물-에탄올 공비증류공정의 최적화

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조 정 호

목 차: (1)

목　차: (2)

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공비 혼합물을 형성하는 이성분계의 분리

1. 공비 혼합물을 형성하는 이성분계의 분리

1.1 공비혼합물을 형성하는 이성분계의 종류 및 분리방법 개요:
1.2 공비점 분리제를 사용하는 공비증류공정
1.3 용매를 사용하는 추출증류공정
1.4 압력변환 증류공정
1.5 초임계 이산화탄소를 이용한 초임계 추출공정
1.6 진공증류공정
1.7 투과증발공정

1.1 공비 혼합물을 형성하는 이성분계의 종류 및 분리방법 개요

- Some azeotropic distillation cases:

No.	**Components to be separated**	**Entrainers**
1	Ethanol/water; isopropanol/water; tert-butanol/water	Benzene, toluene, hexane, cyclohexane, methanol, normal pentane
2	Acetone/n-heptane	Toluene
3	Acetic acid/water	N-butyl acetate
4	Isopropanol/toluene	Acetone

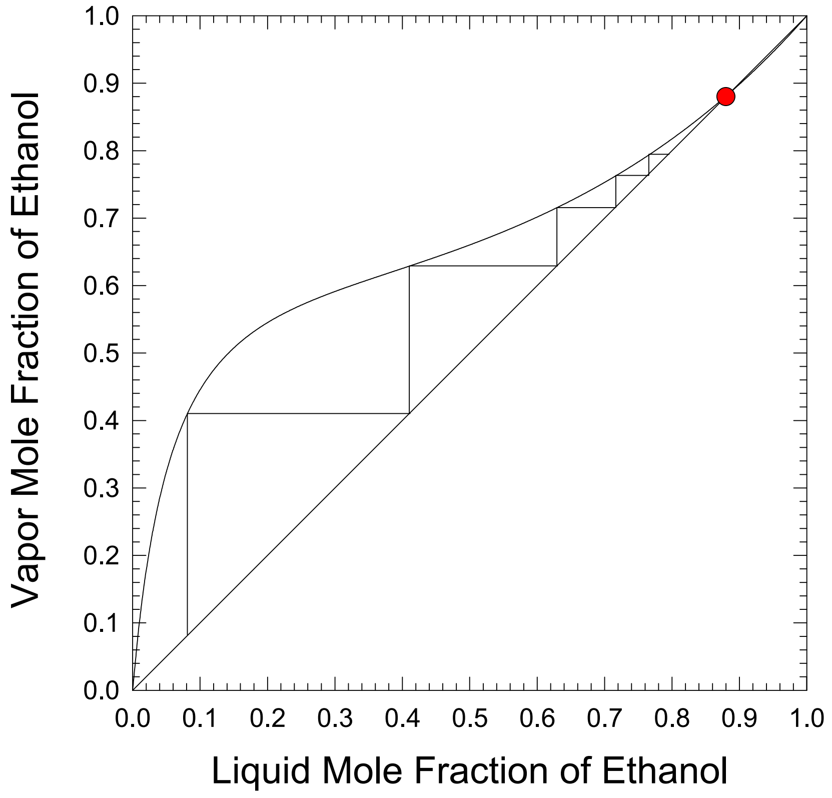
- 위의 책(책은 내가 pdf 파일로 전달해 줄 것 임.)의 참고문헌을 찾아서 박회경 박사가 모두 논문을 작성할 수 있도록 준비할 것

1.1 공비 혼합물을 형성하는 이성분계의 종류 및 분리방법 개요

- Shift the Azeotropic Point by Changing Pressure
  - Pressure Swing Distillation
- Supercritical Fluid Extraction Using Supercritical CO_2 Solvent
- Pervaporation Method: Proposed by SKEC
- Vacuum Distillation
  - Azeotrope between ethanol and water disappears at 11.5kPa.
- Add the Third Component.
  - Azeotropic Distillation: Entrainer (Benzene, CHX, NC5)
  - Extractive Distillation: Solvent (Ethylene Glycol, DMSO)

1.2 공비점 분리제를 사용하는 공비증류공정

Ethanol / Water System



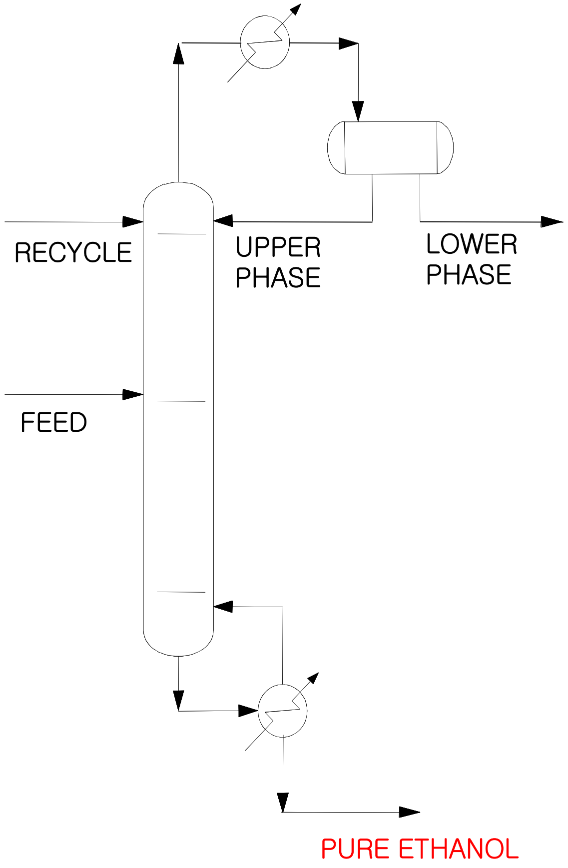
- ➢ Limit of Azeotropic Distillation
  - ✓ Distillation range is restricted by the azeotropic point.
  - ✓ Binary azeotropic mixtures, such as ethanol/water and IPA/water, can be separated into their pure components by distillation by the addition of a third component, so called the entrainer, which forms a ternary azeotrope with a lower boiling point than any binary azeotrope

1.2 공비점 분리제를 사용하는 공비증류공정: 원리 (1)

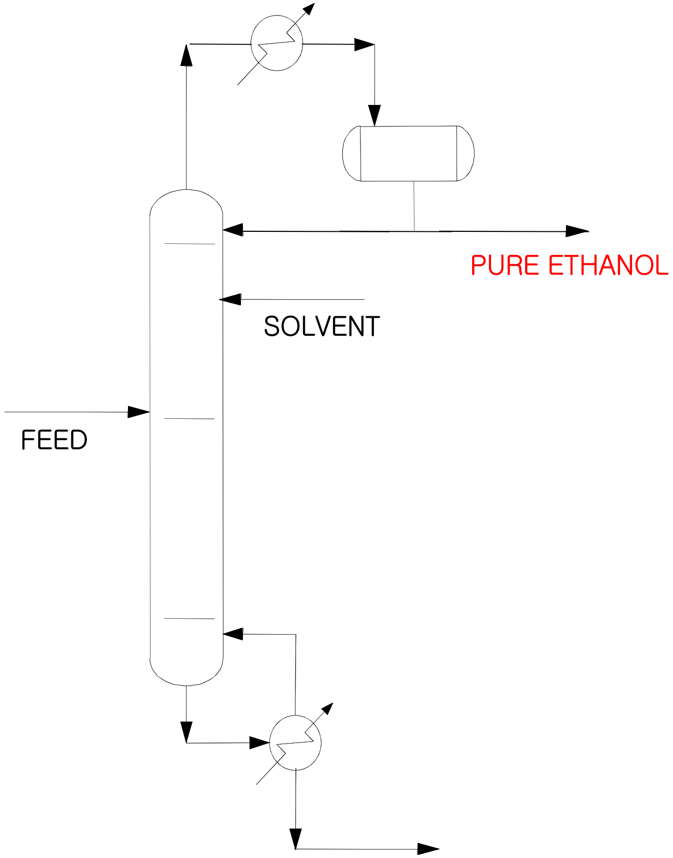
- Azeotropic distillation
  - By forming a ternary heterogeneous azeotrope lower than any other binary azeotropic temperatures, nearly pure ethanol can be obtained as a bottom product in an azeotropic distillation column.
  - Ethanol is obtained *as a bottom product* from an azeotropic distillation column using an entrainer such as benzene or normal pentane.
- Extractive distillation
  - By adding a solvent which is exclusively familiar with a wanted component in a feed mixture, a desired component can be obtained in an extractive distillation column overhead.
  - Ethanol is obtained *as a top product* from an extractive distillation with ethylene glycol solvent.

1.2 공비점 분리제를 사용하는 공비증류공정: 비교

- 공비증류공정과 추출증류공정의 원리 비교

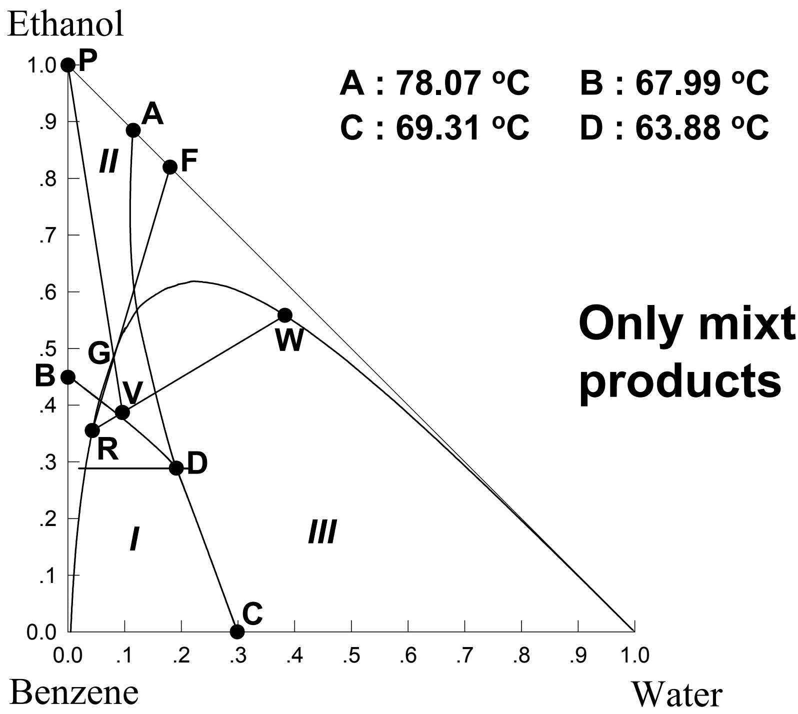


Azeotropic Distillation



Extractive Distillation

1.2 공비점 분리제를 사용하는 공비증류공정: 원리(2)



Only mixtures in region *II* will give the desired products of pure ethanol as a bottom product.

- Aqueous ethanol can be separated into their pure components by distillation by the addition of a third component, so called the entrainer, which forms a ternary heterogeneous azeotrope with a lower than any other binary azeotropes.

1.3 용매를 사용하는 추출증류공정: 원리

➢ 추출증류공정에 적용 가능한 시스템들:

No.	Component 1	Component 2	Solvents
1	Alcohol (ethanol or isopropanol)	Water	Ethylene glycol, DMSO
2	Acetic acid	Water	Tributyl amine
3	Acetone	Water	Water, ethylene glycol
4	Methanol	Methanol	Water
5	Propylene	Propane	ACN(Acetonitrile)
6	C4 hydrocarbons	C4 hydrocarbons	ACN, Acetone, DMF, NMP
7	Tetrahydrofuran	Water	Ethylene glycol, DMSO
8	C5 hydrocarbons	C5 hydrocarbons	DMF
9	Aromatics	Non-aromatics	DMF, NMP, NFM
10	Methanol	DMC	2-Ethoxyethanol 4-Methyl-2-pentanone

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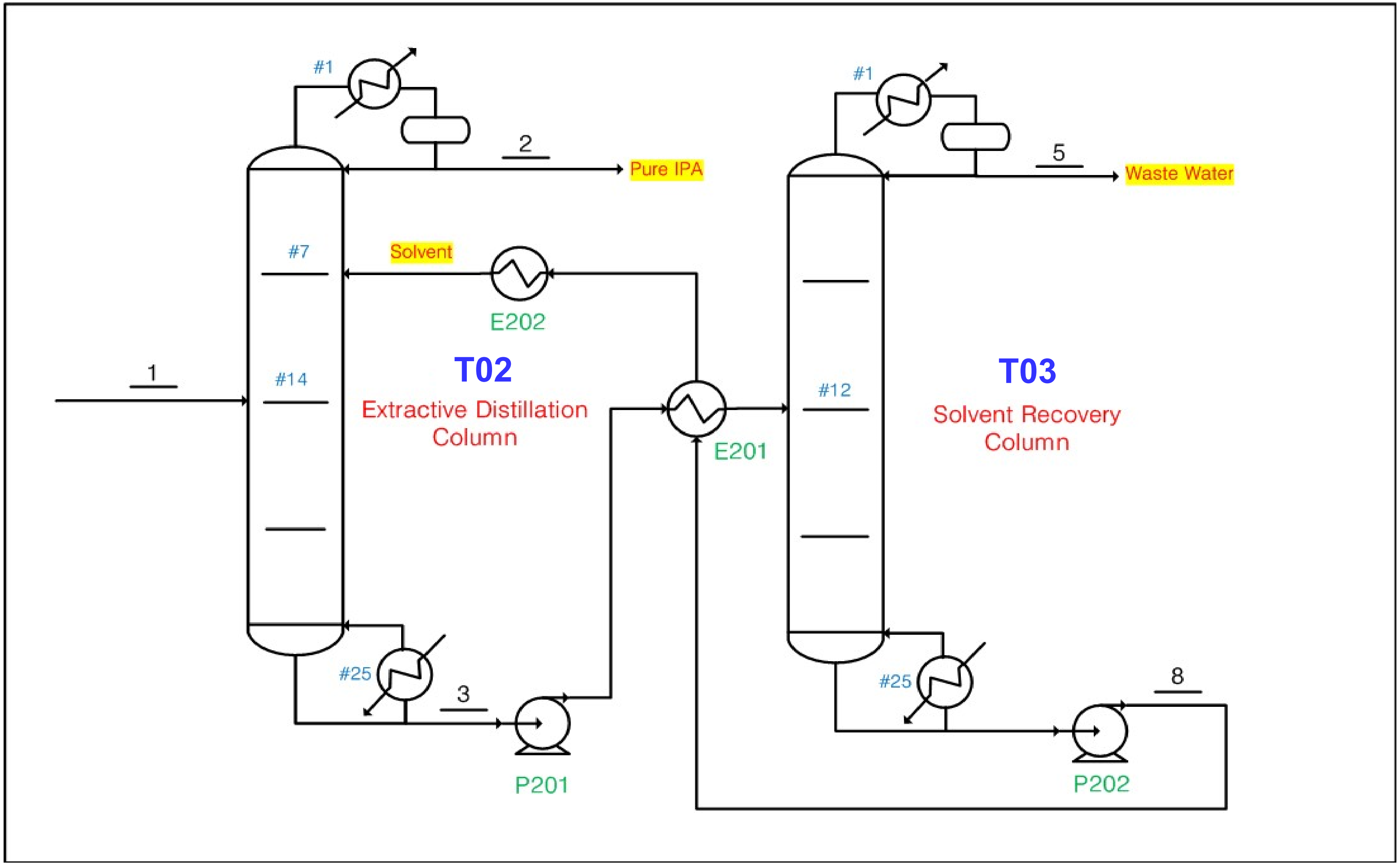
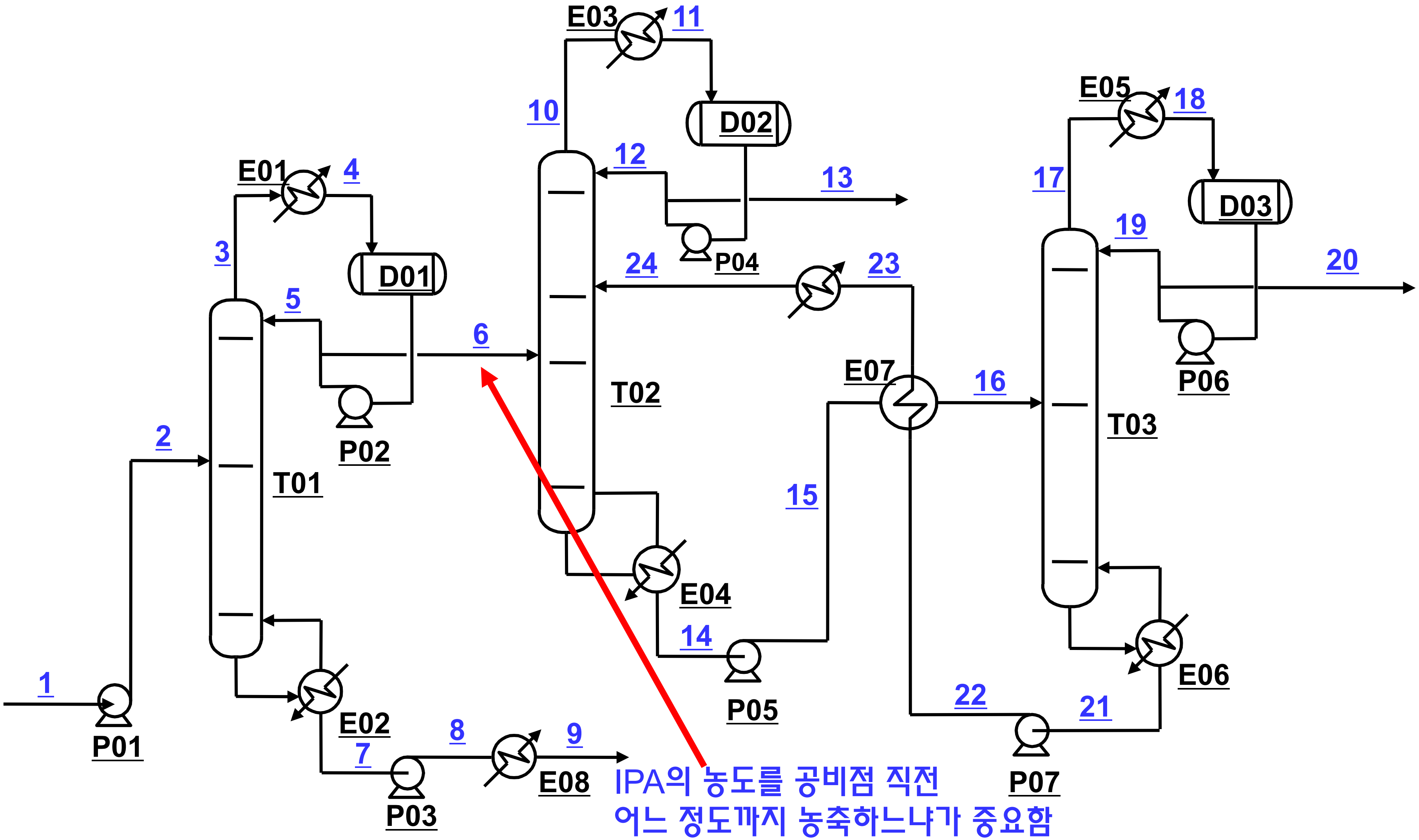
1.3 용매를 사용하는 추출증류공정: 원리

- IPA Dehydration Using Solvent: Two-columns configuration



1.3 용매를 사용하는 추출증류공정: 원리

- IPA Dehydration Using Solvent: Three-columns configuration

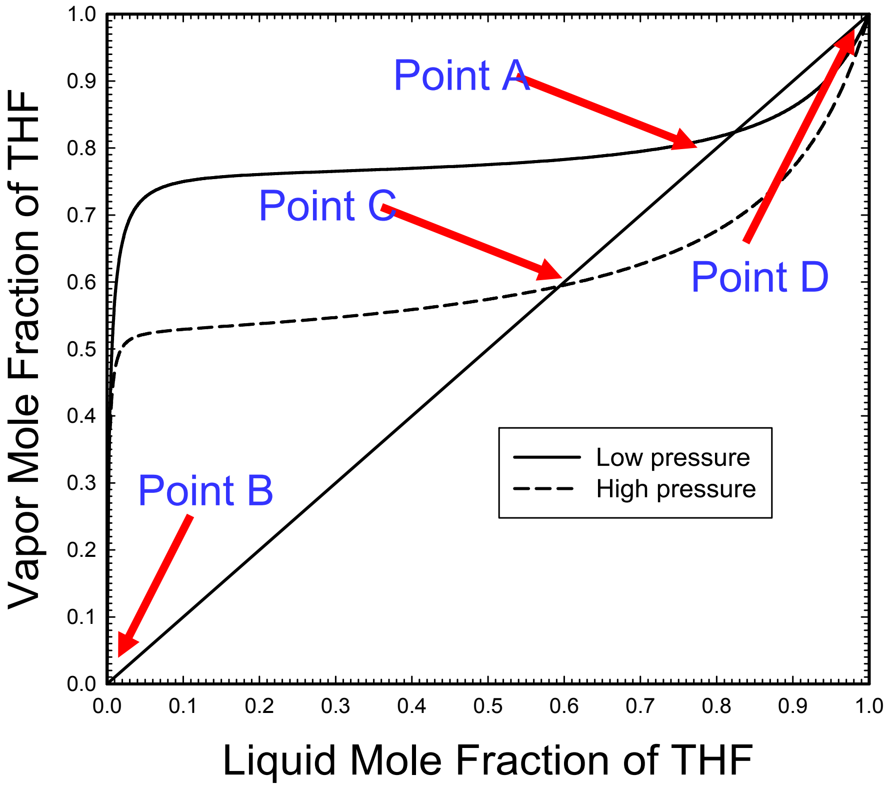


IPA의 농도를 공비점 직전 어느 정도까지 농축하느냐가 중요함

1.4 압력변환 증류공정: 원리

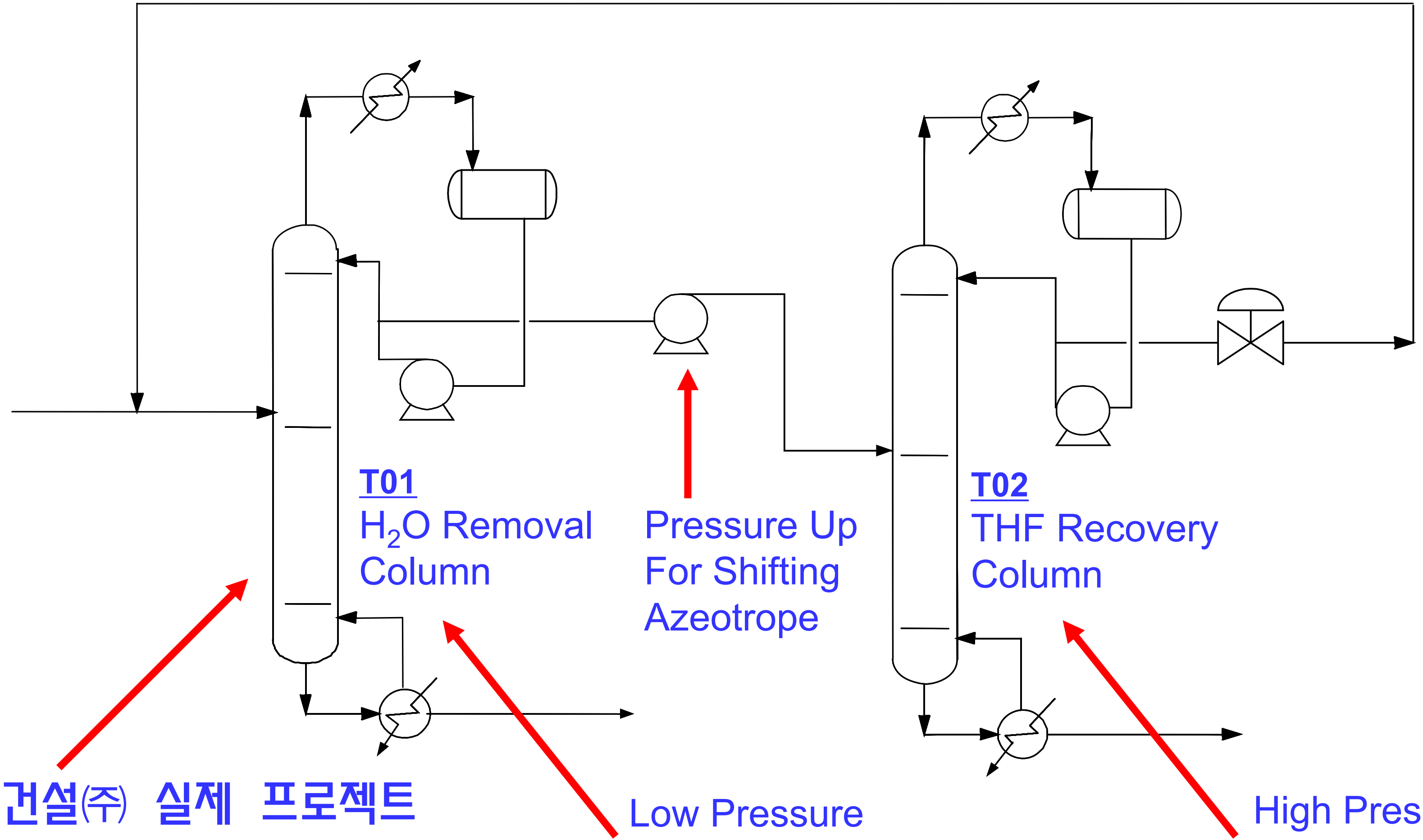
- 압력변화에 따라서 공비조성이 민감하게 변화하는 계에 적용할 수 있다.

THF / Water System



- Distillation range is restricted by the azeotropic point.
- Pressure-sensitive binary azeotropic mixture, such as THF and water system can be separated into their pure components by pressure swing distillation.
- 낮은 압력에서 Point A까지 농축함.
- 높은 압력으로 변경시키면, Point D까지 얻을 수 있음.

1.4 압력변환 증류공정: 공정의 구성



T01
H_2O Removal
Column

Pressure Up
For Shifting
Azeotrope

T02
THF Recovery
Column

한화건설㈜ 실제 프로젝트
원용덕 상무님 과제

Low Pressure
Column

High Pressure
Column

1.4 압력변환 증류공정: 예

- **압력변환 증류공정에 적용 가능한 예**

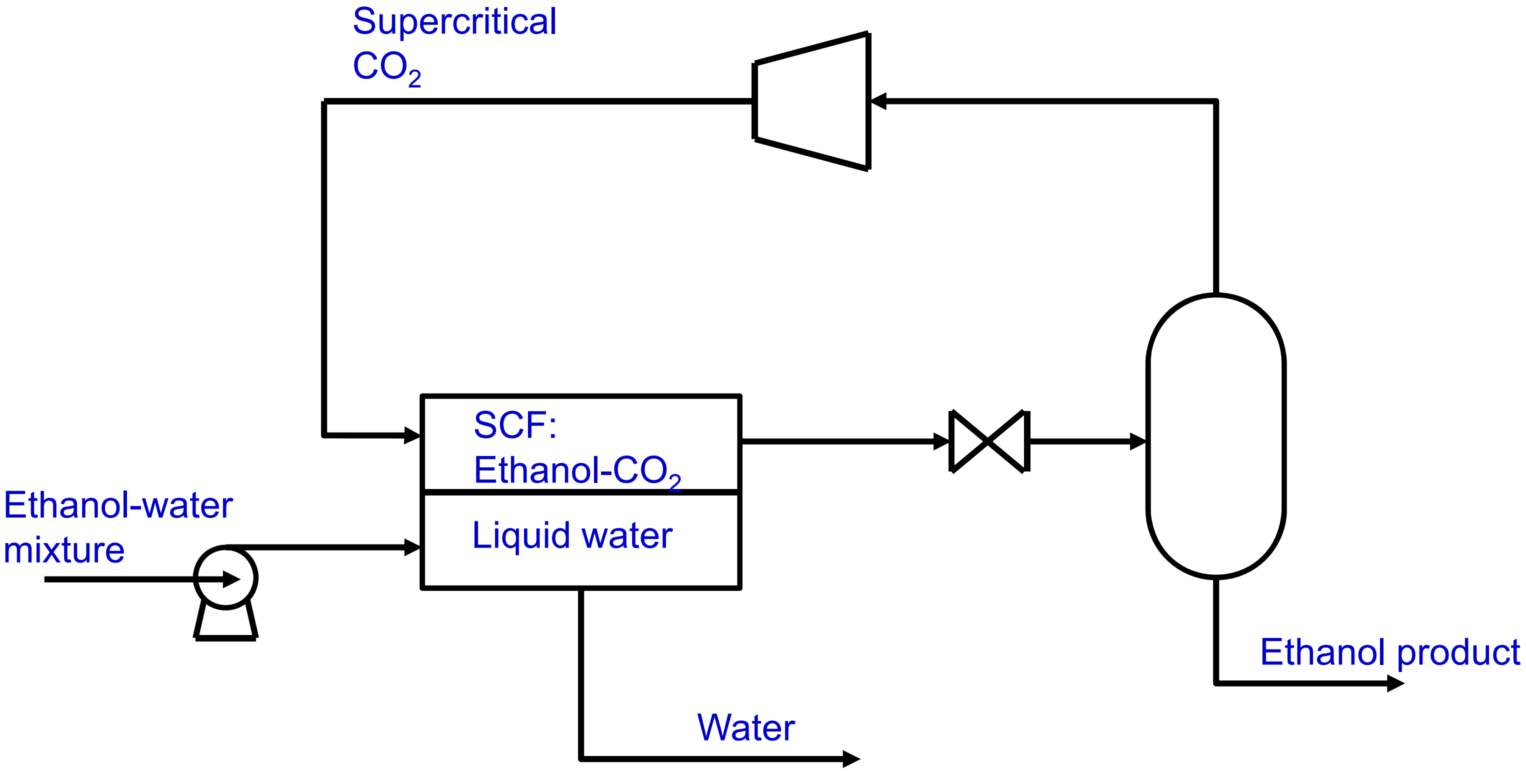
No.	Component 1	Component 2	BIP's in P2	BIP's in A+
1	Carbon dioxide	Ethylene	○	X
2	Hydrochloric acid	Water	○	X
3	Water	Acetonitrile	○	○
4	Water	Ethanol	○	○
5	Water	Acrylic acid	○	○
6	Water	Acetone	○	○
7	Water	Propylene oxide	○	○
8	Water	Methyl acetate	○	○
9	Water	Propionic acid	○	X
10	Water	2-methoxyethanol	○	○
11	Water	2-butanone (MEK)	○	○
12	Water	Tetrahydrofuran (THF)	○	○
13	Carbon tetrachloride	Ethanol	○	○
14	Carbon tetrachloride	Ethyl acetate	○	○
15	Carbon tetrachloride	Ethyl acetate	○	○
16	Carbon tetrachloride	Benzene	○	○
17	Methanol	Acetone	○	○
18	Methanol	2-butanone (MEK)	○	○
19	Methanol	Methyl propyl ketone	○	○

1.4 압력변환 증류공정: 예

➢ **압력변환 증류공정에 적용 가능한 예**

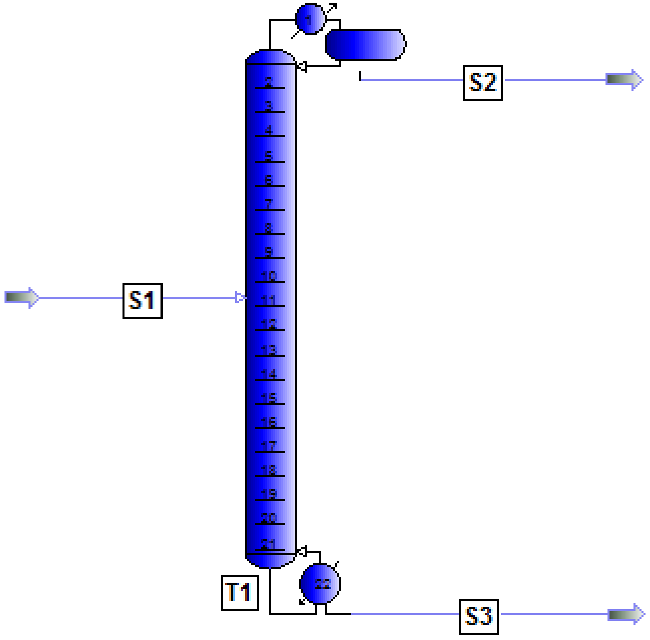
No.	Component 1	Component 2	BIP's in P2	BIP's in A+
20	Methanol	Methyl acetate	○	○
21	Methanol	Ethyl acetate	○	○
22	Methanol	Benzene	○	○
23	Methanol	Dichloromethane	○	○
24	Methylamine	Trimethylamine	○	○
25	Ethanol	Dioxane	○	○
26	Ethanol	Benzene	○	○
27	Ethanol	Heptane	○	○
28	Dimethylamine	Trimethylamine	○	X
29	2-propanol	Benzene	○	○
30	Propanol	Benzene	○	○
31	Propanol	Cyclohexane	○	X
32	2-butanone (MEK)	Benzene	○	○
33	2-butanone (MEK)	Cyclohexane	○	○
34	Isobutyl alcohol	Benzene	○	○
35	Benzene	Cyclohexane	○	○
36	Benzene	Hexane	○	○
37	Phenol	Butyl acetate	○	○
38	Aniline	Octane	X	X

1.5 초임계 이산화탄소를 이용한 초임계 추출공정



1.6 진공증류공정:

- Azeotrope between ethanol and water disappears below the pressure, 0.1 bar.



```
STREAM ID                                 S1            S2            S3
       NAME
       PHASE                          LIQUID        LIQUID        LIQUID
   THERMO ID                         IDEA01        IDEA01        IDEA01

FLUID MOLAR PERCENTS
   1  ETHANOL                       60.0000       99.8060        0.2910
   2  WATER                         40.0000        0.1940       99.7090

TOTAL RATE, KG-MOL/HR              100.0000       60.0000       40.0000

TEMPERATURE, C                      25.0000       79.2444      109.2417
PRESSURE, BAR                        2.5000        1.0500        1.4000
ENTHALPY, M*KCAL/HR                  0.0567        0.1355        0.0790
MOLECULAR WEIGHT                    34.8475       46.0146       18.0969
MOLE FRAC VAPOR                      0.0000        0.0000        0.0000
MOLE FRAC LIQUID                     1.0000        1.0000        1.0000
```

2

공비 혼합물의 분류

2. 공비 혼합물의 분류

2.1 공비 혼합물의 정의

2.2 Homogeneous azeotrope와 heterogeneous azeotrope

2.3 이성분계 공비와 삼성분계 공비 혼합물

2.4 실험적인 공비온도 및 조성과 계산 결과 사이의 비교

2.1 공비 혼합물의 정의

- Azeotrope:
  - Boiling at the same temperature and composition both at the vapor and the liquid phases
- 공비(共沸)
  - 일정한 온도에서 용액의 성분비와 증기의 성분비가 같아지는 현상을 나타내는 것을 말하며, 이러한 상태의 조성을 공비조성이라고 한다.

2.2 균일 공비와 불균일 공비 및 이성분계 공비와 삼성분계 공비

- Homogeneous azeotrope:
  - 액상이 서로 다른 액상으로 상 분리가 일어나지 않는다.
  - 예: IPA-Water, Benzene-IPA
- Heterogeneous azeotropes:
  - 액상의 서로 다른 두 개의 액상으로 상 분리가 일어난다.
  - 종류: Binary and ternary heterogeneous azeotropes
  - 예: Water-Benzene, IPA-Water-Benzene

2.3 실험적인 공비온도 및 조성과 계산 결과 사이의 비교: (1)

- Binary homogeneous azeotrope: “exp vs. ***P2***”

Component	**BP(^{o}C)**	**Azeotropic Temperature (^{o}C)**	**Azeo. Weight %**
IPA Water	82.3 100.0	80.4	87.8 12.2
Benzene Ethanol	80.1 82.3	71.5	66.7 33.3

- Binary heterogeneous azeotrope: “exp vs. ***P2***”

Component	**BP(^{o}C)**	**Azeotropic Temperature (^{o}C)**	**Azeo. Weight %**	**Upper Layer**	**Lower Layer**
IPA Water	80.1 100.0	71.5 ()	66.7 33.3	99.94 0.06	0.07 99.93

- Ternary heterogeneous azeotrope: “exp vs. ***P2***”

Component	**BP(^{o}C)**	**Azeotropic Temperature (^{o}C)**	**Azeo. Weight %**	**Upper Layer**	**Lower Layer**
Benzene IPA Water	80.1 82.3 100.0	65.7 ()	72.0 19.8 8.2	77.5 20.2 2.3	0.5 14.4 85.1

2.3 실험적인 공비온도 및 조성과 계산 결과 사이의 비교: (2)

- Binary homogeneous azeotrope: "exp ***vs. Aspen Plus***"

Component	**BP(°C)**	**Azeotropic Temperature (°C)**	**Azeo. Weight %**
IPA Water	82.3 100.0	80.4	87.8 12.2
Benzene IPA	80.1 82.3	71.5	66.7 33.3

- Binary heterogeneous azeotrope: "exp ***vs. Aspen Plus***"

Component	**BP(°C)**	**Azeotropic Temperature (°C)**	**Azeo. Weight %**	**Upper Layer**	**Lower Layer**
Benzene Water	80.1 100.0	71.5 ()	66.7 33.3	99.94 0.06	0.07 99.93

- Ternary heterogeneous azeotrope: "exp ***vs. Aspen Plus***"

Component	**BP(°C)**	**Azeotropic Temperature (°C)**	**Azeo. Weight %**	**Upper Layer**	**Lower Layer**
Benzene IPA Water	80.1 82.3 100.0	65.7 ()	72.0 19.8 8.2	77.5 20.2 2.3	0.5 14.4 85.1

3

올바른 열역학 모델식의 선정

3. 올바른 열역학 모델식의 선정

3.1 기액 상평형과 액액 상평형 원리
3.2 활동도계수와 퓨개시티계수의 정의
3.3 One constant Margules 모델식
3.4 van Laar 모델식
3.5 Wilson 모델식과 Local composition concept
3.6 NRTL 모델식
3.7 UNIQUAC 모델식
3.8 UNIFAC 모델식

3.1 기액 상평형과 액액 상평형 원리

- Four criteria for equilibria:

Situation	Condition
$T^{\alpha} = T^{\beta}$	Thermal Equilibrium
$P^{\alpha} = P^{\beta}$	Mechanical Equilibrium
$\mu_i^{v} = \mu_i^{l}$, $\mu_i^{l1} = \mu_i^{l2}$	Phase Equilibria (VLE, LLE)
$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$	Chemical Equilibrium

- Fugacity (or chemical potential) is defined as an escaping tendency of a component '*i*' in a certain phase into another phase.

3.1 기액 상평형과 액액 상평형 원리

- Vapor-liquid equilibrium calculations

The basic relationship for every component in vapor-liquid equilibrium is:

$$\hat{f}_i^{\,v}\left(T, P, y_i\right) = \hat{f}_i^{\,l}\left(T, P, x_i\right) \qquad (1)$$

where

$\hat{f}_i^{\,v}$: the fugacity of component i in the vapor phase

$\hat{f}_i^{\,l}$: the fugacity of component i in the liquid phase

3.1 기액 상평형과 액액 상평형 원리

- There are two methods for representing liquid fugacities.
  - Equation of state method
  - Liquid activity coefficient method

3.1 기액 상평형과 액액 상평형 원리

- The equation of state method defines fugacities as:

$$\hat{f}_i^{\,v} = \hat{\phi}_i^{v} y_i P \tag{2}$$

$$\hat{f}_i^{\,l} = \hat{\phi}_i^{l} x_i P \tag{3}$$

where:

ϕ_i^v	is the vapor phase fugacity coefficient
ϕ_i^l	is the liquid phase fugacity coefficient
y_i	is the mole fraction of i in the vapor
x_i	is the mole fraction of i in the liquid
P	is the system pressure

3.1 기액 상평형과 액액 상평형 원리

- We can then rewrite equation 1 as:

$$\hat{\phi}_i^v y_i = \hat{\phi}_i^l x_i \qquad (4)$$

- This is the standard equation used to represent vapor-liquid equilibrium using the equation-of-state method.

- ϕ_i^v and ϕ_i^l are both calculated by the equation-of-state.

- Note that K-values are defined as:

$$K_i = \frac{y_i}{x_i} \qquad (5)$$

3.1 기액 상평형과 액액 상평형 원리: 활동도계수(VLE)

The activity coefficient method defines liquid fugacities as:

$$\hat{f}_i^{\,l} = \gamma_i x_i f_i^{\,0} \qquad (6)$$

The vapor fugacity is the same as the EOS approach:

$$\hat{f}_i^{\,v} = \hat{\phi}_i^{\,v} y_i P \qquad (7)$$

where:

γ_i is the liquid activity coefficient of component *i*

$f_i^{\,0}$ is the standard liquid fugacity of component *i*

$\hat{\phi}_i^{\,v}$ is calculated from an equation-of-state model

We can then rewrite equation 1 as:

$$\hat{\phi}_i^{\,v} y_i P = x_i \gamma_i f_i^{\,0} \qquad (8)$$

3.1 기액 상평형과 액액 상평형 원리: 활동도계수(LLE)

- For Liquid-Liquid Equilibrium (LLE) the relationship is:

$$\hat{f}_i^{l1} = \hat{f}_i^{l2} \qquad (9)$$

where the designators 1 and 2 represent the two separate liquid phases.

- Using the activity coefficient definition of fugacity, this can be rewritten and simplified as:

$$x_i^{l1}\gamma_i^{l1} = x_i^{l2}\gamma_i^{l2} \qquad (10)$$

3.2 One constant Margules 모델식

- The simplest polynomial representation is:

$$G^{ex} = Ax_1x_2$$

- Thus, $\ln\gamma_1 = \left.\frac{\partial(nG^{ex})}{\partial n_1}\right|_{T,P,n_2} = \frac{\partial}{\partial n_1}\left(\frac{An_1n_2}{n_1+n_2}\right) = A\left\{\frac{n_2}{n_1+n_2} - \frac{n_1n_2}{(n_1+n_2)^2}\right\} = Ax_2^2$

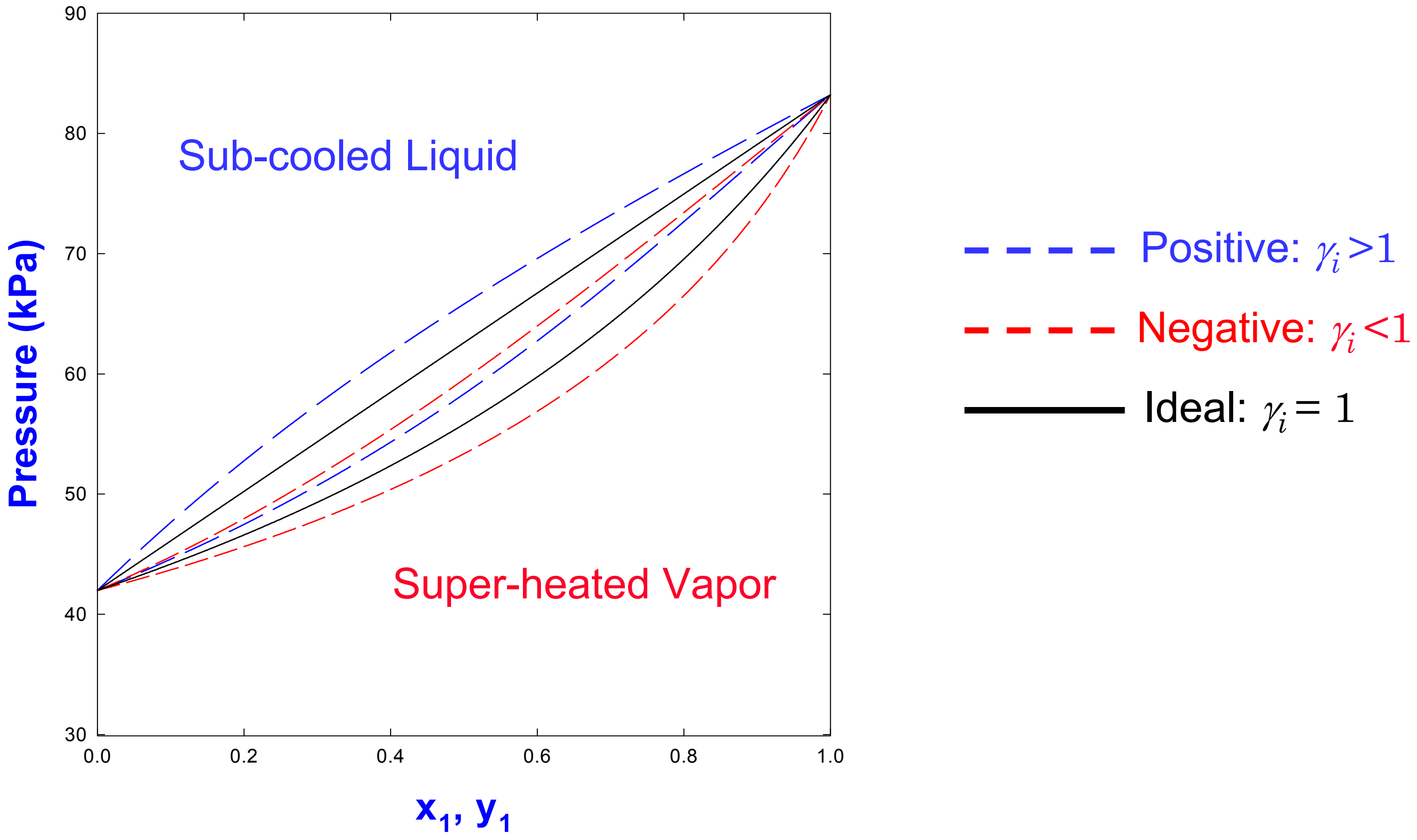
- So that $\gamma_1 = \exp\left(\frac{Ax_2^2}{RT}\right)$ and $\gamma_2 = \exp\left(\frac{Ax_1^2}{RT}\right)$

- The two species activity coefficients are mirror images of each other as a function of composition.

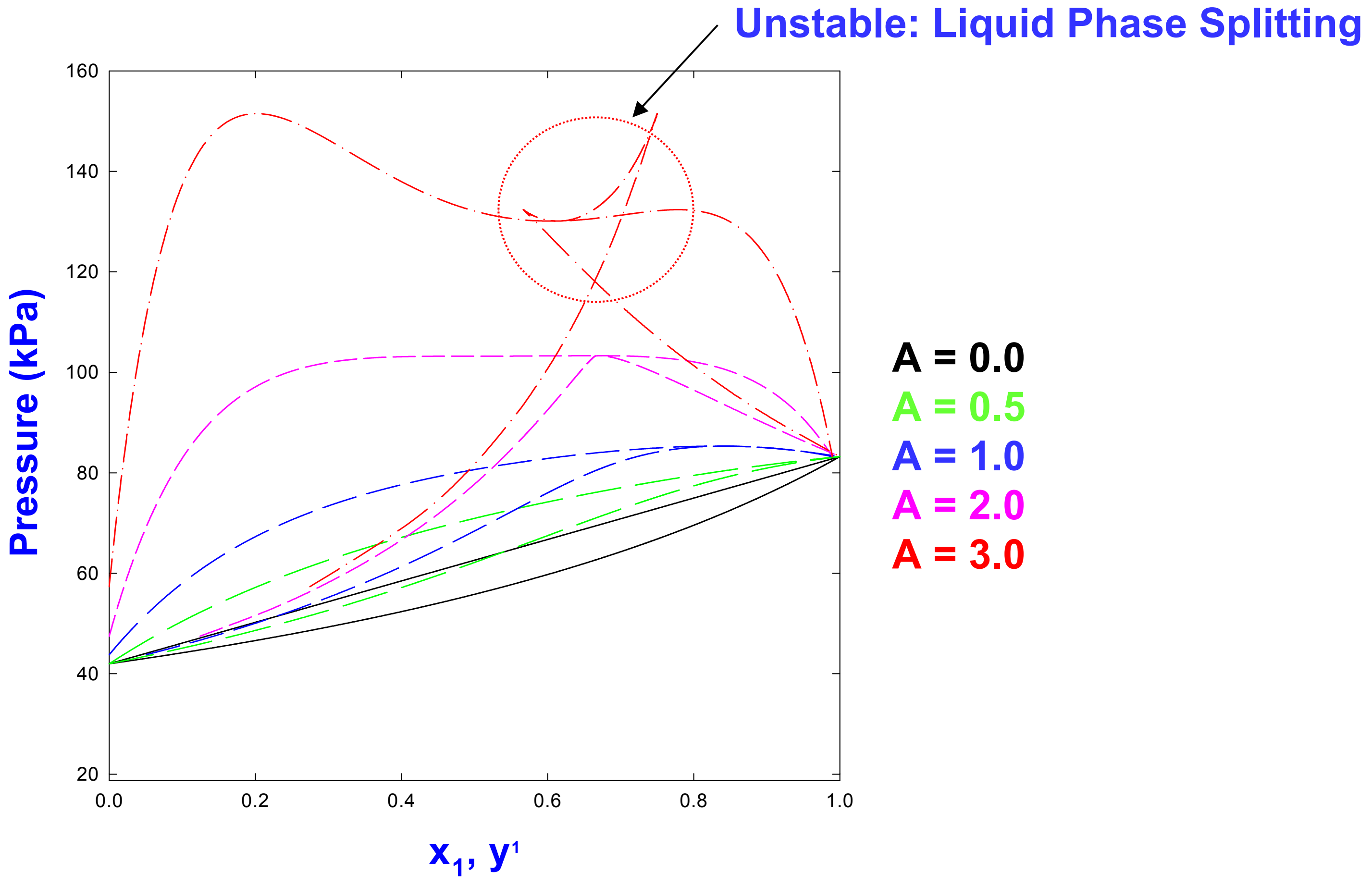
3.2 One constant Margules: Non-ideal Mixtures

- A mixture is non-ideal if γ_i are not equal to 1.
- The value of γ_i indicates the degree of nonideality:
  - If γ_i is less than 1, component interactions are attractive.
  - If γ_i is greater than 1, component interactions are repulsive. If much greater than 1, the formation of 2 liquid phases is possible.
  - For most activity coefficient property methods, non-ideal interactions of components i and j will affect component k.

3.2 One constant Margules: For a Binary VLE



3.2 One constant Margules: For Much Larger Value of γ_i



3.2 One constant Margules: Types of Liquid Mixtures (1)

- Completely Miscible System
  - Always forms single liquid phase iregardless of mixture composition and temperature Ideal Gas Law (for vapor phase).
  - Double derivative of Gibbs free energy change due to mixing is always positive. (stable)
- Immiscible System
  - Mutual solubility is nearly zero.
  - Gibbs free energy change due to mixing is always positive. (unstable)
- Partially Miscible System
  - Liquid mixture forms a stable single liquid phase for some concentration range but splits into the two liquid phases when some more A (or B) is added.

3.2 One constant Margules: Types of Liquid Mixtures (2)

- Completely Miscible System (Stable)

$$\left[\frac{\partial^2\left(\Delta G^{mix}/RT\right)}{\partial x^2}\right]_{T,P} > 0$$

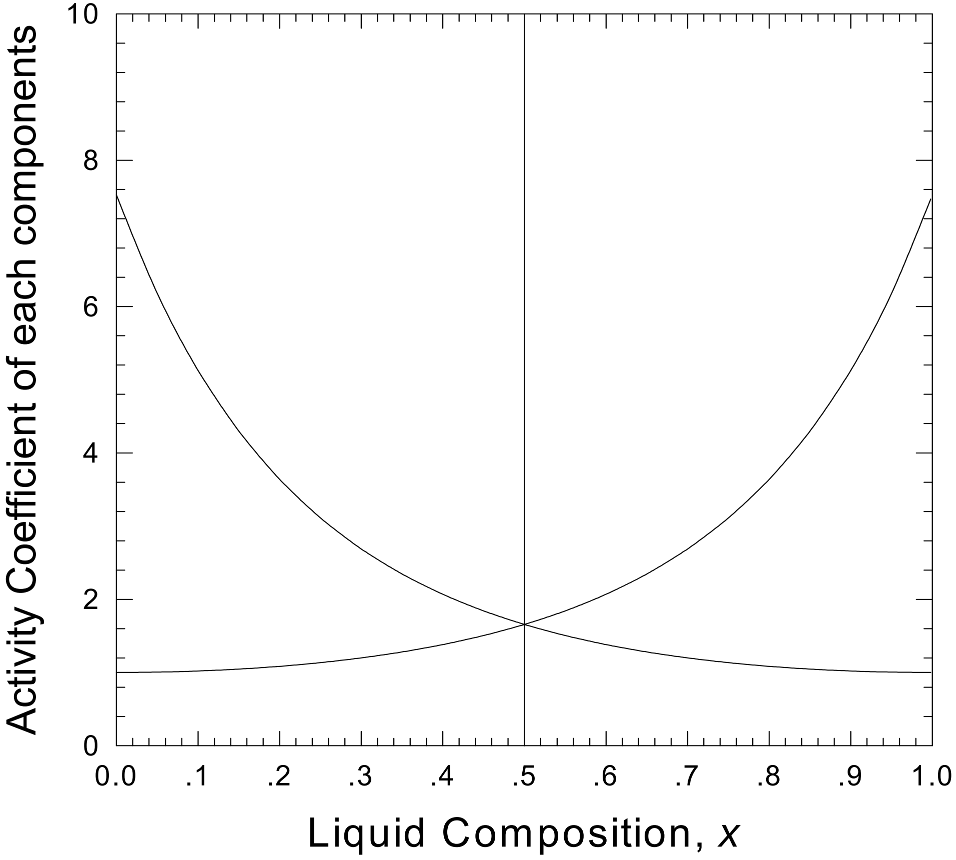
- Immiscible System (Unstable)

$$\left[\frac{\partial^2\left(\Delta G^{mix}/RT\right)}{\partial x^2}\right]_{T,P} < 0$$

- Partially Miscible System (Conditionally Stable)

$$\left[\frac{\partial^2\left(\Delta G^{mix}/RT\right)}{\partial x^2}\right]_{T,P} = 0$$

3.2 One constant Margules 모델식



This model can be applied for chemically not dissimilar systems.

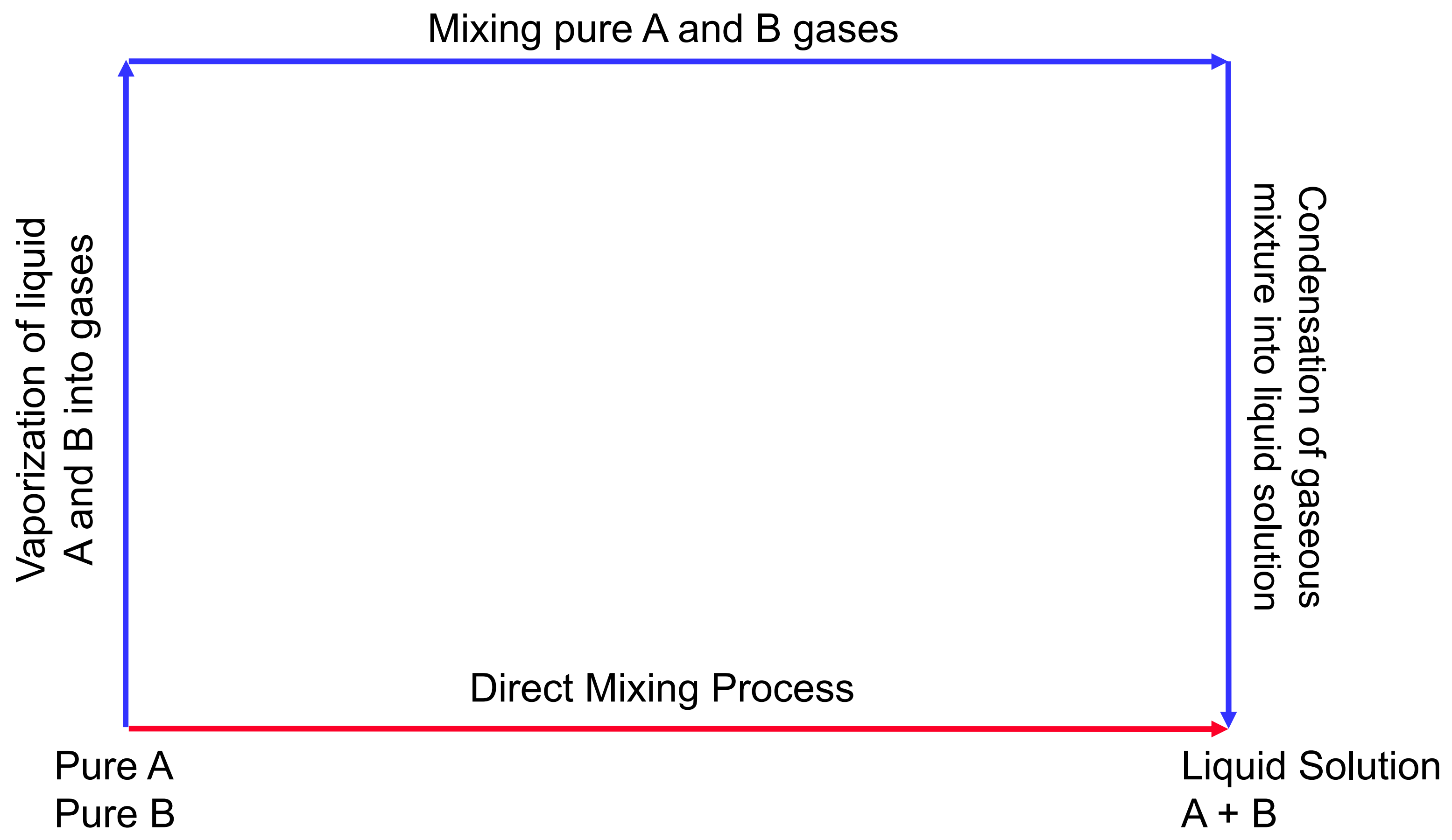
3.2 One constant Margules 모델식

- References

1. Margules, 1895, Sitzber., Akad. Wiss. Wien, *Math. Naturw*., (2A). 104, 1234.

3.3 van Laar 모델식

- van Laar was one of the students of van der Waals.



Mixing pure A and B gases

Vaporization of liquid
A and B into gases

Condensation of gaseous
mixture into liquid solution

Direct Mixing Process

Pure A
Pure B

Liquid Solution
A + B

3.3 van Laar 모델식

- Another old correlation which is still frequently used is the van Laar equation. The resulting expression for the activity coefficient is:

$$\ln\gamma_i = \sum_{i=1}^{N} a_{il} Z_l - \sum_{j=1}^{N} a_{ij} Z_i Z_j - \frac{1}{2} \sum_{\substack{j=1 \\ j,k\neq 1}}^{N} a_{j,k} \frac{a_{ij}}{a_{ji}} Z_j Z_k$$

where: $$Z_l = \frac{x_l}{\sum_j x_j \left(\frac{a_{il}}{a_{li}} \right)}$$

- Two parameters, a_{ij} and a_{ji}, are required for each binary.

3.3 van Laar 모델식

- The van Laar equations for the activity coefficients:

$$\ln \gamma_1 = \frac{\alpha}{\left[1+\frac{\alpha x_1}{\beta x_2}\right]^2} \quad \text{and} \quad \ln \gamma_2 = \frac{\beta}{\left[1+\frac{\beta x_2}{\alpha x_1}\right]^2}$$

- With relation to the van der Waals parameter a and b

$$\alpha = \frac{b_1}{RT}\left[\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right]^2 \quad \text{and} \quad \beta = \frac{b_2}{RT}\left[\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right]^2$$

- Since we know the van der Waals equation is not very accurate, it is not surprising that the correlative value of the van Laar equations is different from the regressed values.

3.3 van Laar 모델식

- Comparison of the van Laar constants between parameters obtained from regressed data and parameters calculated from van der Waals equation

	Obtained from regression		Obtained from vdw EOS	
System	α	β	α	β
acetaldehyde-water	1.59	1.80	8.05	2.08
Acetone-methanol	0.58	0.56	0.56	0.33
Acetone-water	2.05	1.50	7.86	2.13

3.3 van Laar 모델식

Table: Application guideline of van Laar equation

Required Pure-component Properties	Application Guidelines	
Vapor Pressure	Components	Use for chemically not dissimilar components

- References

1. van Laar, J. J., 1910, The vapor pressure of binary mixtures, *Z. Phys. Chem*., **72**, 723-751

3.4 Wilson 모델식

➢ Basis

- Derived from the Flory-Huggins model, by assuming that the local composition is not equal to the overall composition to account for non-randomness of mixture composition.
- The activity coefficient model to use *“local composition concept”.*
- Cannot predict two liquid phases regardless of binary parameter values

  - Will never predict two liquid phases.

  - Not recommended it process has two liquid phases such as decanters.

3.4 Wilson 모델식

- The Wilson equation was the first to incorporate the concept of “local Composition.” The basic idea is that, because of differences in intermolecular forces, the composition in the neighborhood of a specific molecule in solution will differ from that of the bulk liquid.
- The two parameters per binary are, at least in principle, associated with the degree to which each molecule can produce a change in the composition of the local environment.

3.4 Wilson 모델식

- The expression for the activity coefficient is:

$$\ln\gamma_i = 1 - \ln\sum_{j=1}^{N} x_j A_{ij} - \sum_{k=1}^{N} \frac{x_k A_{ki}}{\sum_{j=1}^{N} x_j A_{kj}}$$

where: $A_{ij} = \frac{v_i^L}{v_j^L}\exp\left[-\frac{a_{ij}}{T}\right]$ *(when unit of a_{ij} is K)*

v_i^L *= the liquid molar volume of component i*

3.4 Wilson 모델식

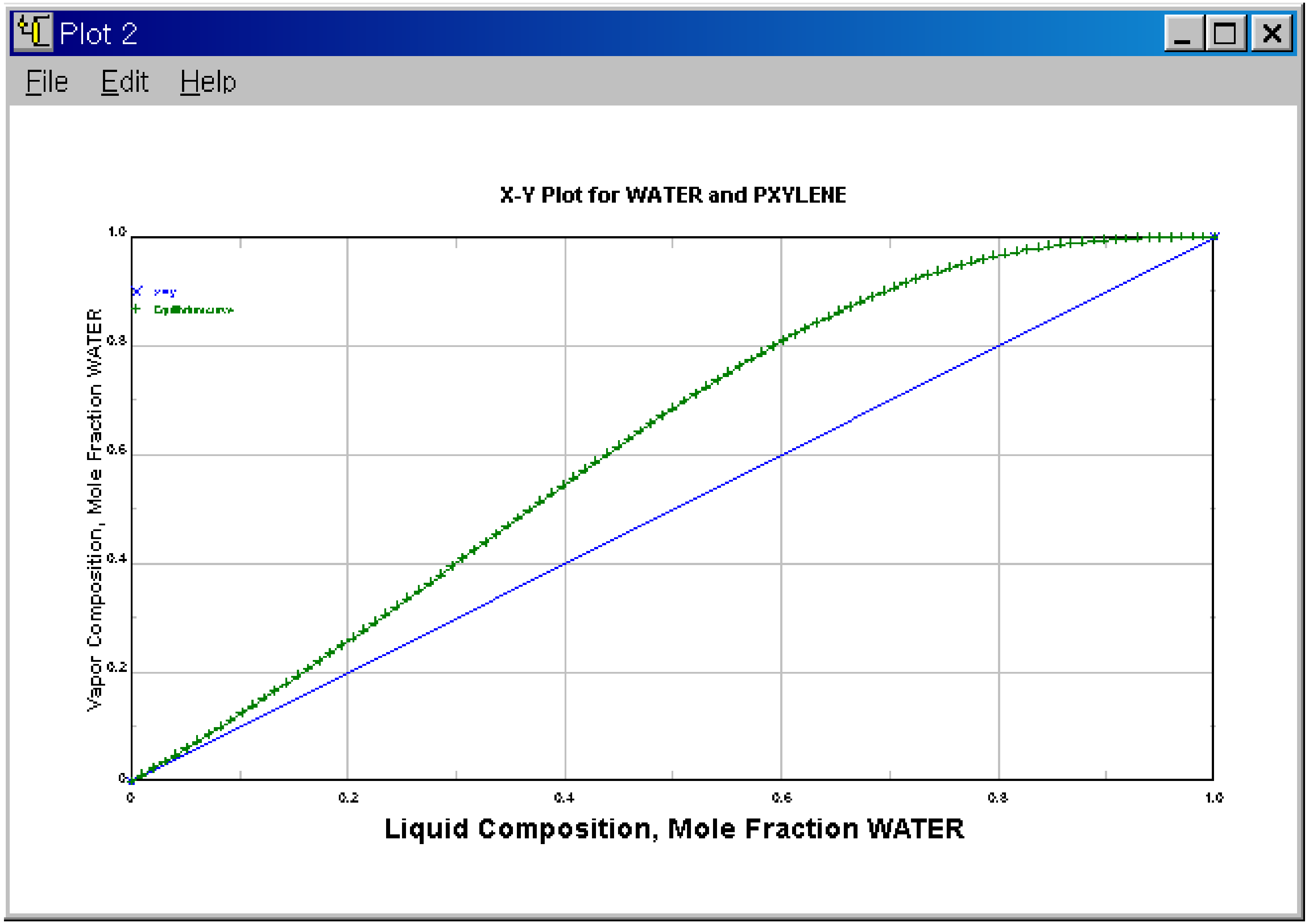
- The Wilson equation cannot describe local maxima or minima in the activity coefficient. Its single significant shortcoming, however, is that it is mathematically unable to predict the splitting of a liquid into two partially miscible phases. It is therefore completely unsuitable for problems involving liquid-liquid equilibria.

- References

  1. Wilson, G. M., 1964, Vapor-Liquid Equilibrium XI. A New Expression for the Excess Free Energy of Mixing, *J. Amer. Chem. Soc.*, **86**, 127.

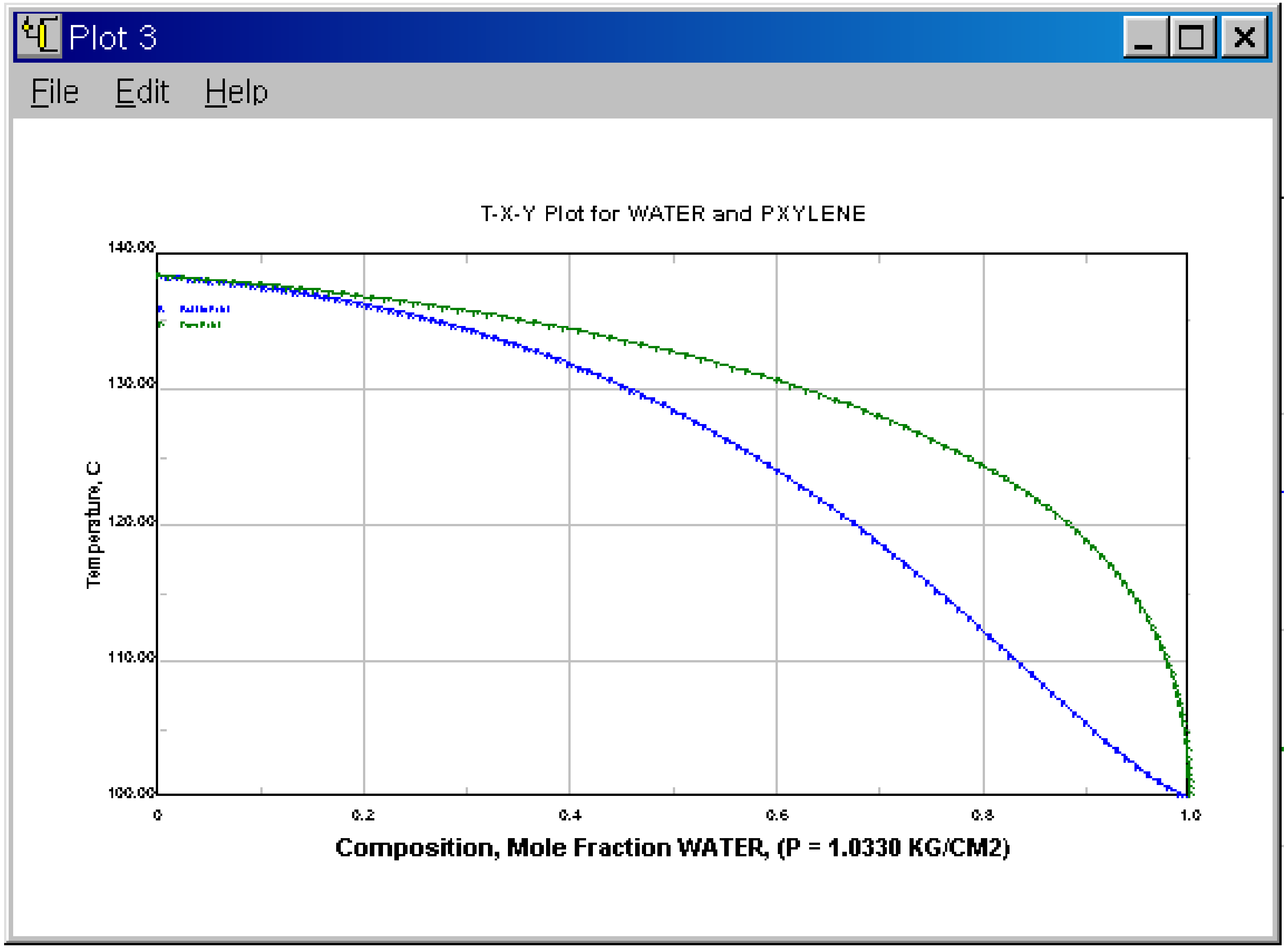
3.4 Wilson 모델식

- Fatal weakness of Wilson model:



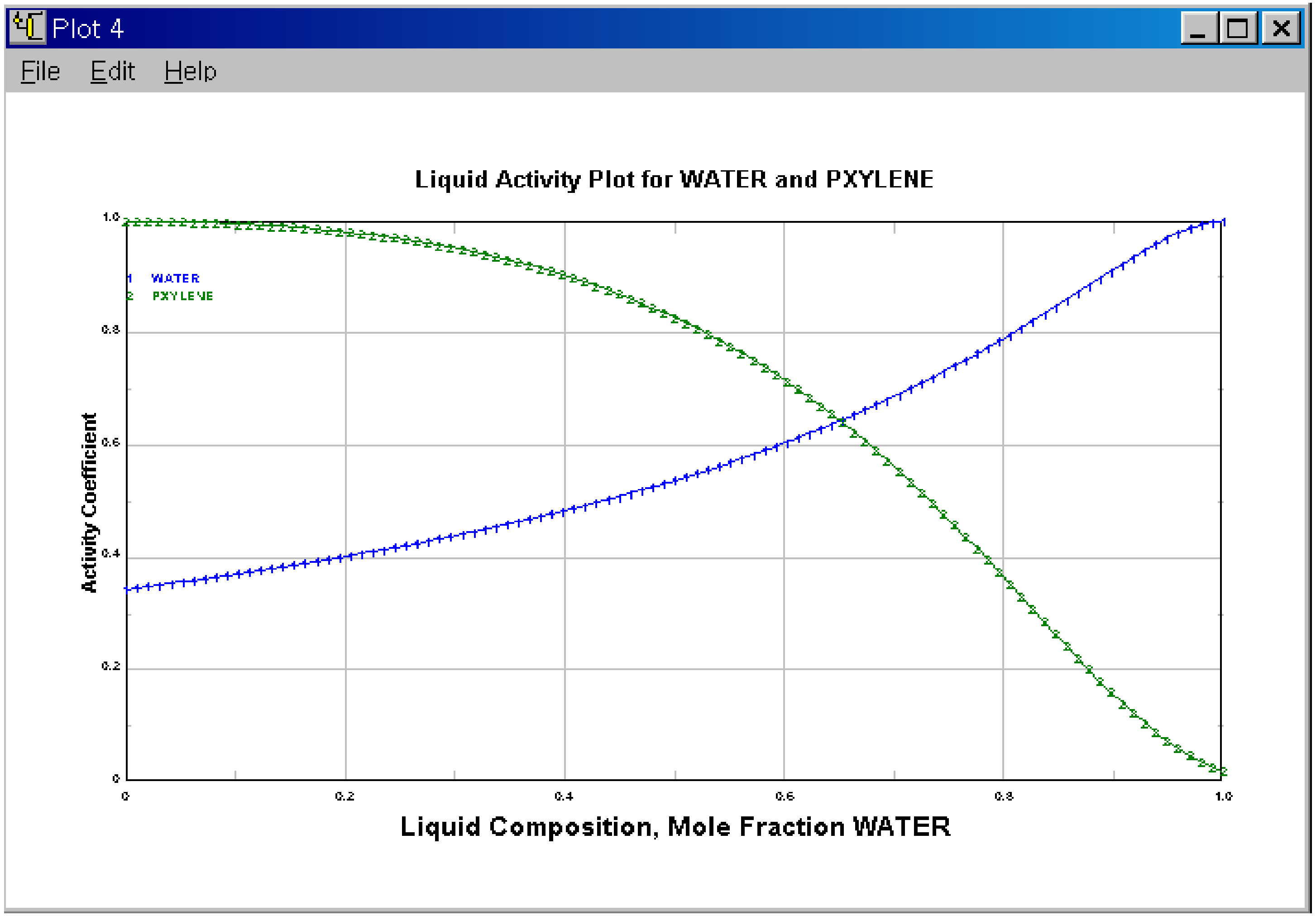
3.4 Wilson 모델식

- Fatal weakness of Wilson model:



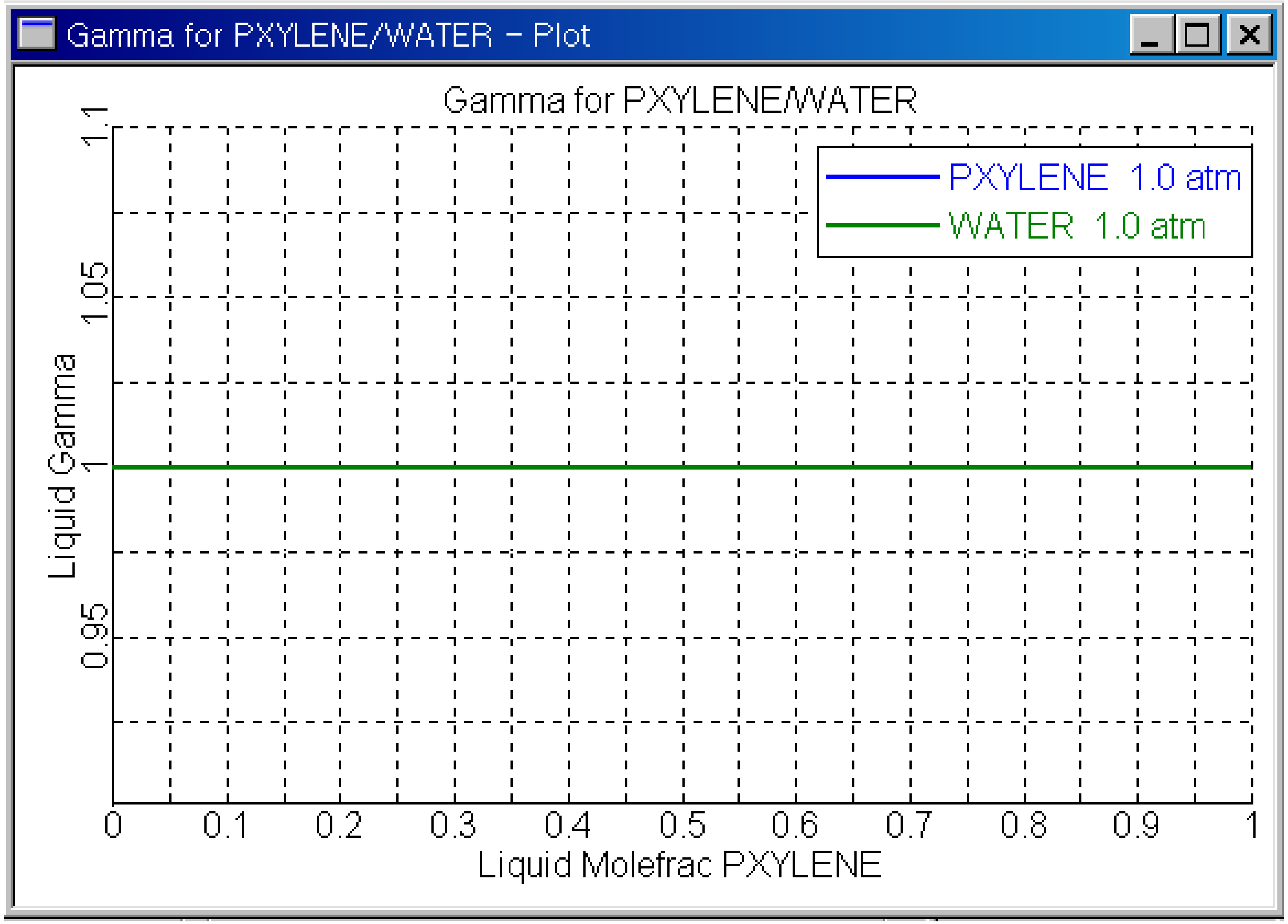
3.4 Wilson 모델식

- It does not return to ideal Raoult's law when the BIP's are not available in DB.



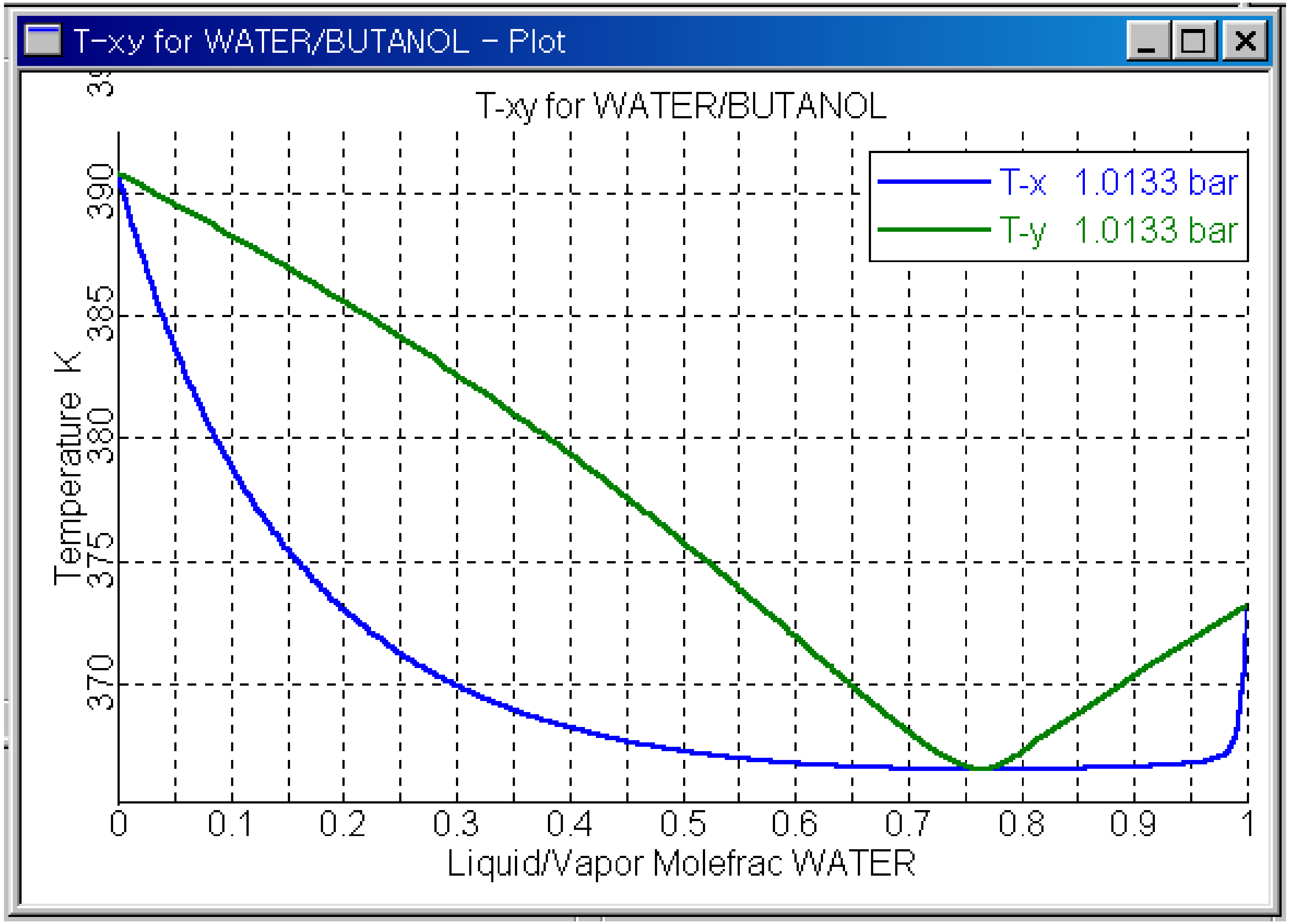
3.4 Wilson 모델식

- How about Aspen Plus?



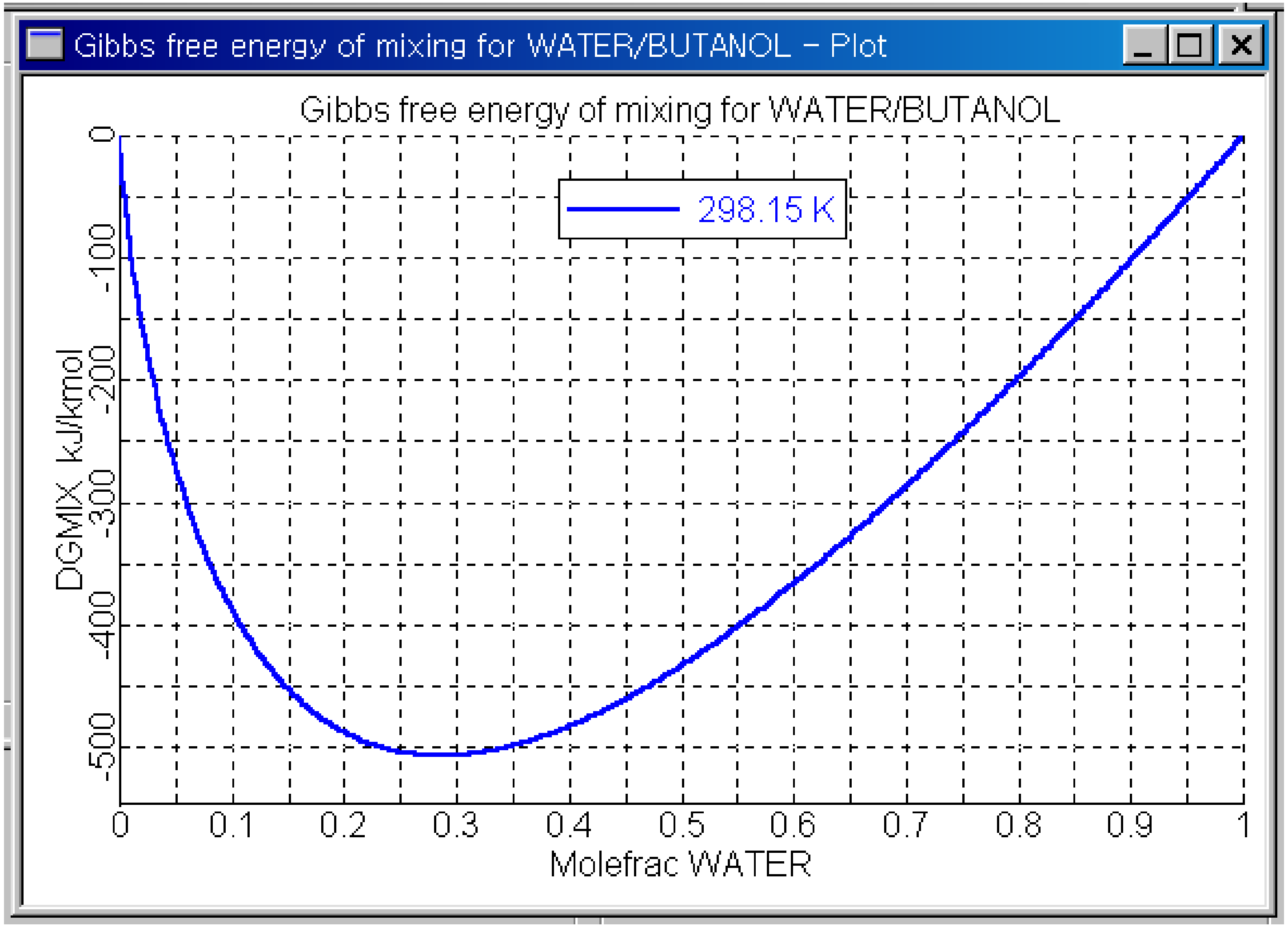
3.4 Wilson 모델식

- Fatal weakness of Wilson model:



3.4 Wilson 모델식

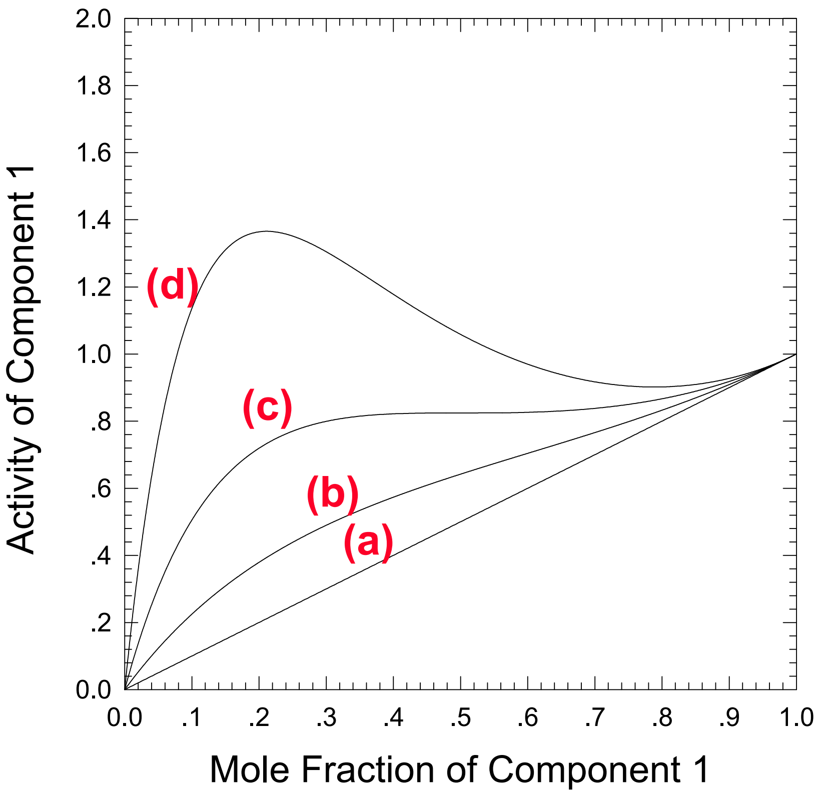
- **Fatal weakness of Wilson model:**



3.4 Wilson 모델식: Stability Criteria for Liquid Mixtures

- If the second derivative of total Gibbs free energy change vs. composition is bigger than zero for any composition, the system satisfies the stability criteria so, liquid mixture forms a single stable liquid mixture.

- (a) Ideal
- (b) Slightly Non-ideal
- (c) Critical Miscibility
- (d) Liquid Phase Splitting



3.4 Wilson 모델식

Table: Application guideline of Wilson equation

Required Pure-component Properties	Application Guidelines	
Vapor Pressure	Components	Useful for polar or associating component in nonpolar solvents. Cannot be used if liquid-liquid immiscibility exists.
Liquid molar volume		

3.5 NRTL 모델식

- The NRTL (non-random-two-liquid) equation was developed by Renon and Prausnitz to make use of the local composition concept, while avoiding the Wilson equation's inability to predict liquid-liquid phase separation. The resulting equation has been quite successful in correlating a wide variety of systems.

- References

  1. Renon, H. and Prausnitz, J. M., 1968, Local Composition in Thermodynamic Excess Functions for Liquid Mixtures, *AIChE J.*, **14**, 135-144.

3.5 NRTL 모델식

- NRTL. This model has up to 8 adjustable binary parameters that can be fitted to data.

$$\ln\gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k}\left[\tau_{ij} - \frac{\sum_l x_l \tau_{lj} G_{lj}}{\sum_k G_{kj} x_k}\right]$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + \frac{c_{ij}}{T^2}$$

$$G_{ij} = \exp\left[-\left(\alpha_{ij} + \beta_{ij} T\right)\tau_{ij}\right]$$

3.5 NRTL 모델식

- Three parameters, τ_{ij}, τ_{ji}, and $\alpha_{ij} = \alpha_{ji}$, are e NRTL (non-random-two-liquid) equation was developed by Renon and Prausnitz to make use of the local composition concept, while avoiding the Wilson equation's inability to predict liquid-liquid phase separation. The resulting equation has been quite successful in correlating a wide variety of systems.

Table: Application guideline of NRTL equation

Required Pure-component Properties	Application Guidelines	
Vapor Pressure	Components	Use for strongly nonideal mixtures and for partially miscible systems

3.5 NRTL 모델식

- $\alpha_{ij} = 0.3$
  - For mixtures of non-polar substances; mixtures for which deviation from ideality is small; for VLE

- $\alpha_{ij} = 0.2$
  - For systems that exhibit liquid-liquid immiscibility

- $\alpha_{ij} = 0.47$
  - For mixtures of strongly self-associated substances with Non-polar substances, but not recommended since alternative equations are available, Hayden-O'Connell model for dimers and hexamer model for hexamers.

3.6 UNIQUAC 모델식

➢ Basis

- Derived from Derived from on ideas of Guggenheim quasi-chemical theory to introduce local area fraction in a similar way to local fraction in Wilson model and local mole fraction in Renon model.
- Takes into account differences in molecular size and shape by introducing area parameter *"q"* and volume parameter *"r"*.
- It is superior to Wilson model since it can predict liquid phase splitting phase behavior.
- Can be used to multi-component phase equilibria with pure and binary parameters only.
- It is superior to NRTL since it has only two adjustable parameters. (NRTL has 3 parameter for each binary pair.)

3.6 UNIQUAC 모델식

- The excess Gibbs energy (and therefore the logarithm of the activity coefficient) is divided into a combinatorial and a residual part. The combinatorial part depends on the sizes and shapes of the individual molecules; it contains no binary parameters. The residual part, which accounts for the energetic interactions, has two adjustable parameters.
- The UNIQUAC equation has, like the NRTL equation, been quite successful in correlating a wide variety of systems involving highly nonideal systems or partially miscible systems.

3.6 UNIQUAC 모델식

- The expression for the activity coefficient is:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R$$

$$\ln\gamma_i^C = \ln\left(\frac{\varphi_i}{x_i}\right) + \frac{\bar{z}}{2} q_i \ln\left(\frac{\theta_i}{\varphi_i}\right) + l_i - \frac{\varphi_i}{x_i}\sum_{j=1}^{N} x_j l_j$$

$$\ln\gamma_i^R = q_i\left(1 - \ln\left(\sum_{j=1}^{M}\theta_j\tau_{ji}\right) - \sum_{j=1}^{M}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{M}\theta_k\tau_{kj}}\right)$$

3.6 UNIQUAC 모델식

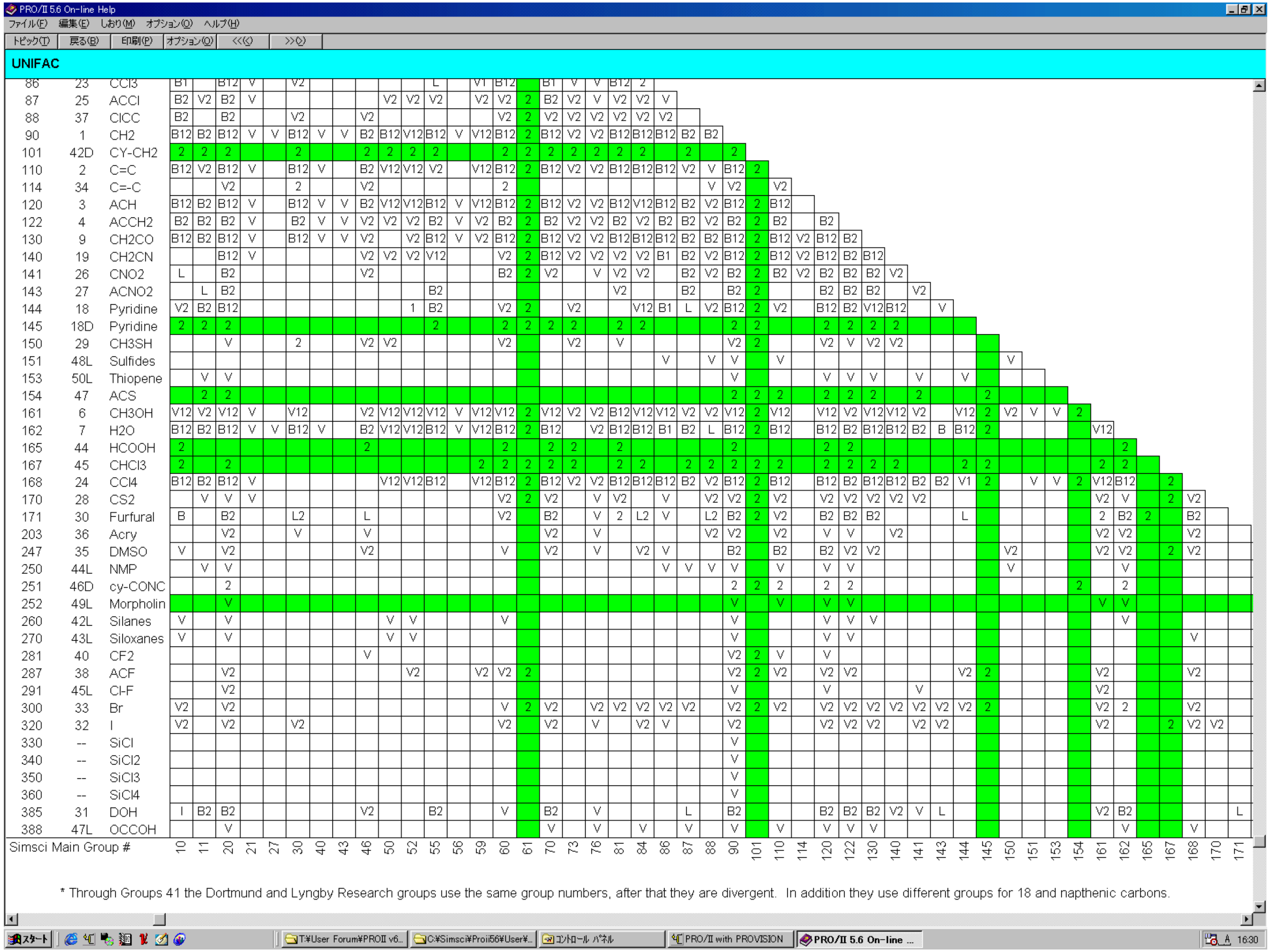
- References

1. Abrams, D. S. and Prausnitz, J. M., 1975, Statistical Thermodynamics of Mixtures: A New Expression for the Excess Gibbs Free Energy of Partly or Completely Miscible Systems, *AIChE J.*, **21**, 116-128

3.7 UNIFAC 모델식

- The UNIFAC (UNIQUAC functional activity coefficient) method was developed in 1975 by Fredenslud, Jones, and Prausnitz.
- This method estimates activity coefficients based on the group contribution concept following the ASOG model.
- Interactions between two molecules are assumed to be a function of group-group interactions.
- Whereas there are thousands of chemical compounds of interest in chemical processing, the number of functional groups is much smaller.

3.7 UNIFAC 모델식



UNIFAC

86	23	CCl3	B1		B12	V		V2						L		V1	B12		B1	V	V	B12	2																										
87	25	ACCl	B2	V2	B2	V						V2	V2	V2		V2	V2	2	B2	V2	V	V2	V2	V																									
88	37	ClCC	B2		B2			V2			V2						V2	2	V2	V2	V2	V2	V2	V2																									
90	1	CH2	B12	B2	B12	V	V	B12	V	V	B2	B12	V12	B12	V	V12	B12	2	B12	V2	V2	B12	B12	B12	B2	B2																							
101	42D	CY-CH2	2	2	2			2			2	2	2	2			2	2	2	2	2	2	2		2		2																						
110	2	C=C	B12	V2	B12	V		B12	V		B2	V12	V12	V2		V12	B12	2	B12	V2	V2	B12	B12	B12	V2	V	B12	2																					
114	34	C=-C			V2			2			V2						2									V	V2		V2																				
120	3	ACH	B12	B2	B12	V		B12	V	V	B2	V12	V12	B12	V	V12	B12	2	B12	V2	V2	B12	V12	B12	B2	V2	B12	2	B12																				
122	4	ACCH2	B2	B2	B2	V		B2	V	V	V2	V2	V2	B2	V	V2	B2	2	B2	V2	V2	B2	V2	B2	B2	V2	B2	2	B2		B2																		
130	9	CH2CO	B12	B2	B12	V		B12	V	V	V2		V2	B12	V	V2	B12	2	B12	V2	V2	B12	B12	B12	B2	B2	B12	2	B12	V2	B12	B2																	
140	19	CH2CN			B12	V					V2	V2	V2	V12			V2	2	B12	V2	V2	V2	V2	B1	B2	V2	B12	2	B12	V2	B12	B2	B12																
141	26	CNO2	L		B2						V2						B2	2	V2		V	V2	V2		B2	V2	B2	2	B2	V2	B2	B2	B2	V2															
143	27	ACNO2		L	B2									B2								V2			B2		B2	2			B2	B2	B2		V2														
144	18	Pyridine	V2	B2	B12								1	B2			V2	2		V2			V12	B1	L	V2	B12	2	V2		B12	B2	V12	B12		V													
145	18D	Pyridine	2	2	2									2			2	2	2	2		2	2				2	2			2	2	2	2															
150	29	CH3SH			V			2			V2	V2					V2			V2		V					V2	2			V2	V	V2	V2															
151	48L	Sulfides																						V		V	V		V										V										
153	50L	Thiopene		V	V																						V				V	V	V		V		V												
154	47	ACS		2	2																						2	2	2		2	2	2		2			2											
161	6	CH3OH	V12	V2	V12	V		V12			V2	V12	V12	V12	V	V12	V12	2	V12	V2	V2	B12	V12	V12	V2	V2	V12	2	V12		V12	V2	V12	V12	V2		V12	2	V2	V	V	2							
162	7	H2O	B12	B2	B12	V	V	B12	V		B2	V12	V12	B12	V	V12	B12	2	B12		V2	B12	B12	B1	B2	L	B12	2	B12		B12	B2	B12	B12	B2	B	B12	2					V12						
165	44	HCOOH	2								2						2		2	2		2					2				2	2												2					
167	45	CHCl3	2		2											2	2	2	2	2		2	2		2	2	2	2	2		2	2	2	2			2	2					2	2					
168	24	CCl4	B12	B2	B12	V						V12	V12	B12		V12	B12	2	B12	V2	V2	B12	B12	B12	B2	V2	B12	2	B12		B12	B2	B12	B12	B2	B2	V1	2		V	V	2	V12	B12		2			
170	28	CS2		V	V	V											V2	2	V2		V	V2		V		V2	V2	2	V2		V2	V2	V2	V2	V2								V2	V		2	V2		
171	30	Furfural	B		B2			L2			L						V2		B2		V	2	L2	V		L2	B2	2	V2		B2	B2	B2				L						2	B2	2		B2		
203	36	Acry			V2			V			V								V2		V					V2	V2		V2		V	V		V2									V2	V2			V2		
247	35	DMSO	V		V2						V2						V		V2		V		V2	V			B2		B2		B2	V2	V2						V2				V2	V2		2	V2		
250	44L	NMP		V	V																			V	V	V	V		V		V	V							V					V					
251	46D	cy-CONC			2																						2	2	2		2	2										2		2					
252	49L	Morpholin			V																						V		V		V	V											V	V					
260	42L	Silanes	V		V							V	V				V										V				V	V	V											V					
270	43L	Siloxanes	V		V							V	V														V				V	V															V		
281	40	CF2									V																V2	2	V		V																		
287	38	ACF			V2								V2			V2	V2	2									V2	2	V2		V2	V2					V2	2					V2				V2		
291	45L	Cl-F			V2																						V				V				V								V2						
300	33	Br	V2		V2												V	2	V2		V2	V2	V2	V2	V2		V2	2	V2		V2	V2	V2	V2	V2	V2	V2	2					V2	2			V2		
320	32	I	V2		V2			V2									V2		V2		V		V2	V			V2				V2	V2	V2		V2	V2							V2			2	V2	V2	
330	--	SiCl																									V																						
340	--	SiCl2																									V																						
350	--	SiCl3																									V																						
360	--	SiCl4																									V																						
385	31	DOH	I	B2	B2						V2			B2			V		B2		V				L		B2				B2	B2	B2	V2	V	L							V2	B2					L
388	47L	OCCOH			V														V		V		V		V		V		V		V	V	V											V			V		
Simsci Main Group #			10	11	20	21	27	30	40	43	46	50	52	55	56	59	60	61	70	73	76	81	84	86	87	88	90	101	110	114	120	122	130	140	141	143	144	145	150	151	153	154	161	162	165	167	168	170	171

* Through Groups 41 the Dortmund and Lyngby Research groups use the same group numbers, after that they are divergent. In addition they use different groups for 18 and napthenic carbons.

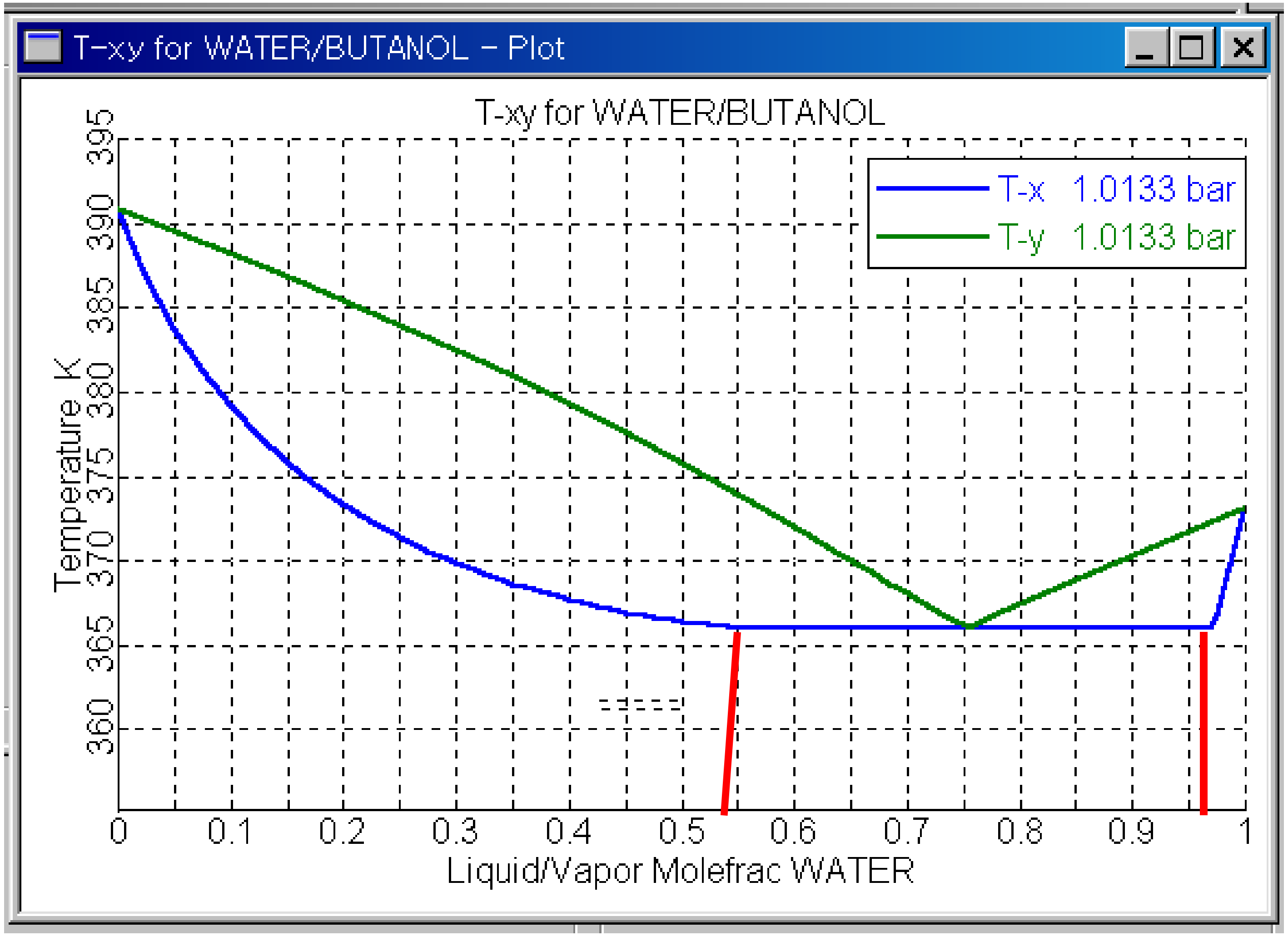
3.7 UNIFAC 모델식

- The UNIFAC method is based on the UNIQIAC model, which represents the excess Gibbs energy (and logarithm of activity coefficient) as a combination of two effects.

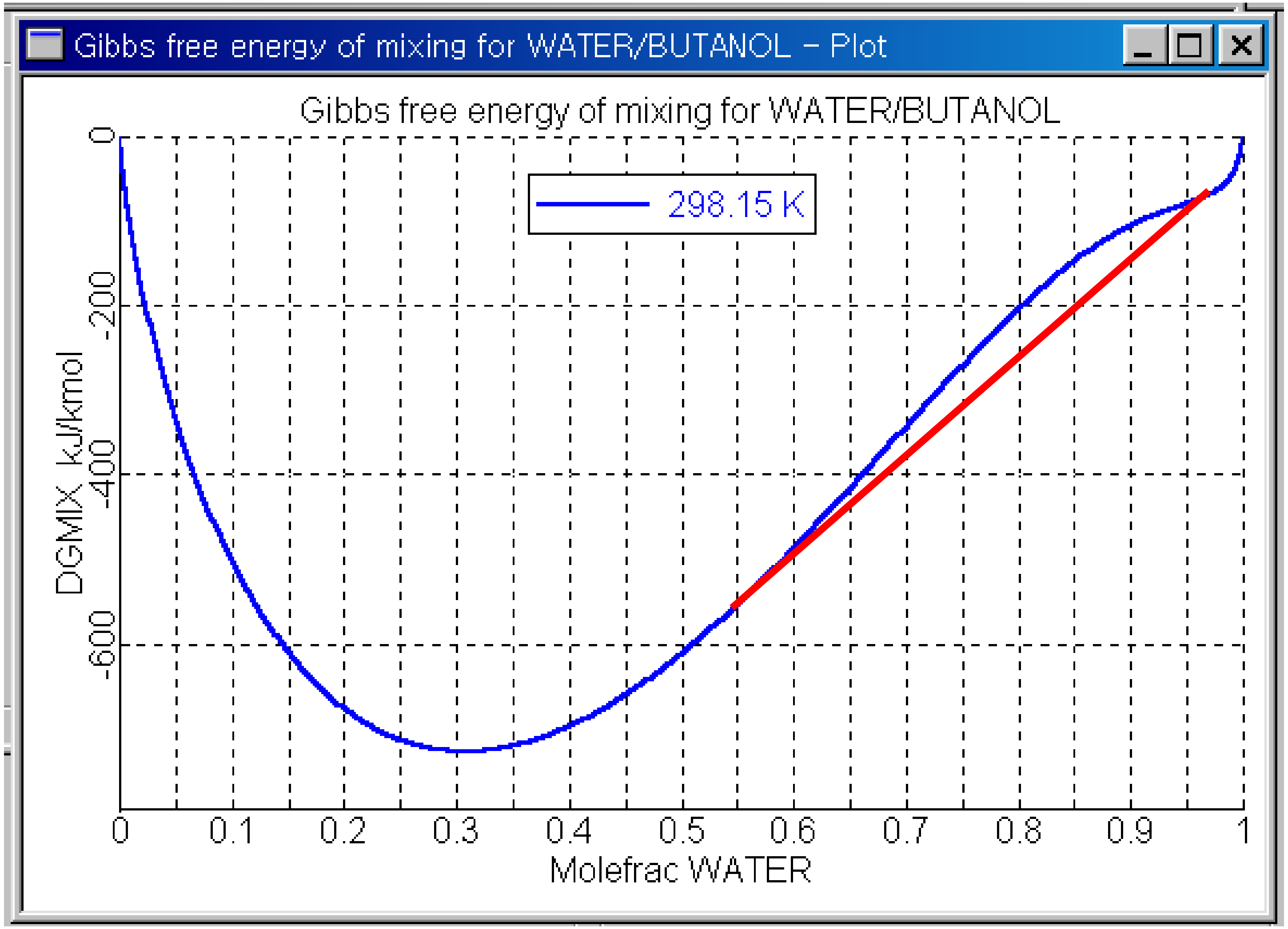
$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

- The combinatorial term is computed from the UNIQUAC equation using the van der Waals are and volume parameter calculated from the individual structural groups.
- A large number of interaction parameters between structural groups for the calculation of residual term, as well as group size and shape parameters habe been incorporated into Aspen Plus.

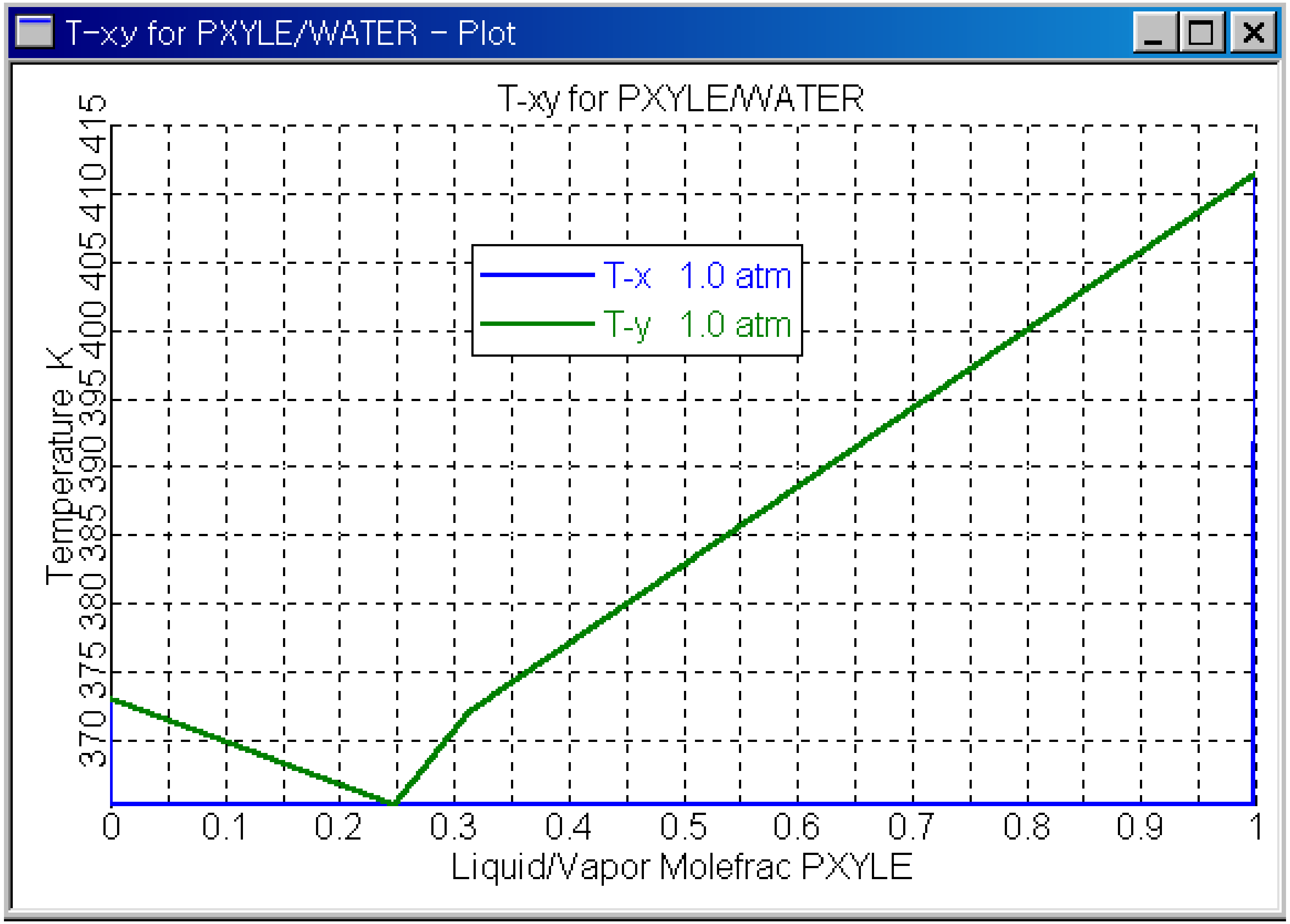
3.7 UNIFAC 모델식



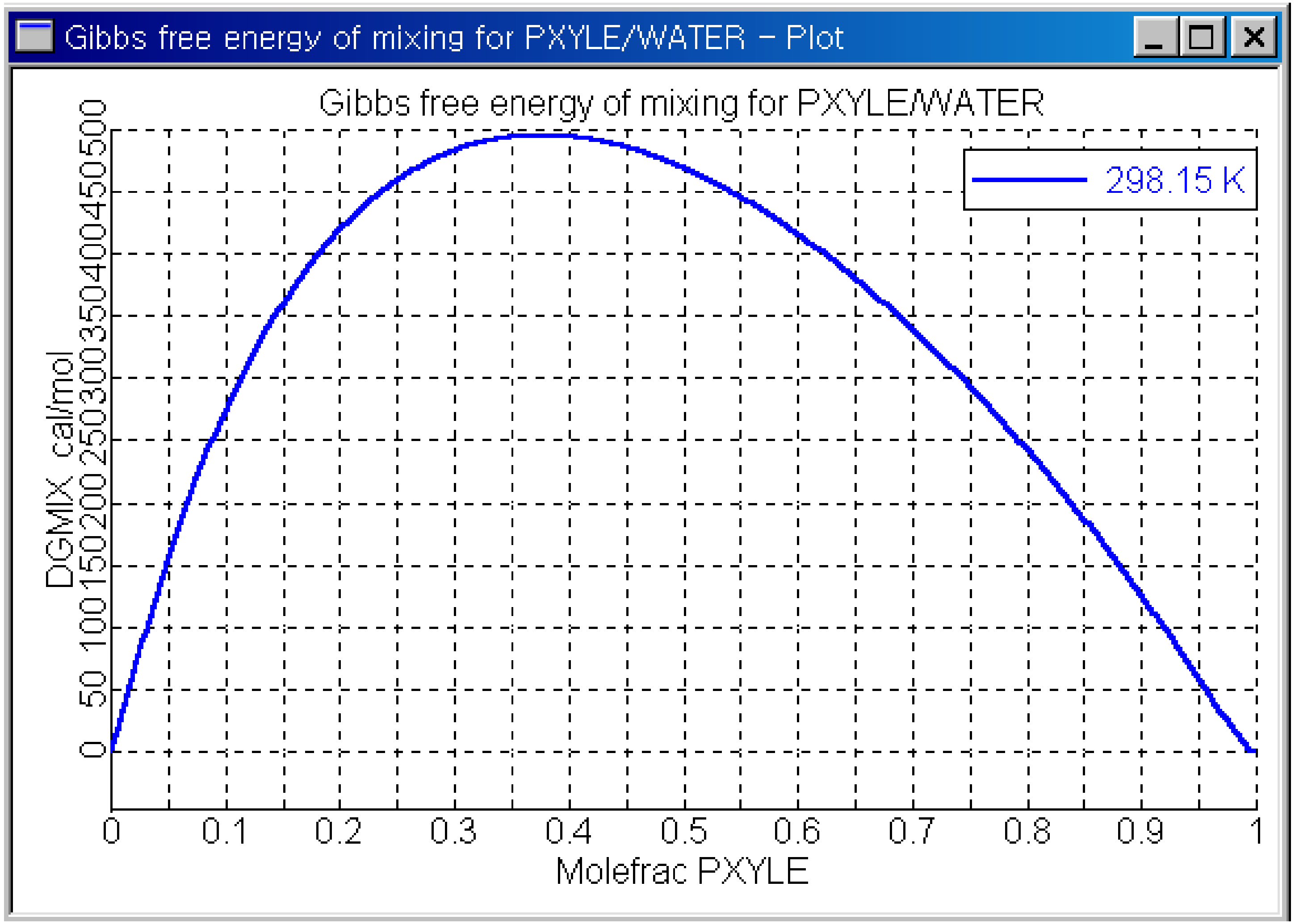
3.7 UNIFAC 모델식



3.7 UNIFAC 모델식



3.7 UNIFAC 모델식



3.7 UNIFAC 모델식

- References

  1. Fredenslund, Aa., Jones, R. L., and Prausnitz, J. M., 1975, Group Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures, *AIChE J.*, **18**, 714-722.

4

원료 조건, 제품 사양 및 유틸리티 조건

4. 원료 조건, 제품 사양 및 유틸리티

4.1 원료 조건

4.2 제품 사양

4.3 사용하는 유틸리티 종류 및 공급 및 회수온도

4.1 원료 조건

- Feedstock Conditions:

Component	**Mole%**
Ethanol	10.0
Water	90.0
Flow (kmol/h)	100.0
Temperature (°C)	45.0
Pressure (bar)	3.5

4.2 제품 사양

- Product Specifications:
  - Ethanol purity: Not less than 99.9% by mole
  - Ethanol recovery: Not less than 99.9%
  - Ethanol content in waste water: Not more than 500 ppm by mole
- Entrainer Selection:
  - Benzene

4.3 사용하는 유틸리티 종류 및 공급 및 회수온도

- Utility Conditions:
  - Steam: 180°C saturated steam
  - Cooling water
    - 32°C supply and 40°C return

5

삼성분계 상평형도 상에서의 공비증류 공정의 설계

5. 삼성분계 상평형도 상에서의 공비증류 공정의 설계

5.1 액-액 상분리선(Binodal curve)의 도시

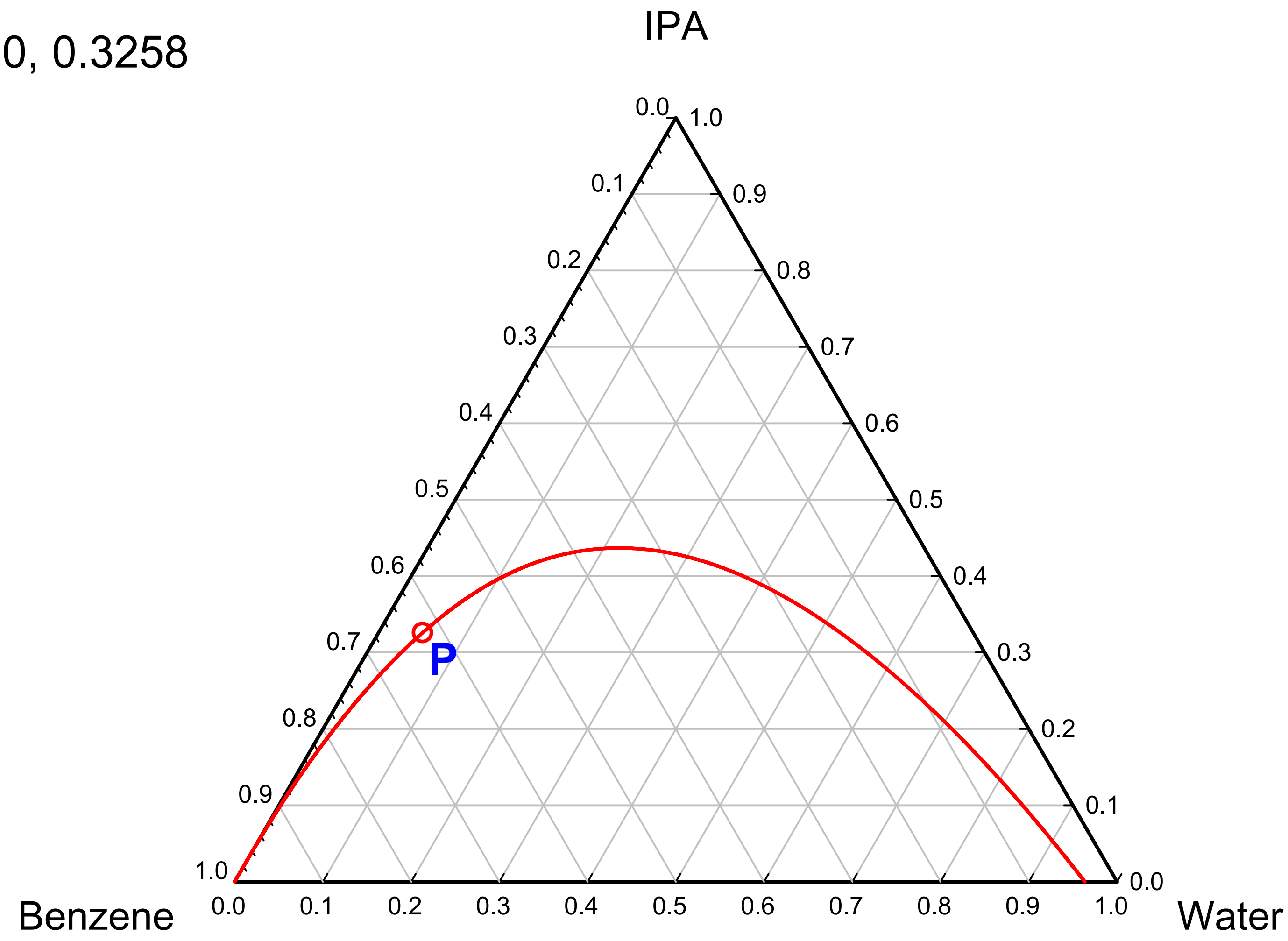
5.2 이성분계 및 삼성분계 공비점의 추산 및 공비온도 계산

5.3 Residual curve의 도시 및 영역 I, II 및 III의 특징

5.4 영역 I, II 및 III에서의 공비증류탑의 전산모사

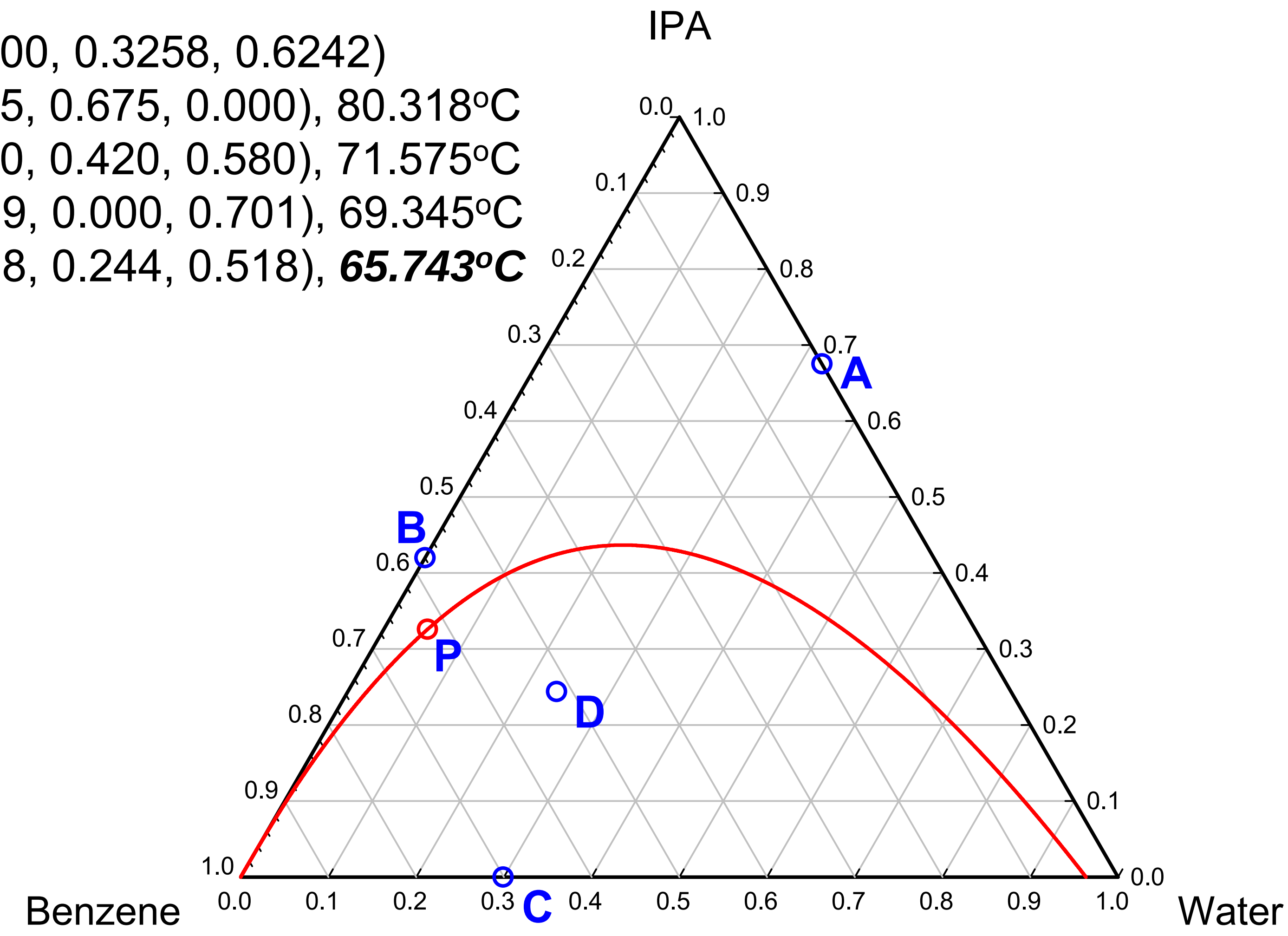
Binodal Curve and Plait Point:

P: 0.0500, 0.3258



Homogeneous & Heterogeneous Azeotropes:

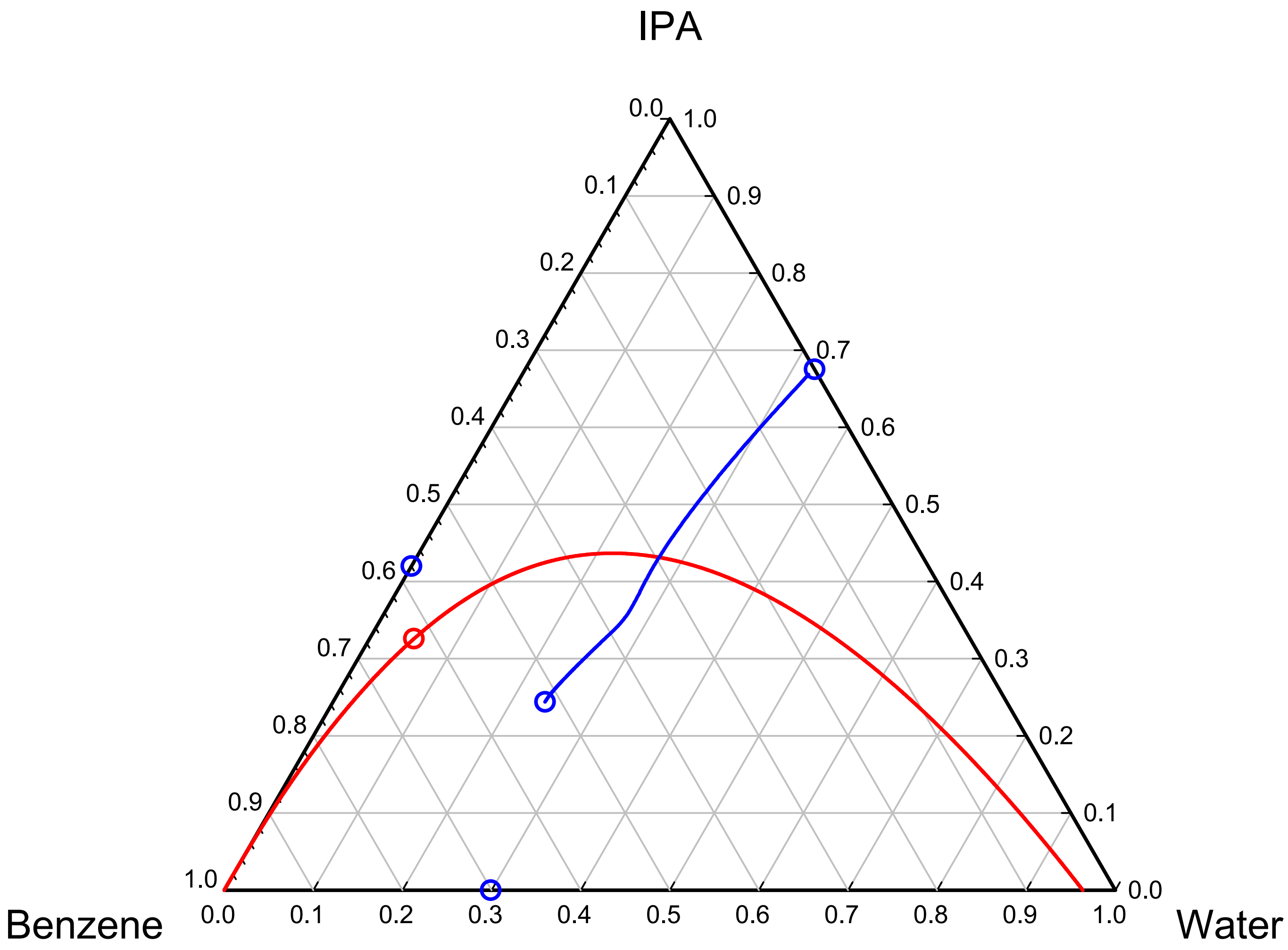
P: (0.0500, 0.3258, 0.6242)
A: (0.325, 0.675, 0.000), 80.318^{o}C
B: (0.000, 0.420, 0.580), 71.575^{o}C
C: (0.299, 0.000, 0.701), 69.345^{o}C
D: (0.328, 0.244, 0.518), ***65.743^{o}C***



Residual Curve for IPA and Water:

Trial	Water	IPA	Benzene
1	0.3216	0.6685	0.0099
5	0.3168	0.6526	0.0306
10	0.3037	0.6074	0.0889
15	0.2878	0.5429	0.1693
20	0.2764	0.4764	0.2472
25	0.2719	0.4156	0.3125
30	0.2739	0.3618	0.3643
35	0.2676	0.3343	0.3981
40	0.2606	0.3169	0.4225
45	0.2551	0.3031	0.4418
50	0.2509	0.2921	0.4569
55	0.2477	0.2833	0.4690
60	0.2453	0.2761	0.4786
65	0.2434	0.2704	0.4862
70	0.2420	0.2657	0.4924
75	0.2409	0.2618	0.4973
80	0.2401	0.2587	0.5012
85	0.2395	0.2561	0.5044
90	0.2390	0.2541	0.5069
95	0.2387	0.2523	0.5090
100	**0.2380**	**0.2440**	**0.5180**

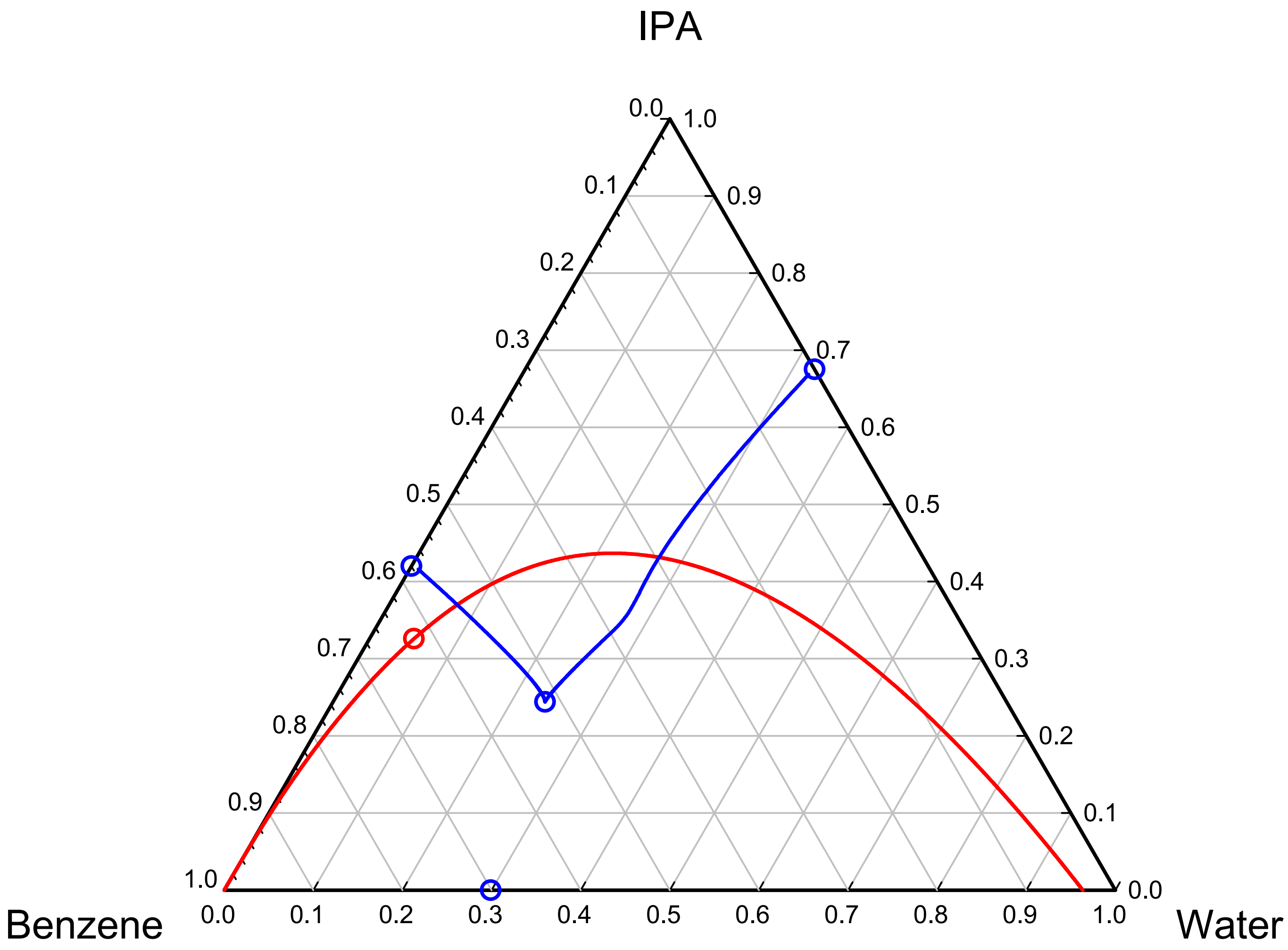
Residual Curve for IPA and Water:



Residual Curve for IPA and Benzene:

Trial	Water	IPA	Benzene
1	0.0099	0.4160	0.5741
5	0.0189	0.4098	0.5713
10	0.0389	0.3961	0.5650
15	0.0707	0.3741	0.5552
20	0.1072	0.3483	0.5445
25	0.1364	0.3273	0.5363
30	0.1591	0.3108	0.5302
35	0.1767	0.2976	0.5257
40	0.1903	0.2872	0.5225
45	0.2009	0.2789	0.5202
50	0.2091	0.2723	0.5187
55	0.2154	0.2669	0.5176
60	0.2204	0.2627	0.5170
65	0.2242	0.2592	0.5166
70	0.2272	0.2564	0.5163
75	0.2296	0.2542	0.5163
80	0.2314	0.2524	0.5163
85	0.2328	0.2509	0.5163
90	0.2339	0.2497	0.5164
95	0.2347	0.2487	0.5165
100	**0.2380**	**0.2440**	**0.5180**

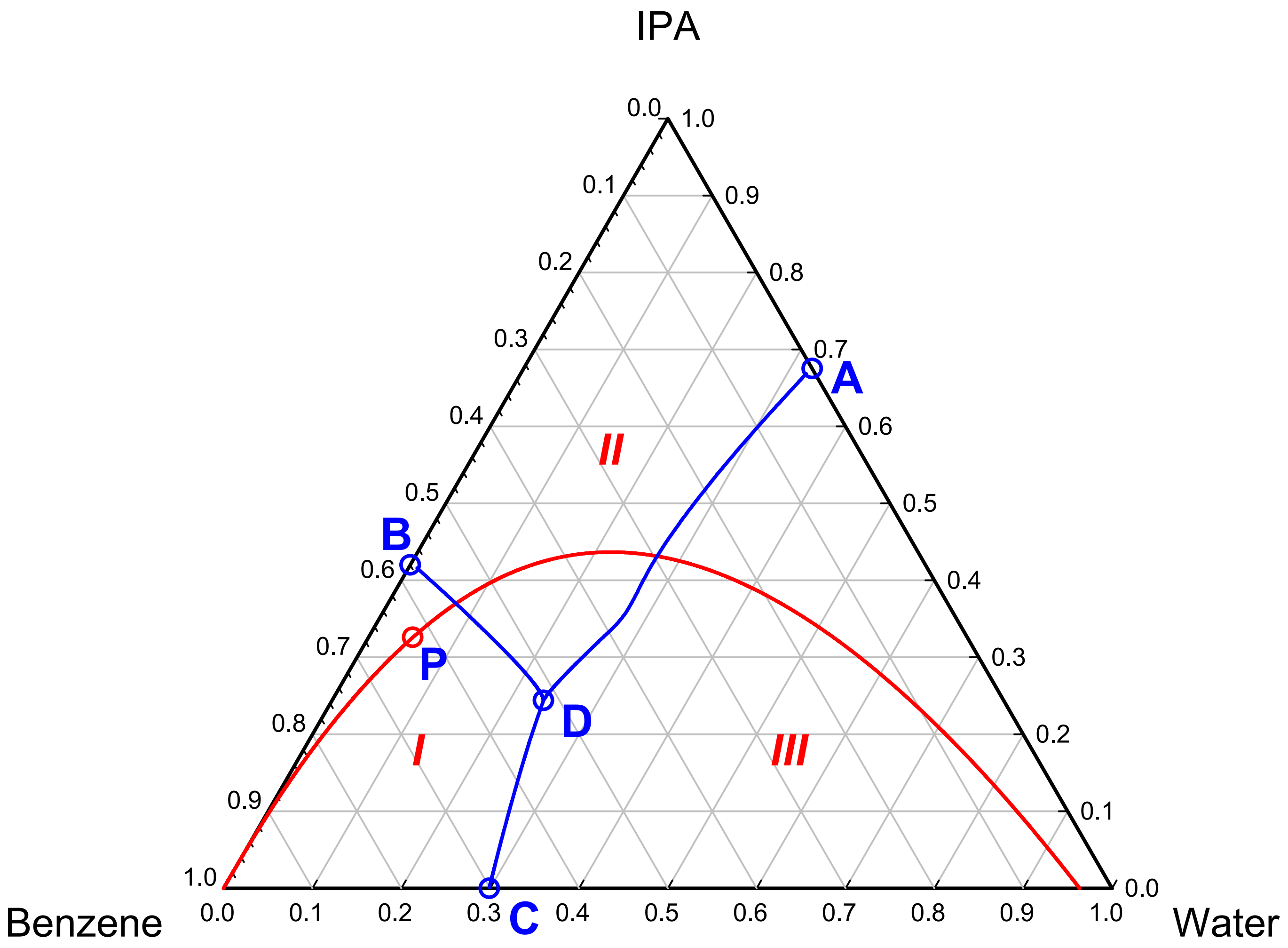
Residual Curve for IPA and Benzene:



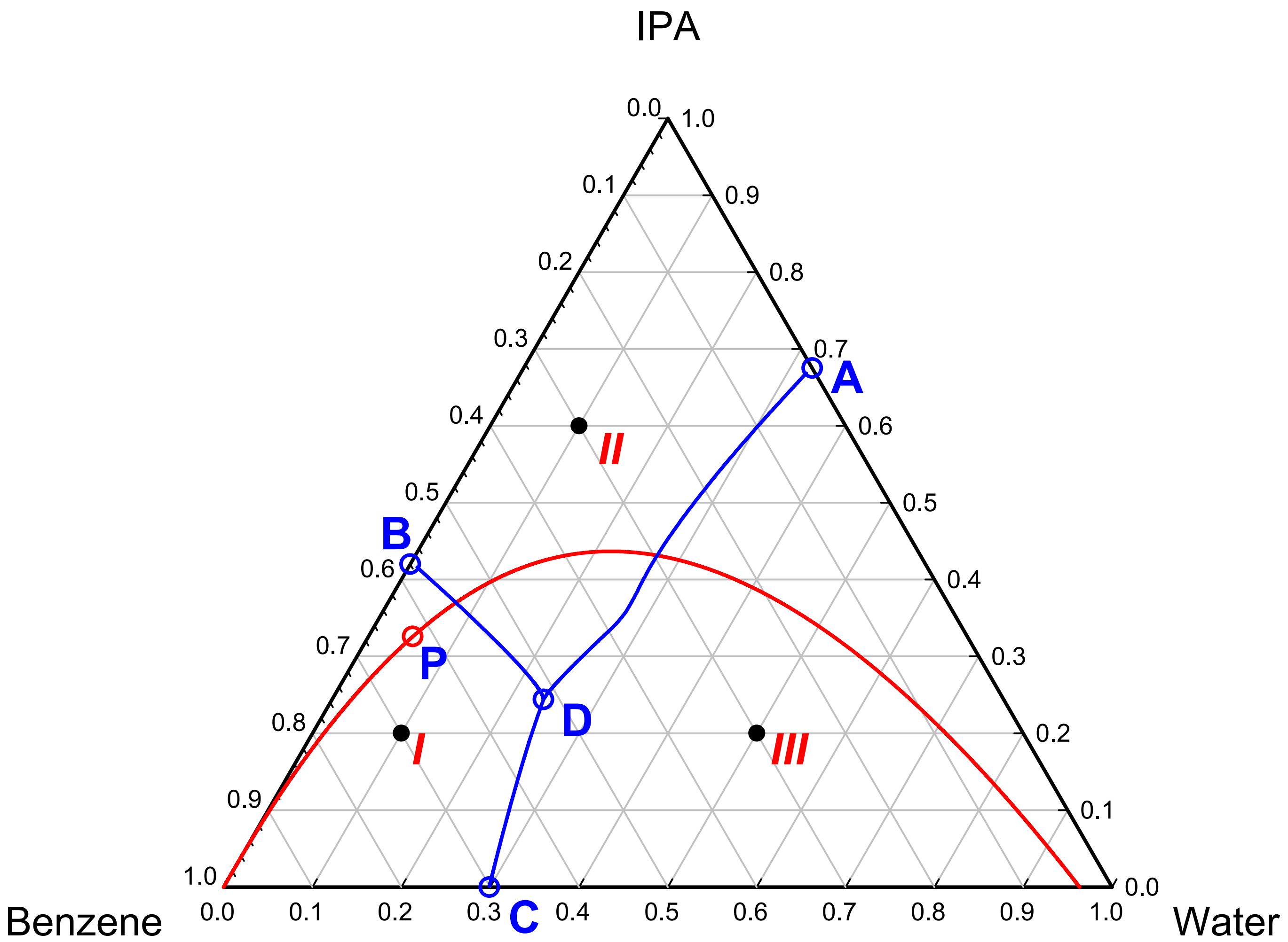
Residual Curve for Water and Benzene:

Trial	Water	IPA	Benzene
1	0.2987	0.0010	0.7003
5	0.2986	0.0015	0.7000
10	0.2983	0.0024	0.6993
15	0.2979	0.0038	0.6983
20	0.2973	0.0061	0.6966
25	0.2962	0.0096	0.6941
30	0.2947	0.0149	0.6904
35	0.2926	0.0224	0.6850
40	0.2897	0.0327	0.6776
45	0.2860	0.0457	0.6682
50	0.2818	0.0613	0.6569
55	0.2771	0.0787	0.6443
60	0.2722	0.0969	0.6309
65	0.2675	0.1150	0.6175
70	0.2631	0.1322	0.6046
75	0.2591	0.1482	0.5927
80	0.2556	0.1626	0.5818
85	0.2526	0.1753	0.5721
90	0.2500	0.1863	0.5636
95	0.2479	0.1958	0.5563
100	**0.2380**	**0.2440**	**0.5180**

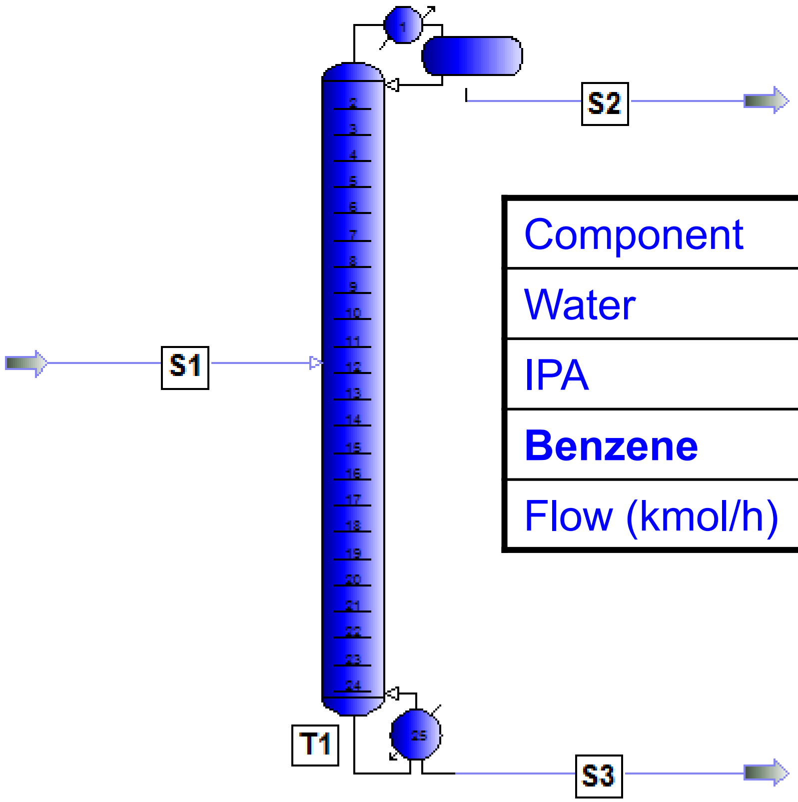
Residual Curve for Water and Benzene:



Composition at Region II can produce pure IPA.

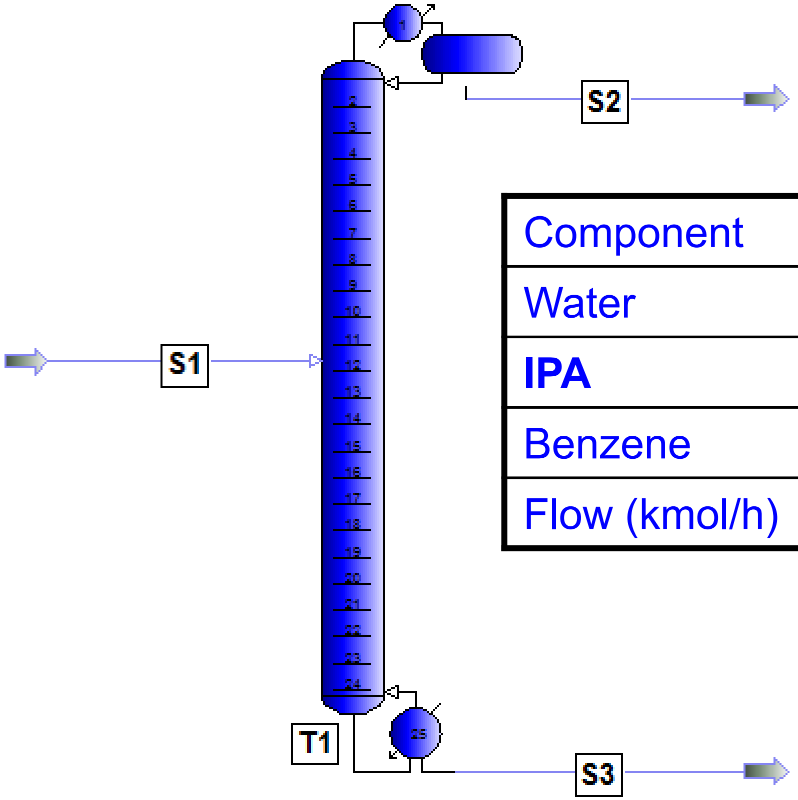


Feedstock in Region *I*.



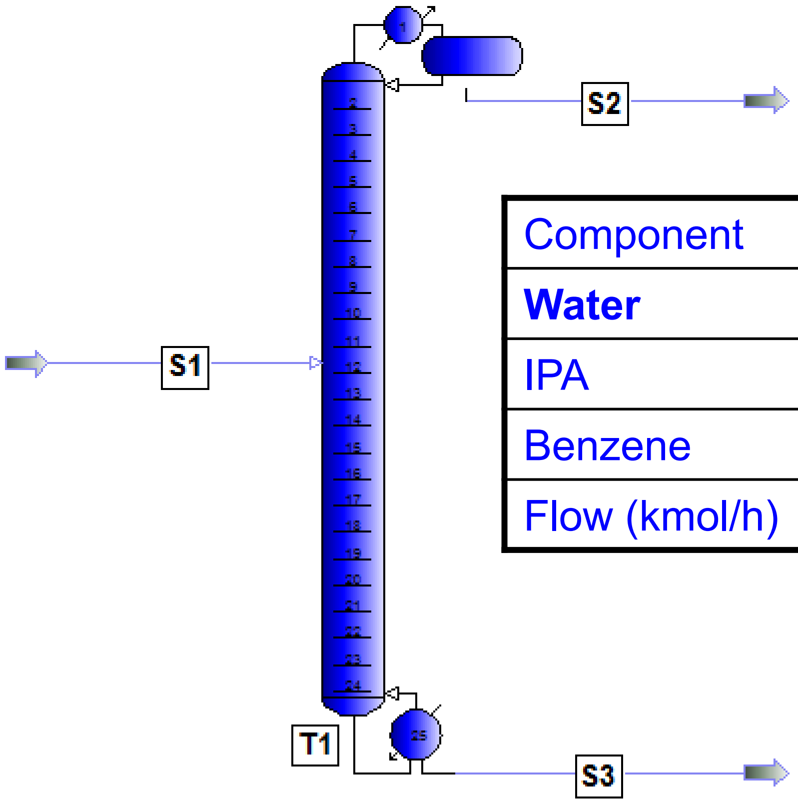
Component	S1	S2	S3
Water	10.0000	16.2421	1.7277E-13
IPA	20.0000	32.4217	0.10000
Benzene	70.0000	51.3362	**99.9000**
Flow (kmol/h)	100.0000	61.5685	38.4315

Feedstock in Region *II*.



Component	S1	S2	S3
Water	10.0000	16.8317	0.1000
IPA	20.0000	32.4661	**99.9000**
Benzene	70.0000	50.7021	2.1407E-6
Flow (kmol/h)	100.0000	59.1691	40.8309

Feedstock in Region *III*.

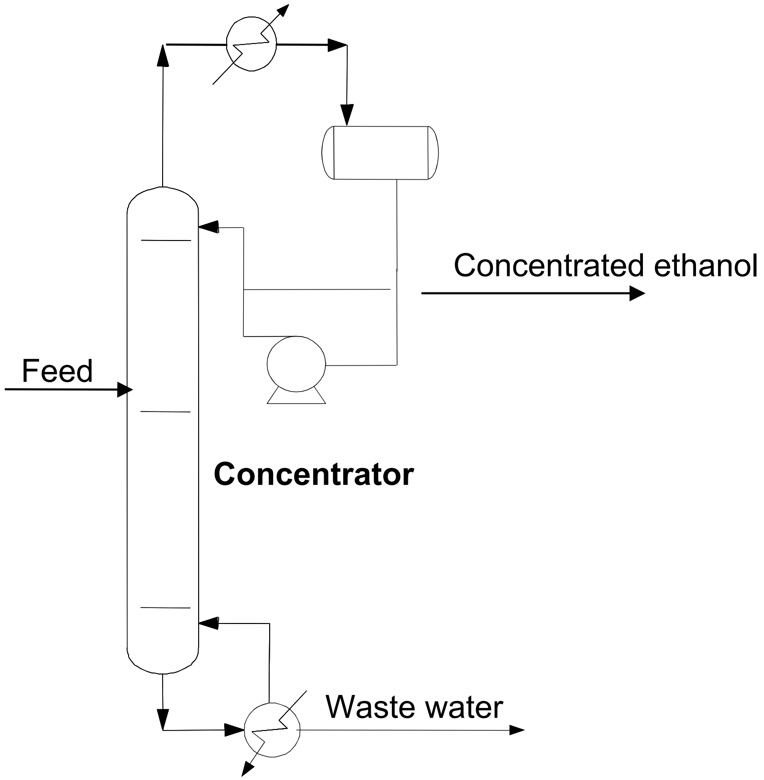


Component	S1	S2	S3
Water	10.0000	23.5506	**99.9000**
IPA	20.0000	30.5480	0.1000
Benzene	70.0000	45.9014	1.1071E-8
Flow (kmol/h)	100.0000	65.3547	34.6426

6

농축기(Concentrator)의 전산모사 기법

Concentrator Simulation:



Basis: Feed = 100 Kg-mole/hr

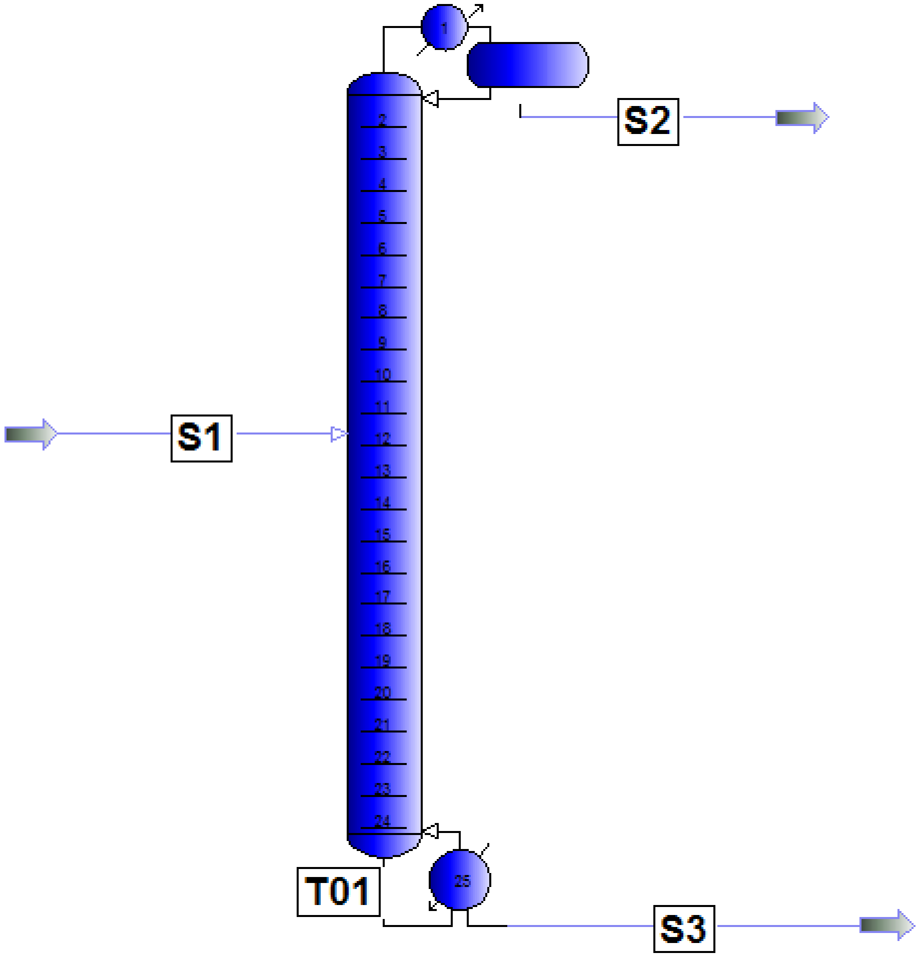
$x_F = 0.10$

Ethanol Mole Balance

$F\ x_F = D\ x_D$ (Nearly Pure Water at Column Bottom)

$$D = \frac{F \cdot x_F}{x_D} = \frac{F \cdot x_F}{x_{azeo}} = \frac{(100) \cdot (0.6)}{(0.88)} = 68.18$$

PRO/II Flow Sheet for a Concentrator:



Column Summary for a Concentrator:

```
COLUMN SUMMARY

                           ---------- NET FLOW RATES -----------     HEATER
  TRAY    TEMP   PRESSURE   LIQUID    VAPOR    FEED     PRODUCT      DUTIES
          DEG C    BAR                    KG/HR                    M*KCAL/HR
 ------  ------- --------  -------- -------- --------- ---------  ------------
      1C    45.0     1.05    3427.9                                685.6L       -0.9728
       2    84.6     1.20    3934.4   4113.5
       3    84.8     1.21    3930.8   4620.0
       4    84.9     1.22    3925.0   4616.4
       5    85.1     1.23    3915.8   4610.6
       6    85.3     1.23    3901.3   4601.4
       7    85.5     1.24    3878.3   4586.8
       8    85.7     1.25    3841.3   4563.9
       9    85.9     1.26    3779.3   4526.8
      10    86.1     1.27    3667.8   4464.9
      11    86.4     1.28    3432.1   4353.4
      12    87.4     1.29    6046.5   4117.7   2222.3L
      13    87.5     1.30    6049.3   4509.7
      14    87.7     1.30    6052.2   4512.6
      15    87.9     1.31    6055.0   4515.4
      16    88.1     1.32    6057.8   4518.2
      17    88.2     1.33    6060.6   4521.0
      18    88.4     1.34    6063.3   4523.8
      19    88.6     1.35    6065.8   4526.6
      20    88.7     1.36    6064.4   4529.0
      21    88.9     1.37    6014.4   4527.7
      22    89.4     1.37    5341.0   4477.6
      23    95.1     1.38    3887.2   3804.2
      24   106.4     1.39    3567.0   2350.4
     25R   109.1     1.40              2030.2             1536.8L        1.0714
```

Distillation Algorithm Selection: (1)

- Inside Out (I/O)
  - Relatively Ideal Thermodynamics including Hydrocarbon with Water Decant
  - Incorporates sidestrippers into column: No recycle!
  - Thermosiphon Reboilers
  - Flash Zone Model
  - Very forgiving of bad initial estimates
  - Fast!
  - No VLLE

Distillation Algorithm Selection: (2)

- CHEMDIST
  - Mechanically simple columns, complex thermo
  - True VLLE
  - Azeotropic and Reactive distillation
  - Sidestrippers solved by recycle
  - No Pumparounds or Thermosiphons
  - More sensitive to bad initial estimates

Distillation Algorithm Selection: (3)

- SURE
  - Very general: Complex column and thermo
  - Use when I/O and Chemdist do not apply
  - Newton Method
  - Very sensitive to bad initial estimates

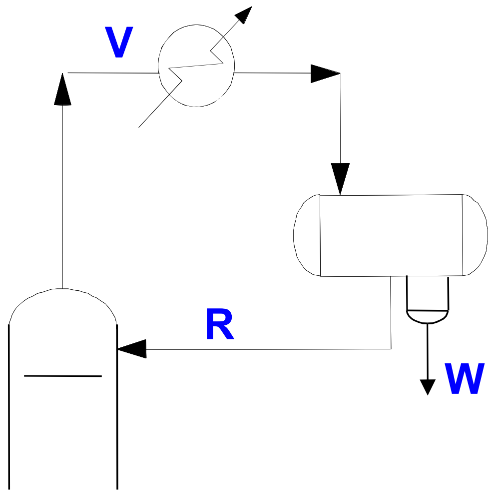
Distillation Algorithm Selection: (4)

	Inside/Out (I/O)	**CHEMDIST**	**SURE**
Unique Features	• Side & main columns solved simultaneously	• Reactive Distillation • VLLE on any tray	• Total Pumparounds • VLWE on any tray • Water draw any tray
Strengths	• Very fast • Insensitive to initial estimates	• Highly Non-Ideal Systems	• Generality
Limitations	• Thermo non-ideality • NO VLLE capability (VLWE at condenser)	• No Pumparounds • Side columns solved as recycles	• Slow • Sensitive to initial guesses
Applicability	• Hydrocarbons • EOS & Slightly non-ideal LACT Thermo • Interlinked columns	• Non-Ideal Systems • Mechanically simple columns • VLLE within column	• Free water or water draw on trays other than condenser • Total pumparounds or vapor bypass

7

경사 분리기(Decanter)의 전산모사 기법

Decanter Simulation:



Assume OVHD Vapor Composition, V around ternary azeotrope

	Mole %
Benzene	53.00
IPA	31.00
Water	16.00

Decanter Simulation:

```
TITLE PROJ=AZEOTROPE, PROB=FLASH,USER=J.H.CHO
  PRINT INPUT=ALL, RATE=M, FRACTION=M, PERCENT=M
  DIMENSION METRIC
COMPONENT DATA
  LIBID 1,BENZENE/2,ETHANOL/3,WATER
THERMODYNAMIC DATA
  METHOD SYSTEM(VLLE)=NRTL, SET=NRTL01
STREAM DATA
  PROP STRM=V, TEMP=70, PRES=1.033, RATE(M)=100, & COMPOSITION(M)=1,53/2,31/3,16
UNIT OPERATIONS
  FLASH UID=COND, NAME=Condenser, KPRINT
      FEED V
      PRODUCT  L=R, W=W
      ISO  TEMPERATURE=45, PRESSURE=1.033
END
```

	V (Mole %)	R (Mole %)	W (Mole %)
Benzene	53.00	73.3072	3.1511
Ethanol	31.00	24.0964	47.9467
Water	16.00	2.5965	48.9022
Flow Rate	100 %	71.05 %	28.95 %

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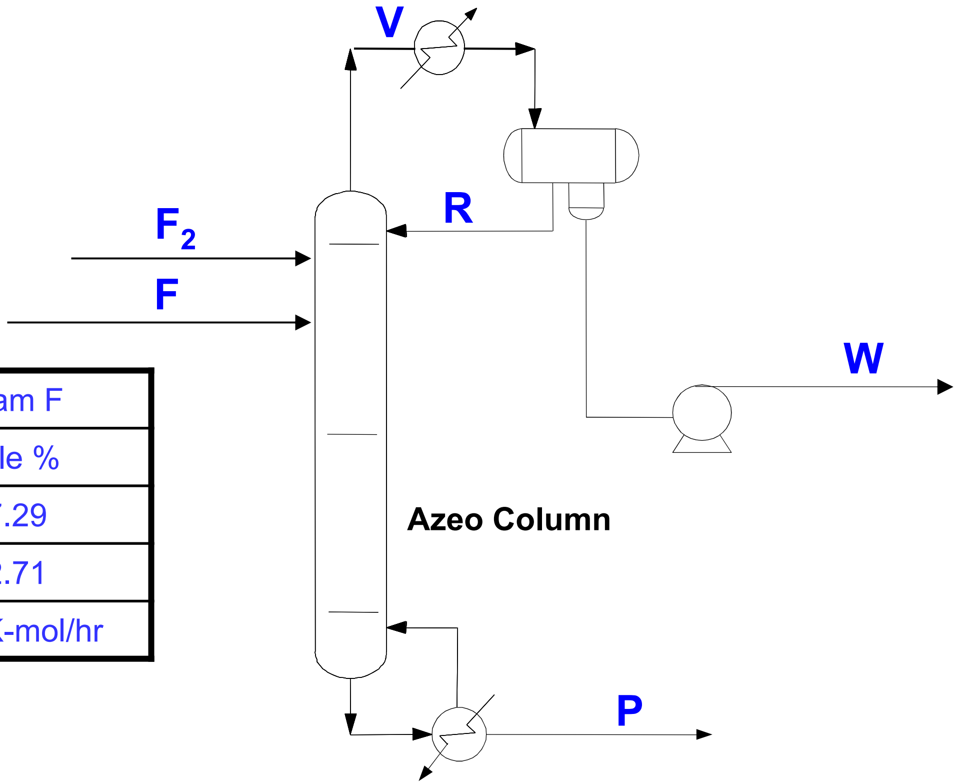
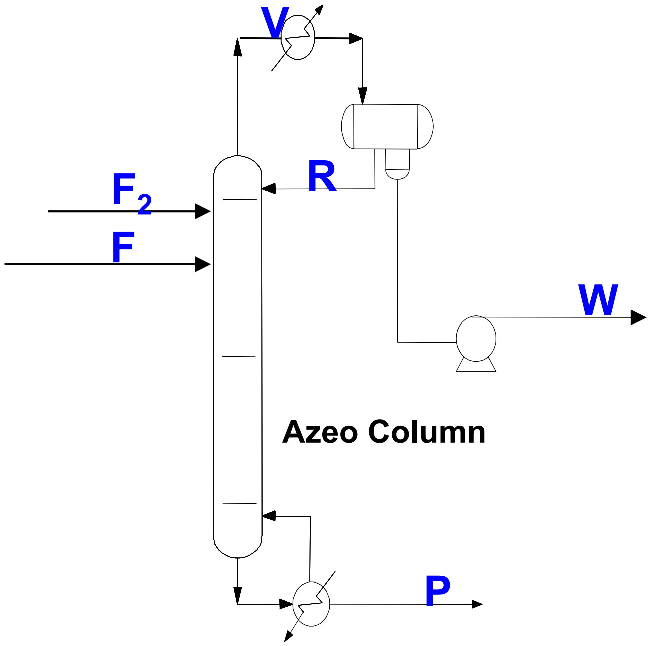
공비 증류탑(Azeotropic Column)의 전산모사 기법

Azeotropic Column Simulation:



Composition of Stream F	
Component	Mole %
IPA	67.29
Water	32.71
Flow Rate	14.8 K-mol/hr

Azeotropic Column Simulation:



- Water balance around Azeotropic Column

$$Azeo\_feed = 73.9\times(1-0.8115)+F_2\times(1-0.8115)$$

$$=13.93+0.1885F_2$$

$$W = V\times(0.489022)\times(0.2895)$$

$$=0.141572\cdot V$$

$$\underline{0.141572\cdot V = 13.93+0.1885\cdot F_2} \quad \text{- (1)}$$

- Ethanol balance around Azeotropic Column

$$V\times(0.2895)\times(0.479467)=(0.8115)\times F_2$$

$$\underline{F_2 = 0.171048\cdot V} \quad \text{- (2)}$$

- Benzene flow from the decanter

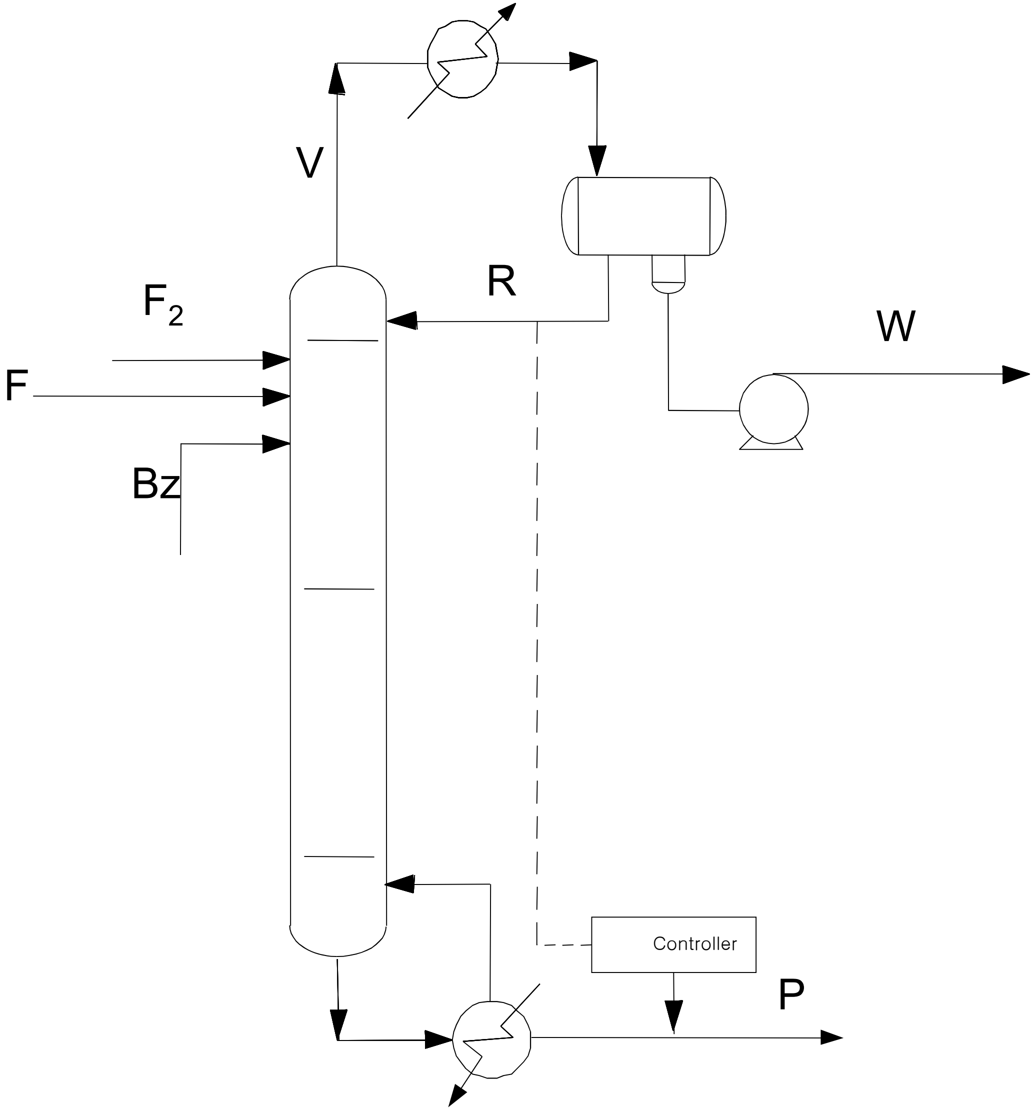
$$=(127.4)\cdot(0.2895)\cdot(0.031511)=1.162$$

K-mol/hr

- Combining Eq. (1) & (2):

$V = 127.4$ K-mol/hr , $F_2 = 21.79$ K-mol/hr

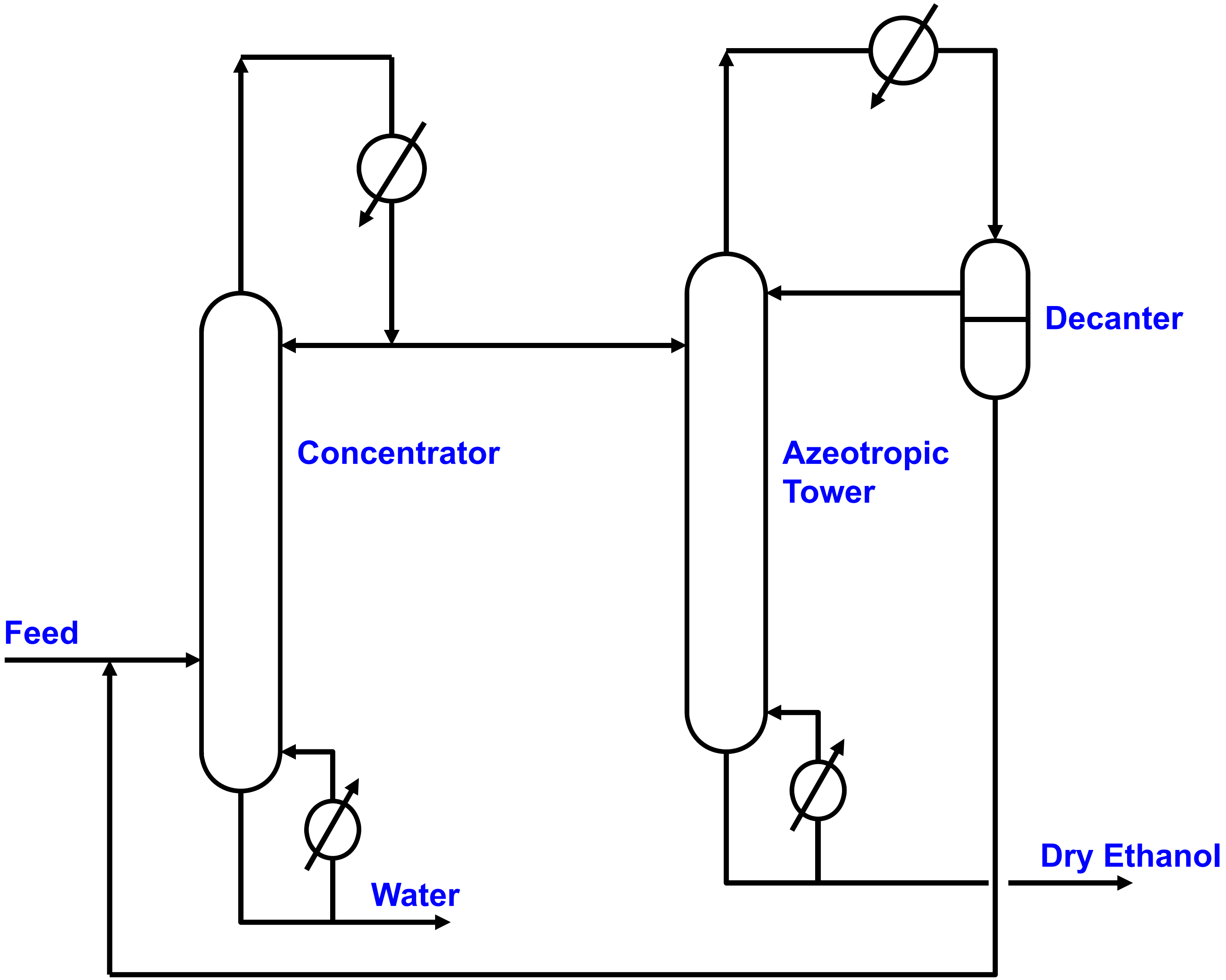
Azeotropic Column Simulation:



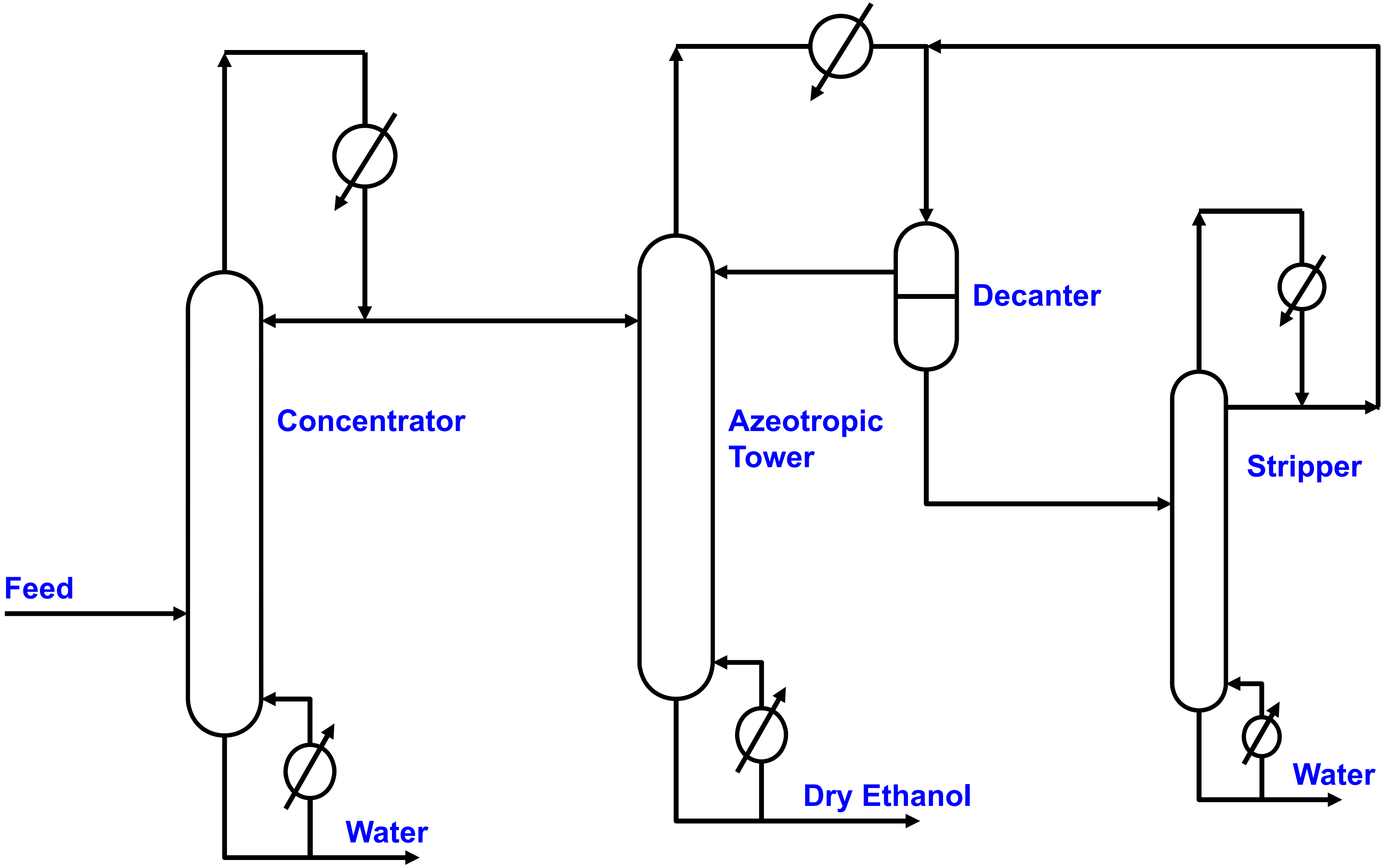
9

Stripper의 전산모사 기법

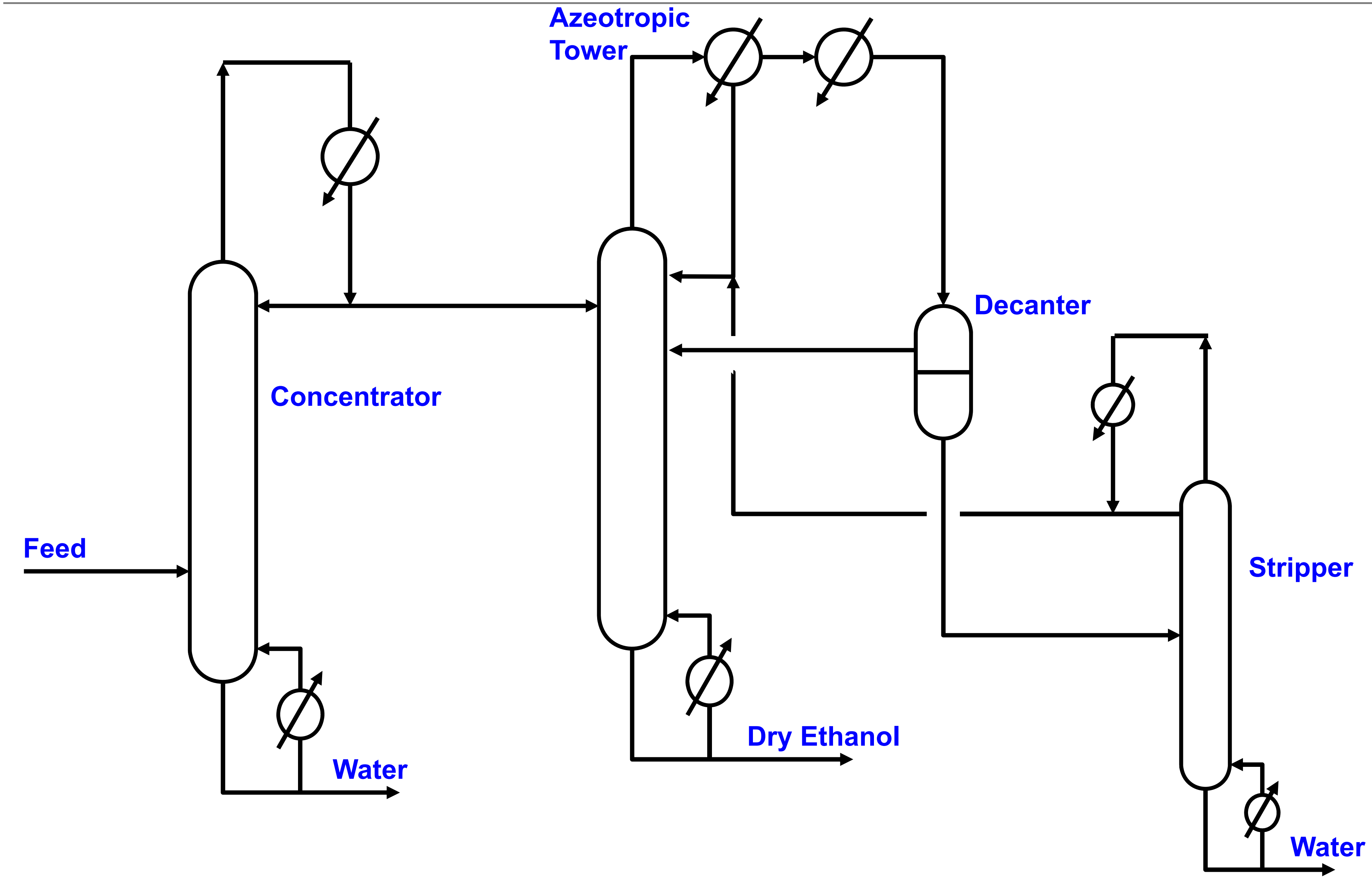
Azeotropic Distillation Process: Scheme 1



Azeotropic Distillation Process: Scheme 2



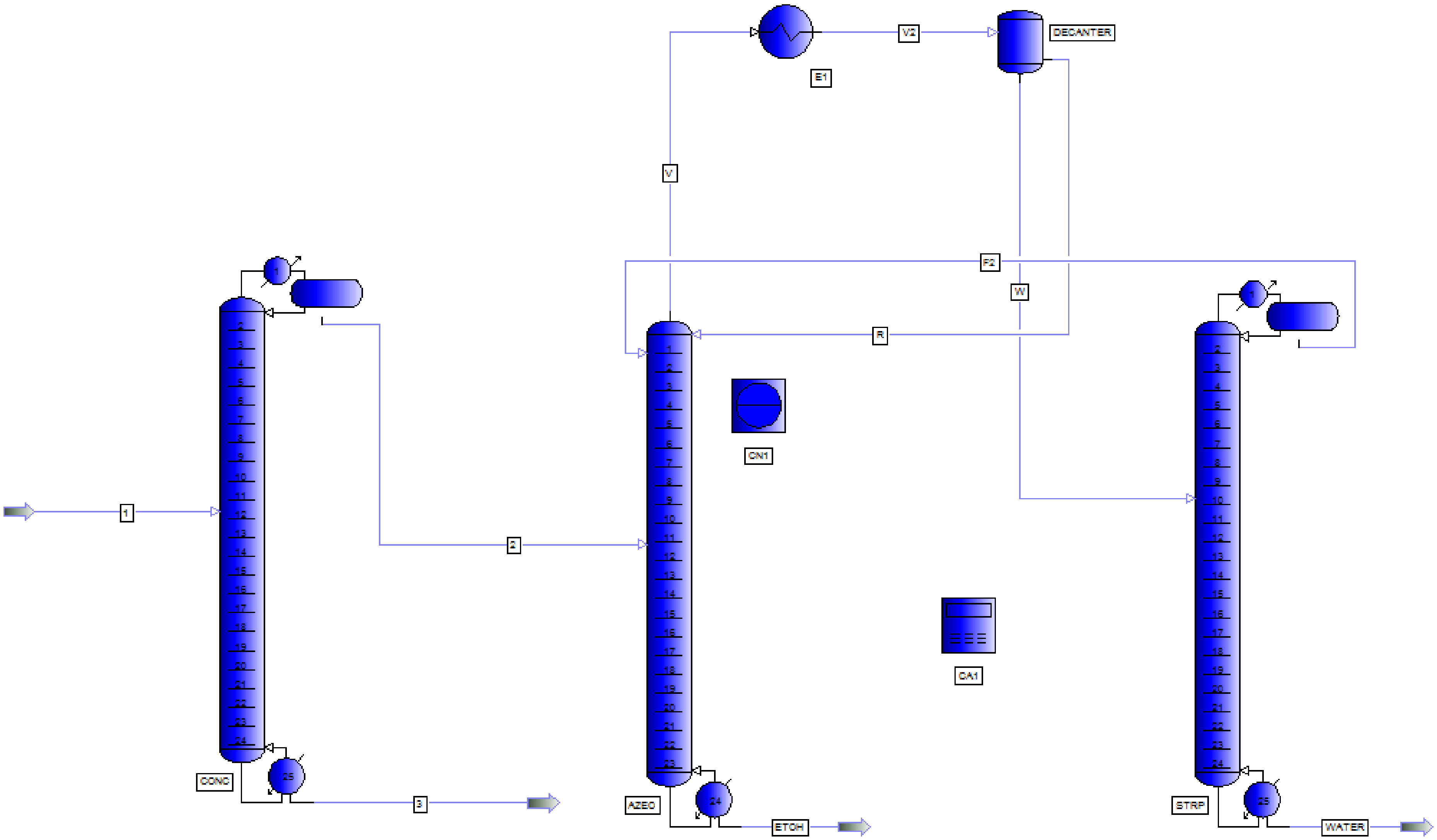
Azeotropic Distillation Process: Scheme 3



10

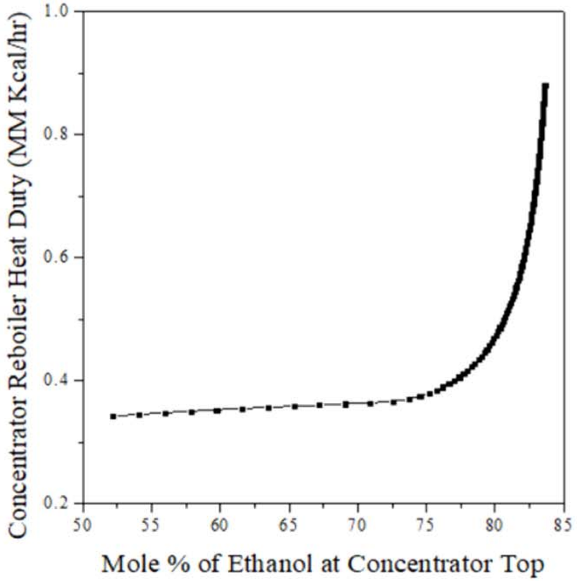
전체 공정에 대한 공정 최적화

전제 공정에 대한 PRO/II Flow Sheet

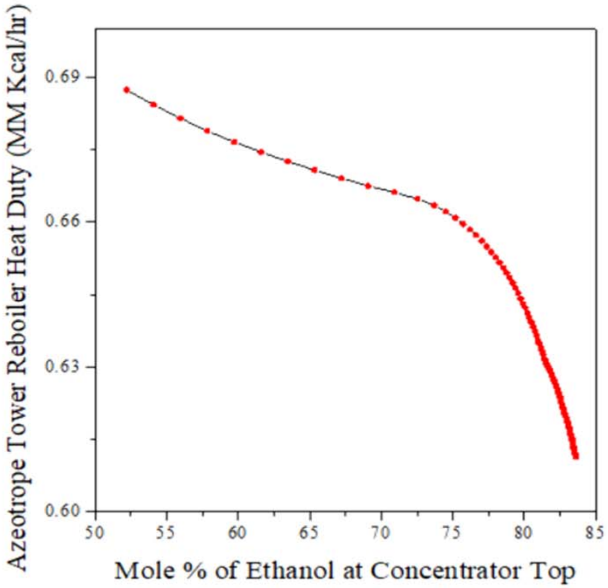


전체 공정에 대한 공정 최적화:

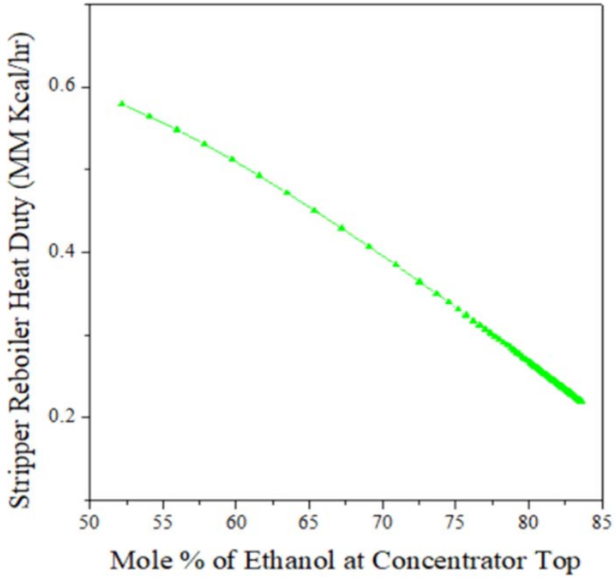
Concentrator



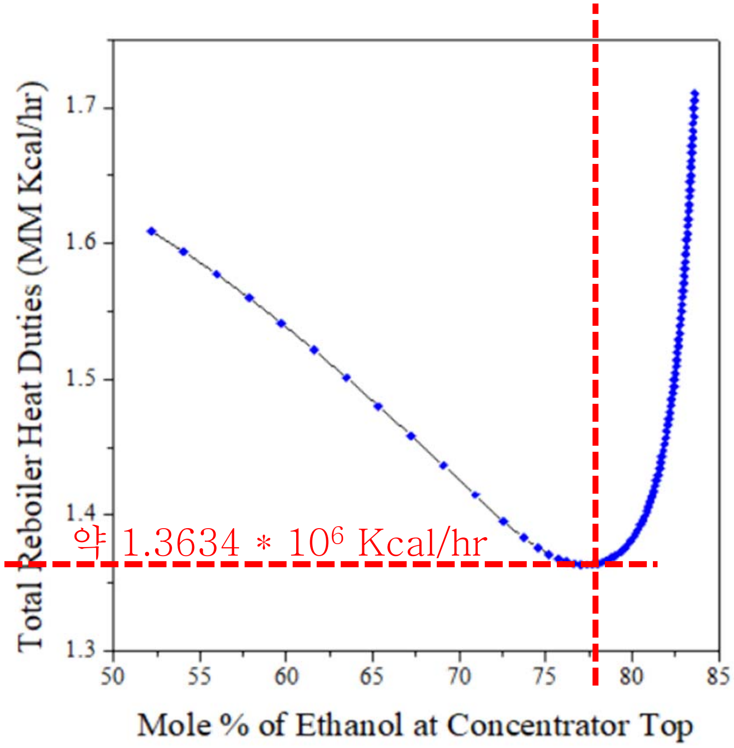
Azeotropic Column



Stripper

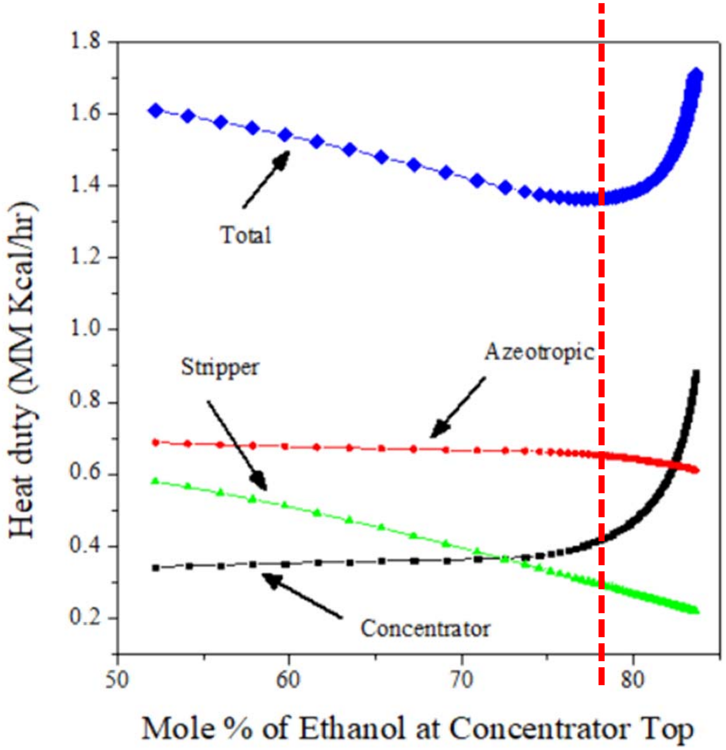


Conclusion:



약 $1.3634 * 10^6$ Kcal/hr

약 77.38%



THANK YOU