glycol (EG) is added in an amount of 80 mol% to an ethanol-water azeotropic mixture. A pseudo binary system in which EG was removed from the mixture was examined, and similar results were obtained.





It can be seen that the mixture can be separated more easily.

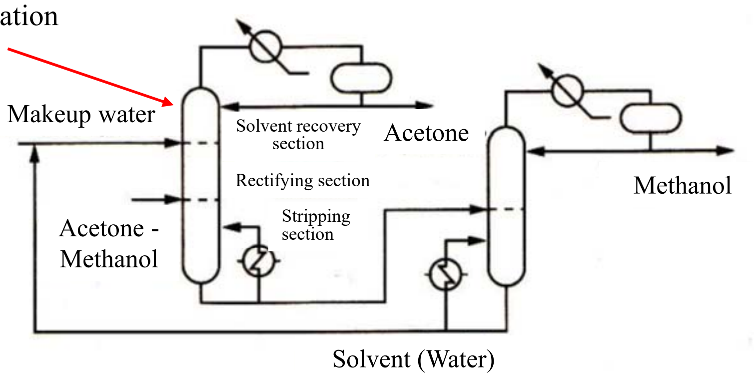
Extractive distillation is a technique that makes use of this principle for separating pure components from azeotropic mixtures.

Extractive Distillation

- Extractive distillation consists of an extractive distillation column and a solvent recovery column. The extractive distillation column can be considered to be divided, depending on the solvent supply stage and the raw material supply stage, into a solvent recovery section, a rectifying section and a stripping section.

Purposes of solvent recovery section:
Achieve a specified solvent concentration and prevent contamination of the distillate.

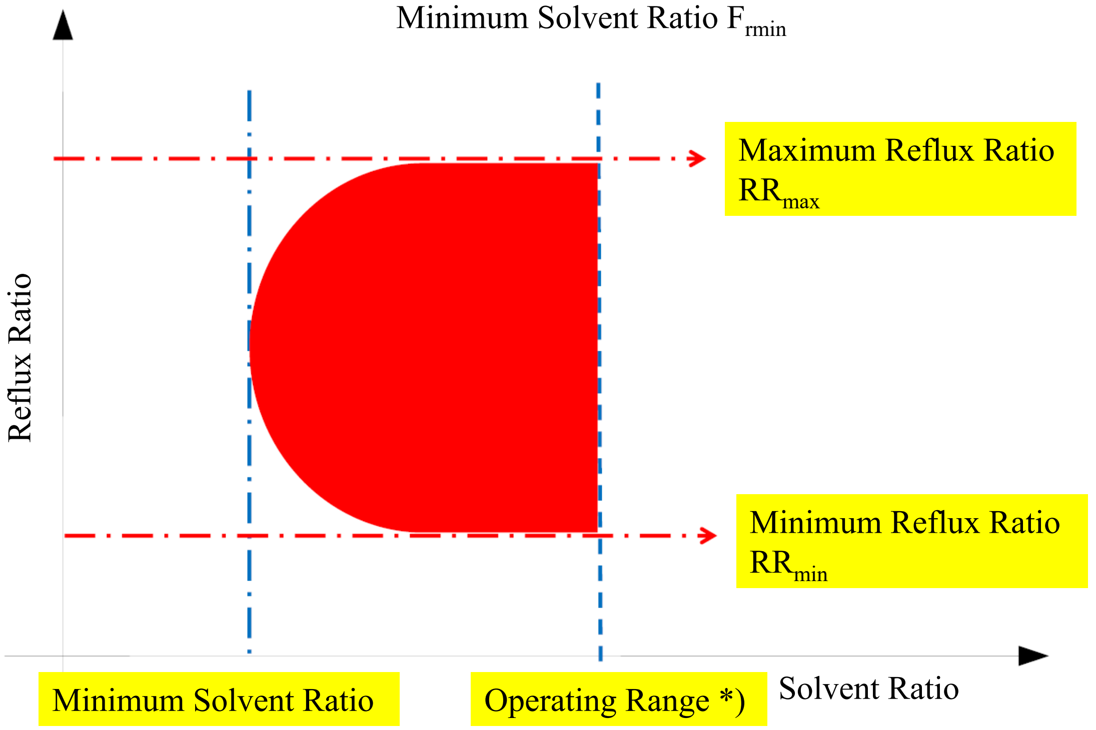
Note: In extractive distillation, when there is excessive reflux, the separation efficiency decreases because the product concentration becomes high (the solvent concentration becomes low), and as a result the extractive effect of the solvent is lost.



Methanol-Acetone based Extractive Distillation System with Water as an Entrainer

“Kagaku Kogaku Binran, 6th ed.” (*in Japanese*: Chemical Engineering Handbook), P.553

Relationship between Solvent Ratio and Reflux Ratio



*) As a guide should be 1.7 times or more the minimum solvent ratio

Conclusion

- Azeotropic point and distillation boundaries move due to pressure fluctuations. In that case, the direction of azeotropic change due to the pressure fluctuation of the system can be predicted based on the magnitude of the latent heat of vaporization.
- The relative volatility of two components increases as the concentration of a third component increases. This property is not limited to azeotropic mixtures, and it can be applied to systems that form tangent azeotropes as well as systems with low relative volatilities.