공비점 분리제로서 벤젠을 이용한 에탄올 탈수공정의 열역학적 연구

2001년 10월 19일 (금)

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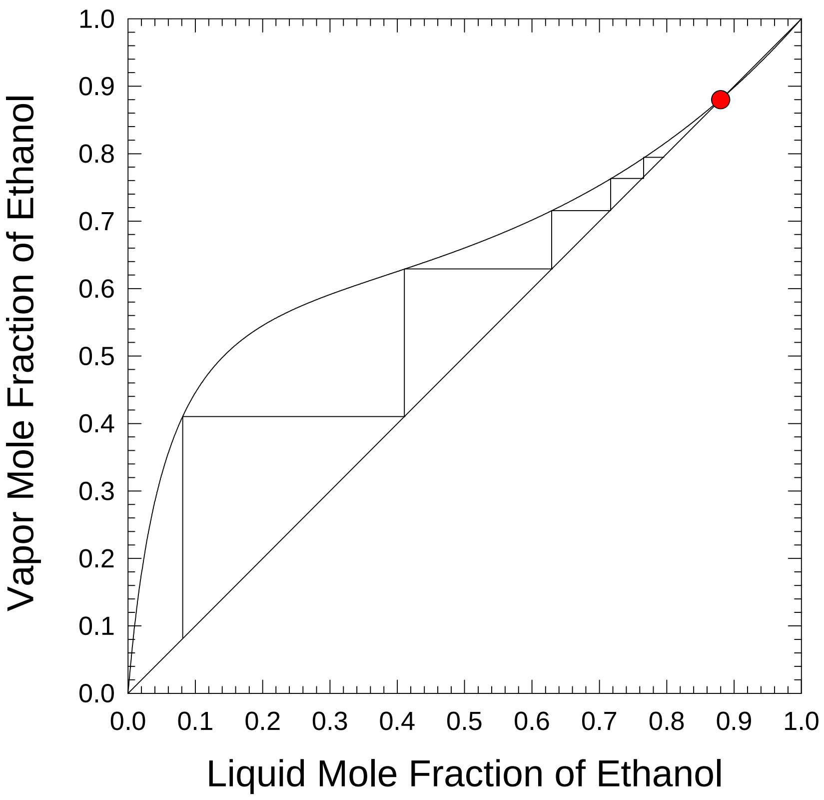
물-에탄올 이성분계



물-에탄올 이성분계와 계단작도

물-에탄올 이성분계는 88mole% 근처에서 공비점을 형성하므로 통상적인 분리방법을 통해서는 각각의 순수한 성분을 얻어내 수 없다.

따라서 제 3의 성분인 벤젠과 같은 공비점 분리제를 사용해서 ...

공비증류와 추출증류

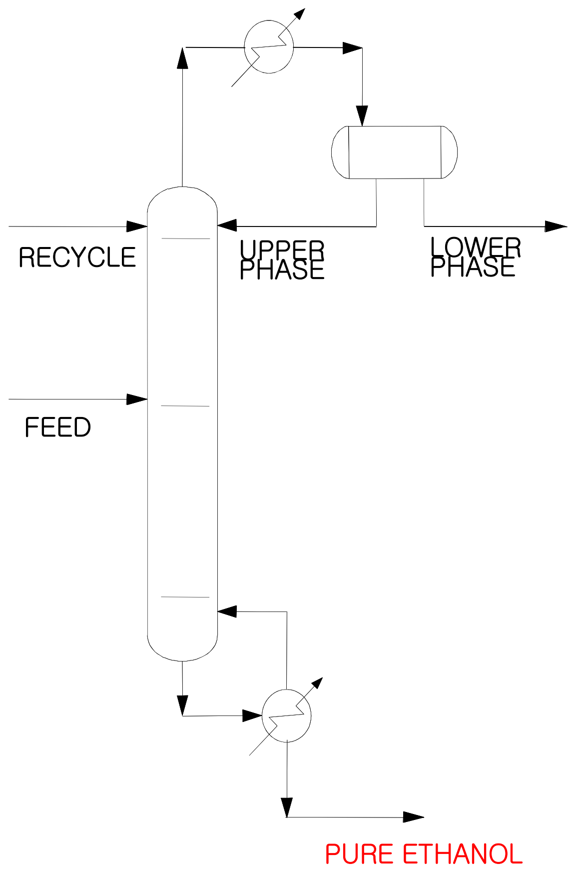
Azeotropic Distillation

- 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.

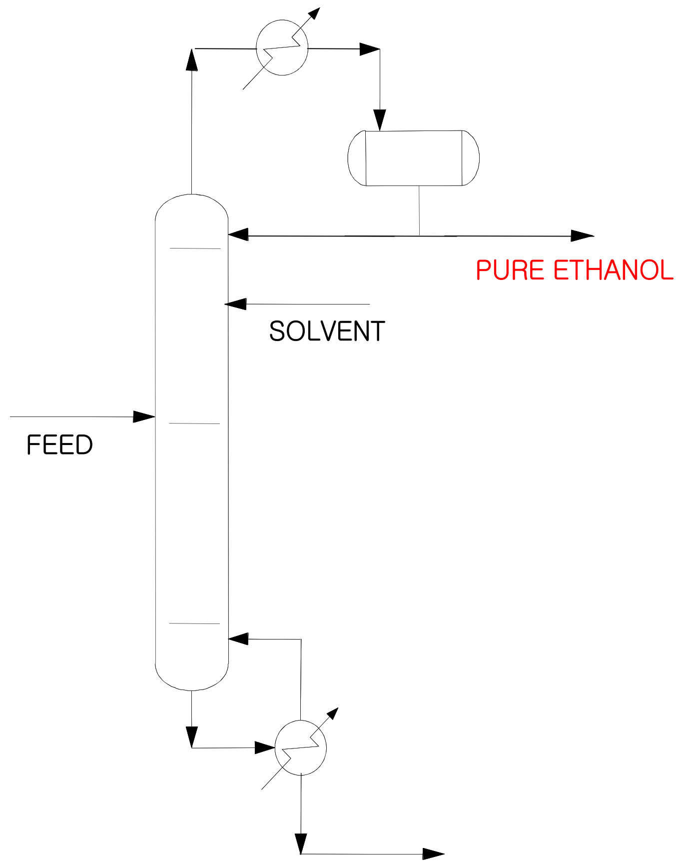
Extractive Distillation

- 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.

공비증류와 추출증류



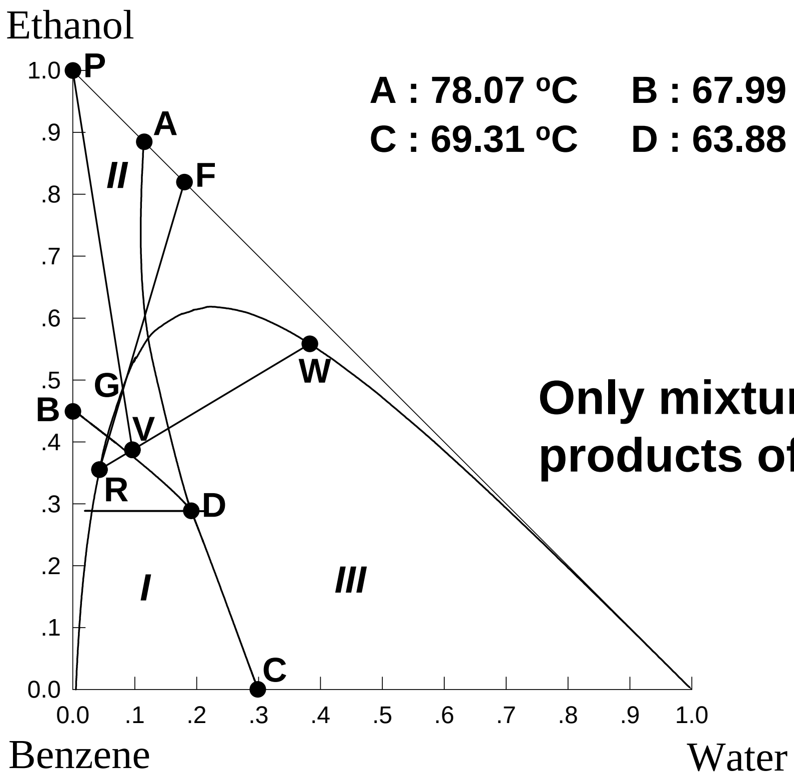
Azeotropic Distillation



Extractive Distillation

공비증류공정의 원리

DONG YANG UNIVERSITY



A : 78.07 ^oC B : 67.99 ^oC

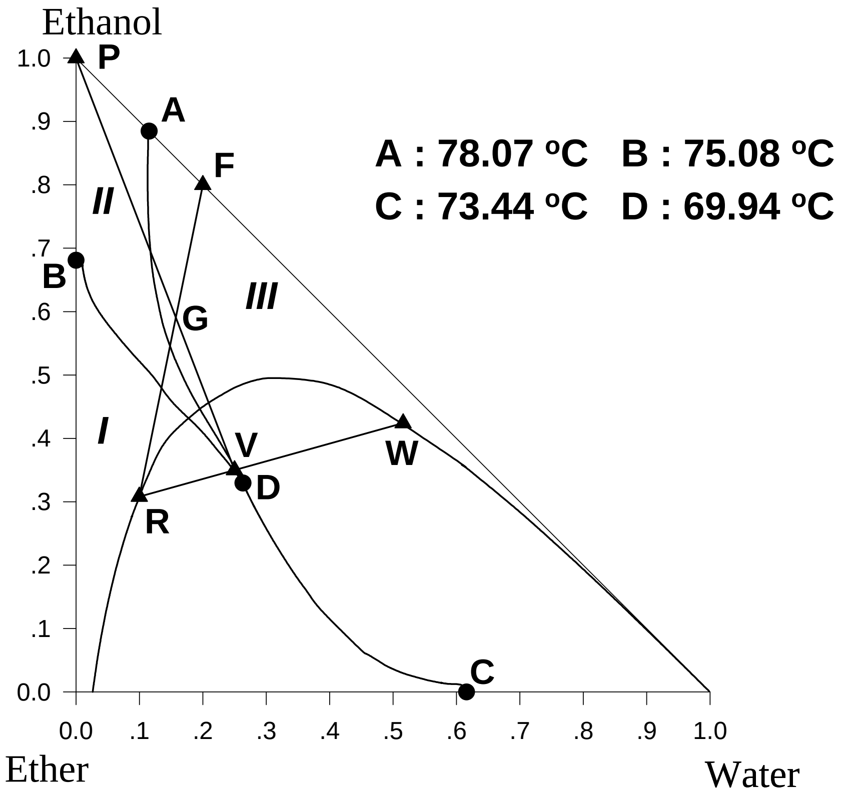
C : 69.31 ^oC D : 63.88 ^oC

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

물-에탄올-벤젠 삼성분계 상평형도와
공비증류탑 설계조건

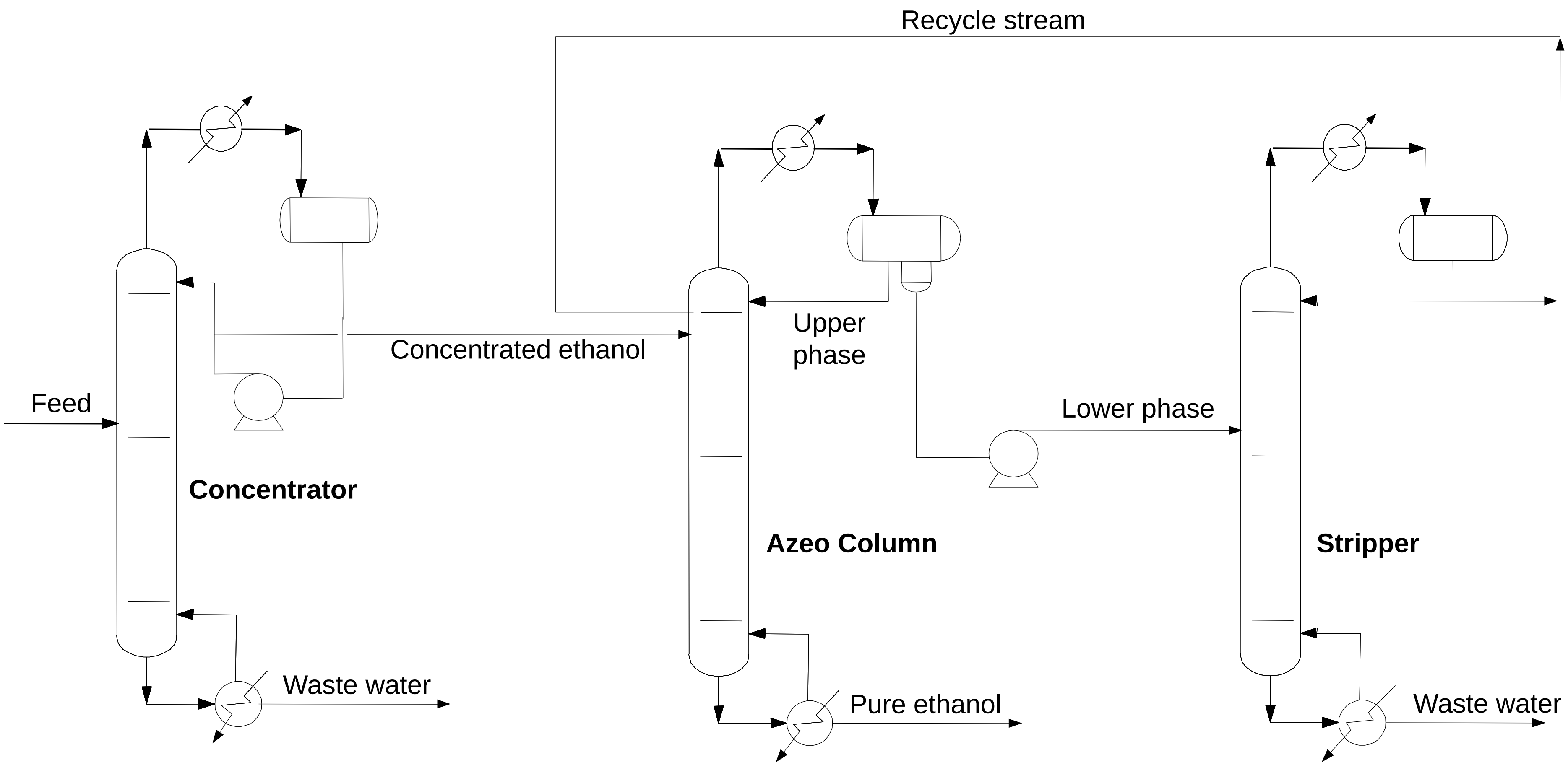
Aqueous ethanol can be separated into their pure components by distillation by the addition of a third component, so called the entrainer, which forms a ternary heterogeneous azeotrope with a lower than any other binary azeotropes.

공비점 분리제의 선정 조건



In this case, pure ethanol cannot be obtained since *G* is in region *III*.

공비증류공정의 구성



에탄올 탈수 공비증류공정 **(Three-columns configuration)**

Problem Description

- Feed

가. Feed Composition

1) Ethanol : 60.0 mole%

2) Water : 40.0 mole%

나. Feed Condition

1) Inlet Temperature : 25℃

2) Inlet Pressure : 3.5 bar

다. Flow Rate

1) 100 Kg-mole/hr

- Entrainer: Benzene

- Cooling Medium: Water

1) In/Out Temperature : 32℃ /40℃

2) Decanter Operating Temperature : 45℃

공비증류공정 모사 Procedure

Step 1: 열역학 모델의 선정 및 Binodal Curve의 작성

Step 2: 이성분계 및 삼성분계의 공비점 계산

Step 3: 이성분계 및 삼성분계의 Residual Curve 작성

Step 4: Concentrator Simulation

Step 5: Azeotropic Tower Simulation

Step 6: Azeo + Dryer (Stripper) Simulation

Step 7: 전체 공비증류공정의 모사

Step 8: Optimization of Ethanol Dehydration Process

Step 1a: 열역학 모델식의 선정

NRTL Equation

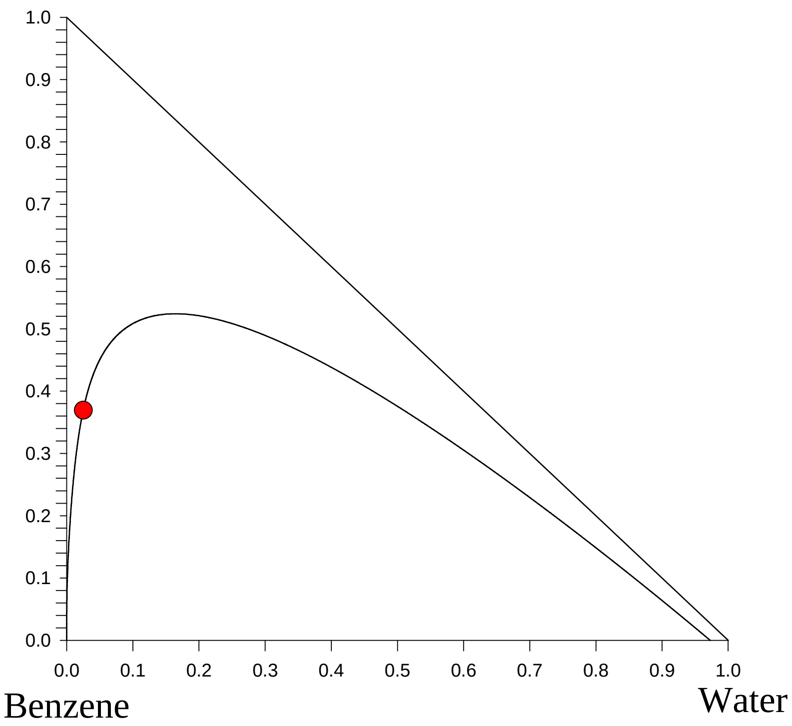
$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right)$$

where

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$$ (when unit is K)

$$G_{ji} = \exp\left(-\alpha_{ji} \tau_{ji}\right)$$

Step 1b: Binodal Curve 의 작성



Binodal Curve Construction using NRTL

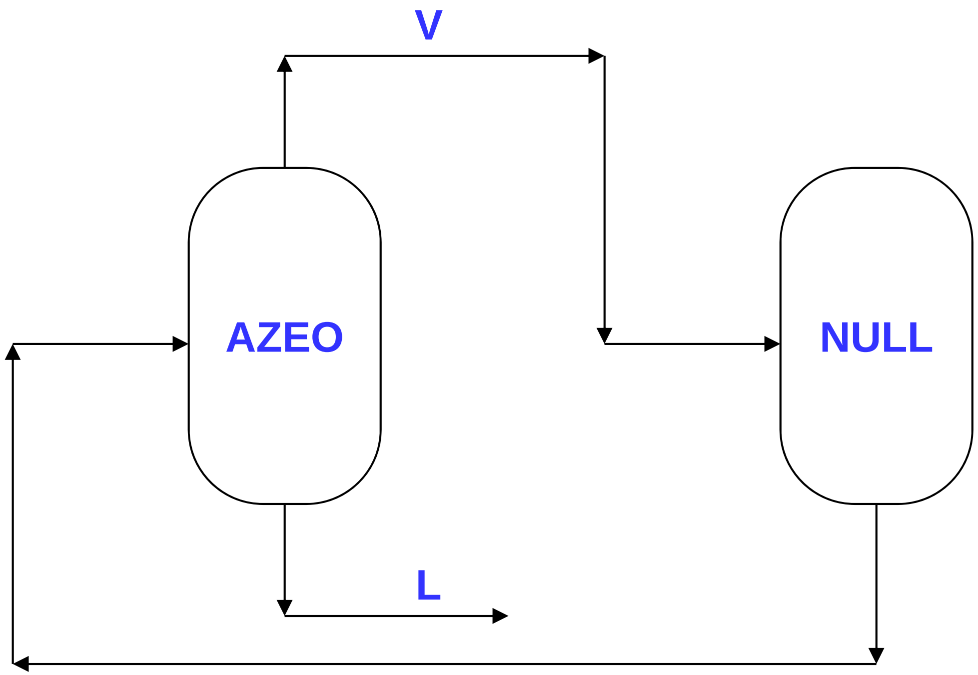
1) Water
2) Ethanol
3) Benzene

Temperature = 45.0°C

Interaction Parameters

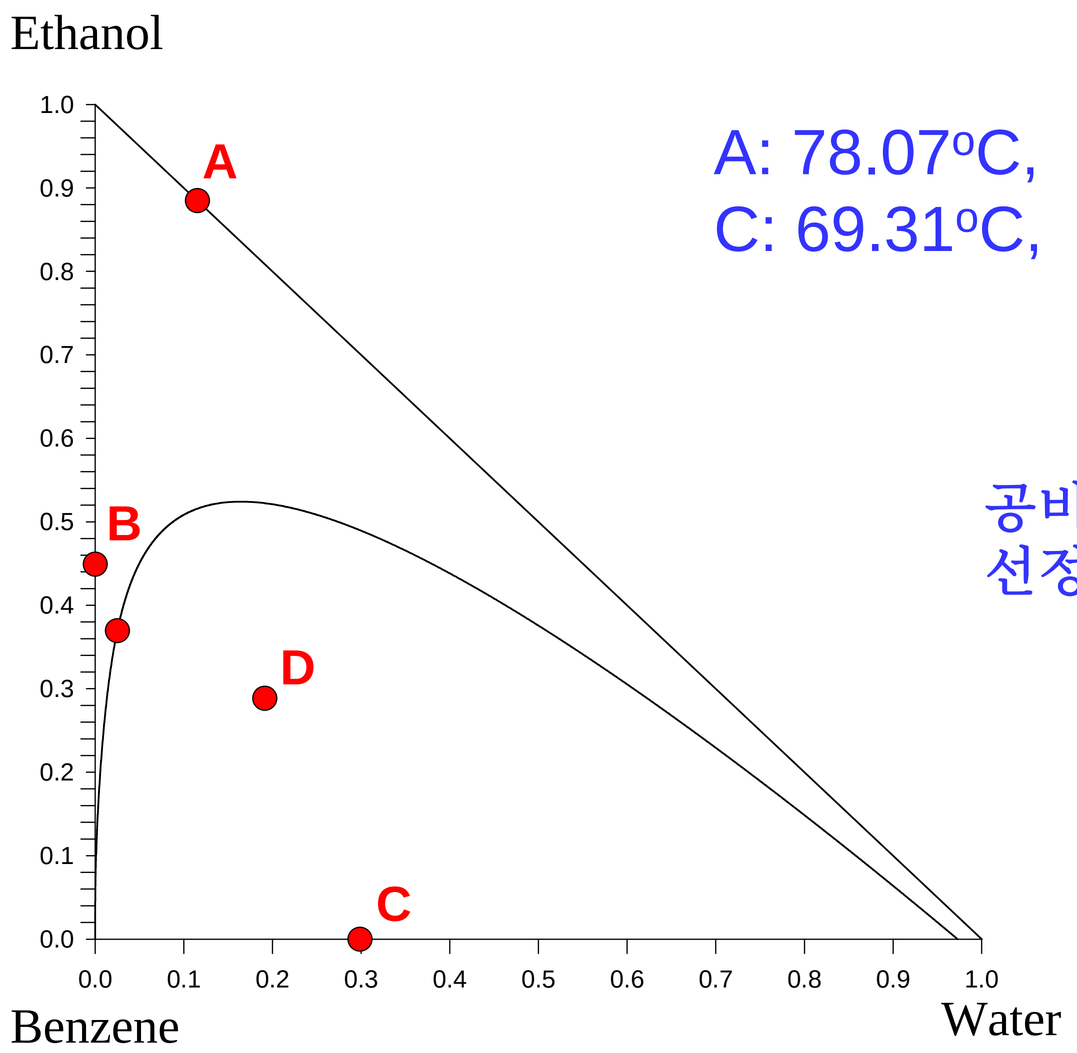
I	J	A(I,J)	A(J,I)	$\alpha(I,J)$
1	2	483.324	195.495	0.291
1	3	2990.025	758.494	0.200
2	3	-60.000	660.00	0.300

Step 2a: 물-에탄올 사이의 이성분계 균일 공비점 찾기



Flash Drum ‘AZEO’에서 증기의 양을 미량(만분의 일) 증발시킨다.
Flash Drum ‘NULL’에서는 1 기압에서 기포점을 계산을 수행한 후 액은 전량 다시 ‘AZEO’로 환류시킨다. 이 과정은 ‘AZEO’에서 각 성분의 K-value 과 같아질 때까지 반복 수행한다.

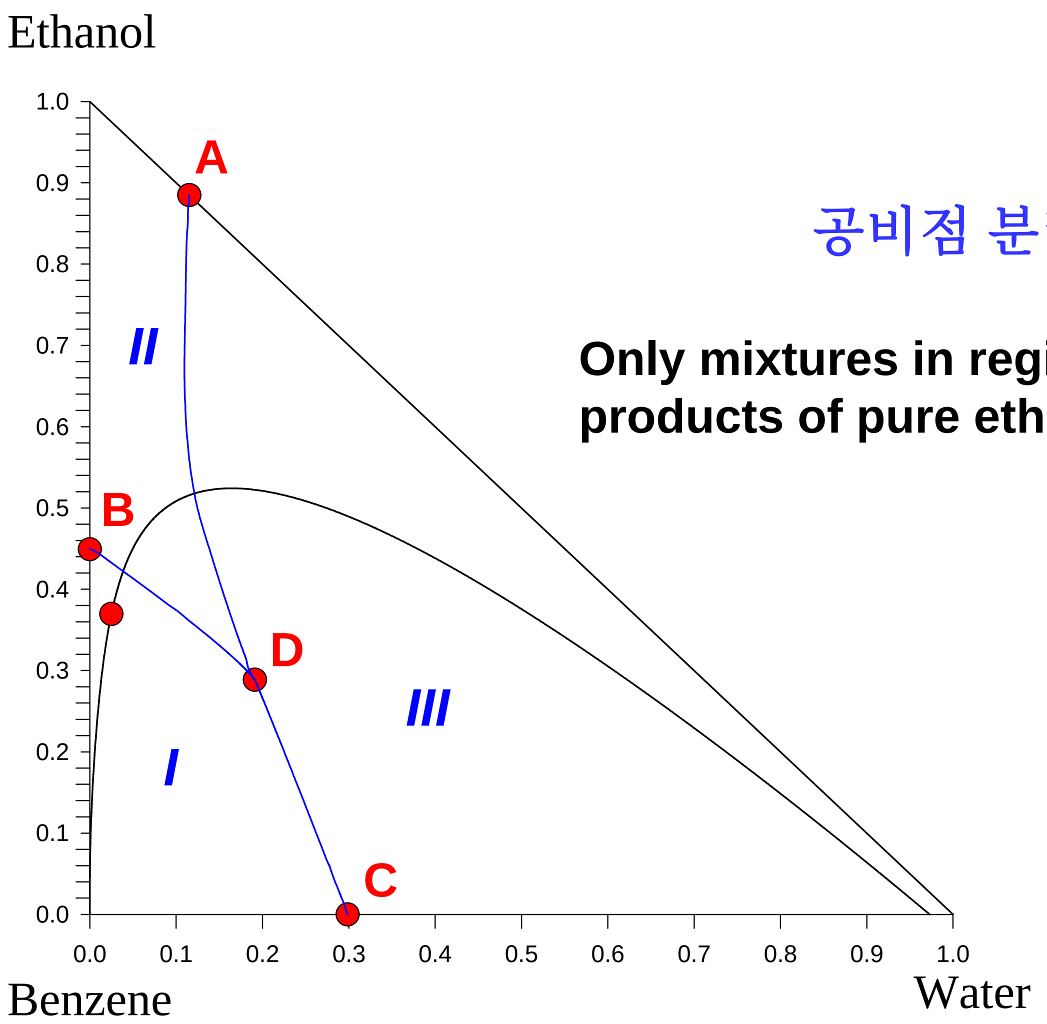
Results for Step 2



A: 78.07^{o}C, B: 69.77^{o}C
C: 69.31^{o}C, *D: 63.88^{o}C*

공비점 분리제
선정 조건 1

Step 3: Residual Curve의 작성 (Curve AD, BD and CD)

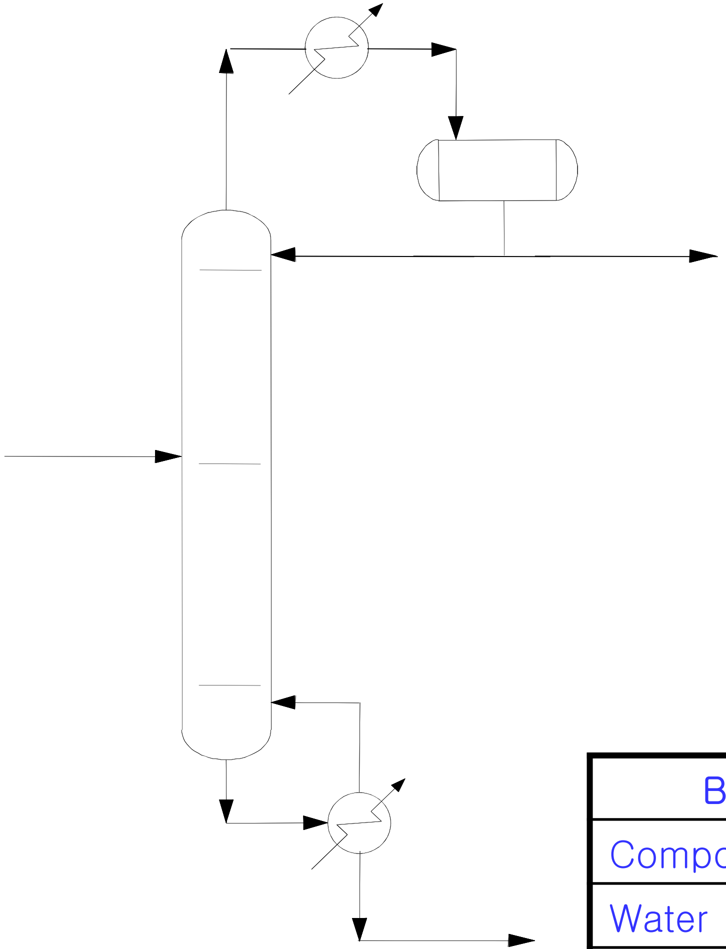


공비점 분리제 선정 조건 2

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

Feed having composition in Region *I* :

Feedstock	
Composition	Mole %
Water	10.00
Ethanol	10.00
Benzene	80.00
Total Flow	100.00

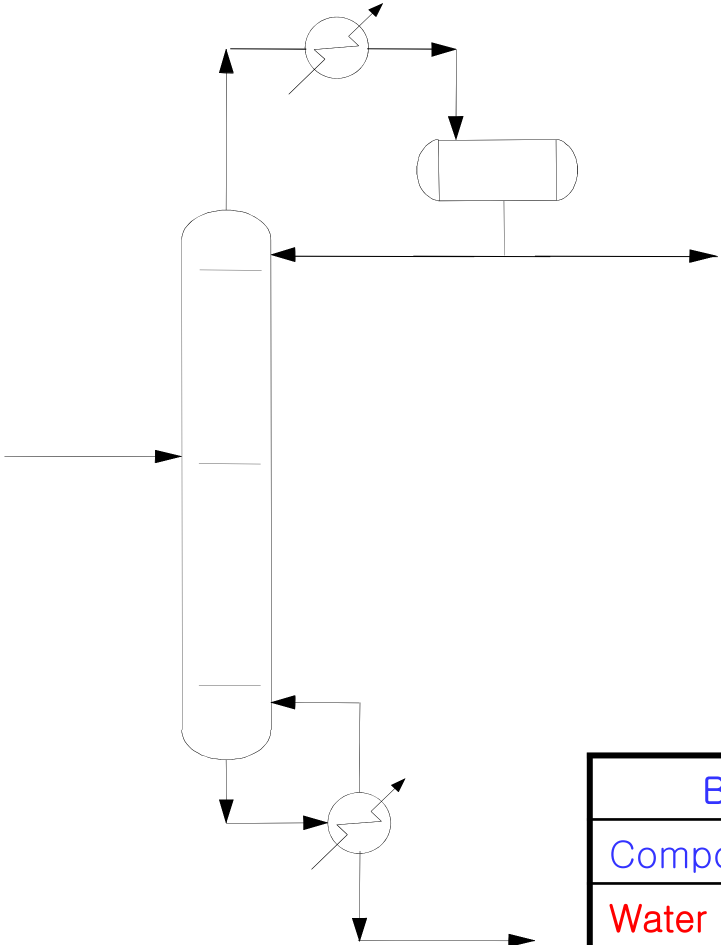


Top Product	
Composition	Mole %
Water	50.63
Ethanol	46.57
Benzene	2.80
Total Flow	19.76

Bottom Product	
Composition	Mole %
Water	0.00
Ethanol	1.00
Benzene	99.00
Total Flow	19.76

Feed having composition in Region *III* :

Feedstock	
Composition	Mole %
Water	50.00
Ethanol	20.00
Benzene	30.00
Total Flow	100.00

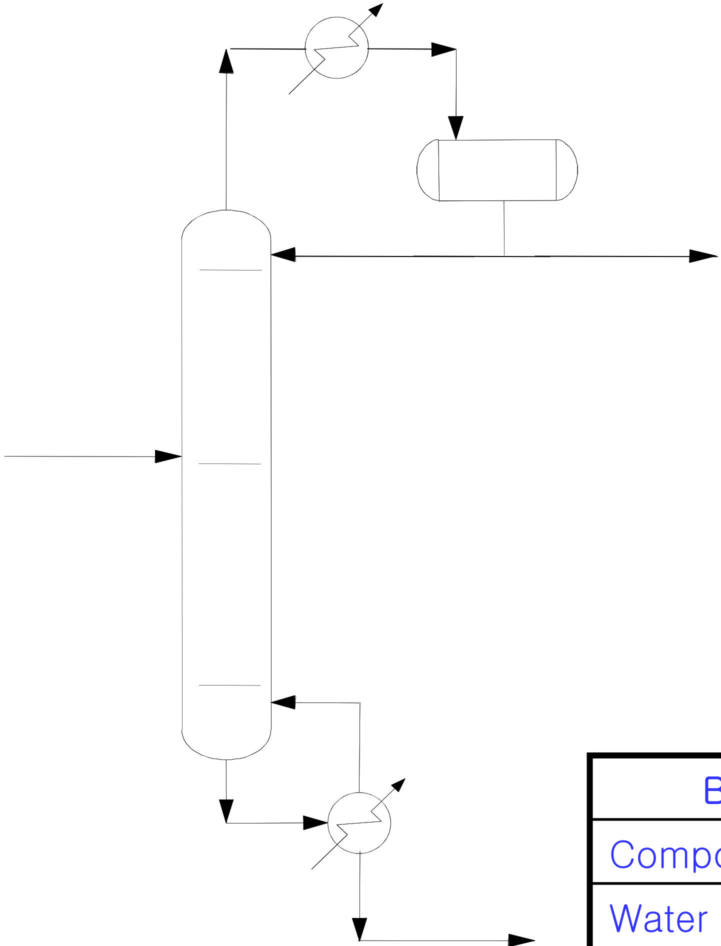


Top Product	
Composition	Mole %
Water	20.10
Ethanol	31.59
Benzene	48.31
Total Flow	62.11

Bottom Product	
Composition	Mole %
Water	99.00
Ethanol	1.00
Benzene	0.00
Total Flow	37.89

Feed having composition in Region *II* :

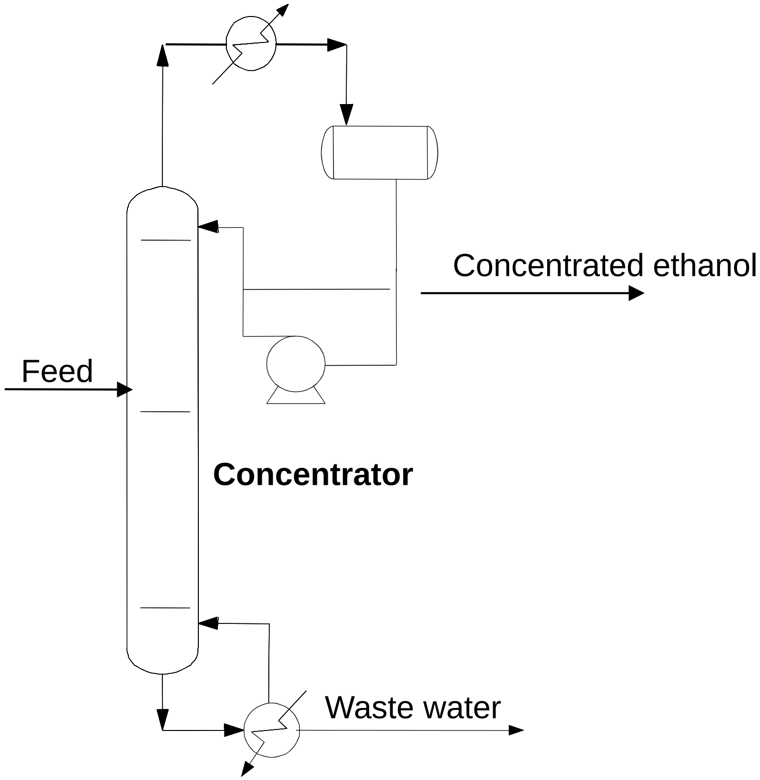
Feedstock	
Composition	Mole %
Water	10.00
Ethanol	70.00
Benzene	20.00
Total Flow	100.00



Top Product	
Composition	Mole %
Water	24.74
Ethanol	27.23
Benzene	48.03
Total Flow	40.41

Bottom Product	
Composition	Mole %
Water	0.00
Ethanol	99.00
Benzene	1.00
Total Flow	59.59

Step 4: Concentrator Simulation



Basis: Feed = 100 Kg-mole/hr

$x_F = 0.60$

Ethanol Mole Balance

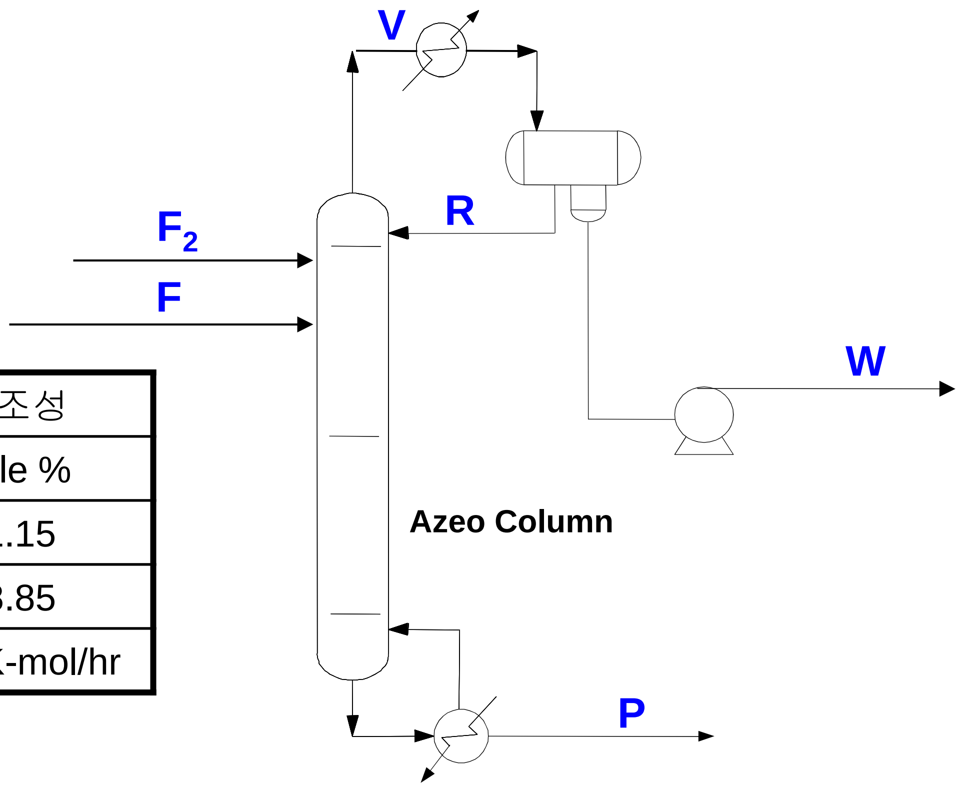
$F\,x_F = D\,x_D$ (Bottom에 에탄올은 거의 없다.)

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

PRO/II Keyword Input for Step 4

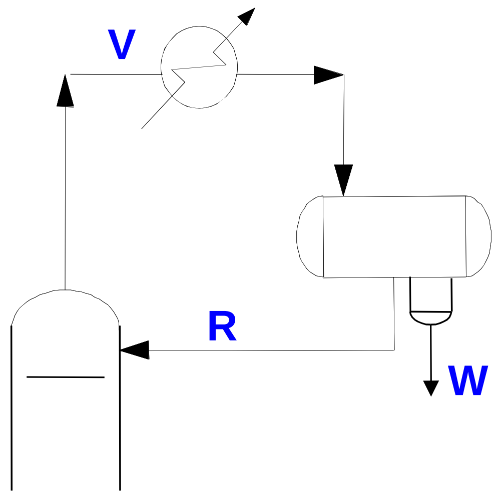
```
UNIT OPERATIONS
  COLUMN UID=CONC, NAME=Concentrator
      PARA TRAY=25,CHEMDIST=150 DAMPING=0.4
      FEED 1,8
      PRODUCT  OVHD(M)=2,68.18, BTMS(M)=3
      COND TYPE=TFIX, PRES=1.033, TEMP=45
      DUTY 1,1/2,25
      PSPEC PTOP=1.379, DPCOLUMN=0.21
      ESTIMATE MODEL=CHEM
      CESTIMATE(L) 1,0.1152,0.8848/25,1,0
      SPEC RRATIO, PHASE=L, VALUE=3.0
      SPEC STREAM=3,FRACTION, COMP=1,WET, VALUE=1
      VARY DUTY=1,2
```

Step 5: Azeotropic Tower Simulation



Stream F에 대한 조성	
Component	Mole %
Ethanol	81.15
Water	18.85
Flow Rate	73.9 K-mol/hr

Step 5: Decanter Simulation – *Step 5 continued*



삼성분계 공비조성 근처의 값으로 OVHD Vapor의 조성 V를 가정한다.

	Mole %
Benzene	53.00
Ethanol	31.00
Water	16.00

Step 5: Decanter Simulation – *Step 5 continued*

```
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 %

Step 5: Component Mass Balance around Azeo Tower

- Water balance around Azeotropic Column

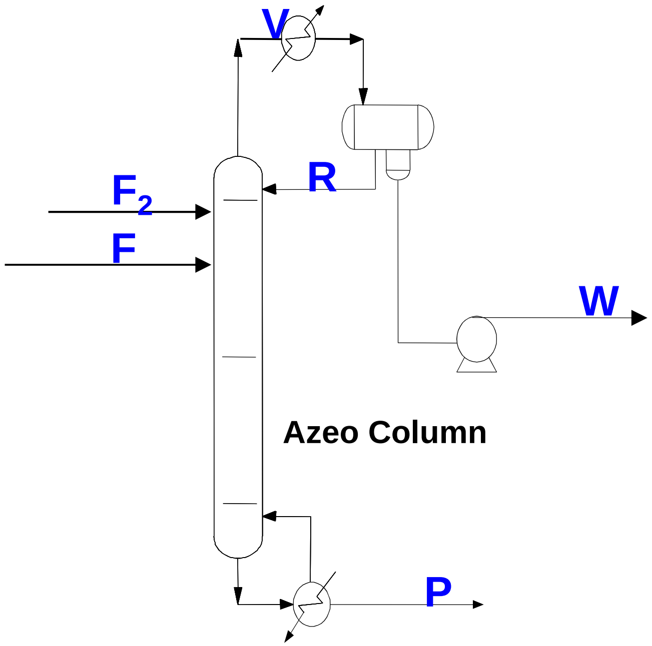
$$Azeo\_feed = 73.9 \times (1 - 0.8115) + F_2 \times (1 - 0.8115)$$

$$= 13.93 + 0.1885 F_2$$

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

$$= 0.141572 \cdot V$$

$$0.141572 \cdot V = 13.93 + 0.1885 \cdot F_2 \quad - (1)$$



- Ethanol balance around Azeotropic Column

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

$$F_2 = 0.171048 \cdot V \quad - (2)$$

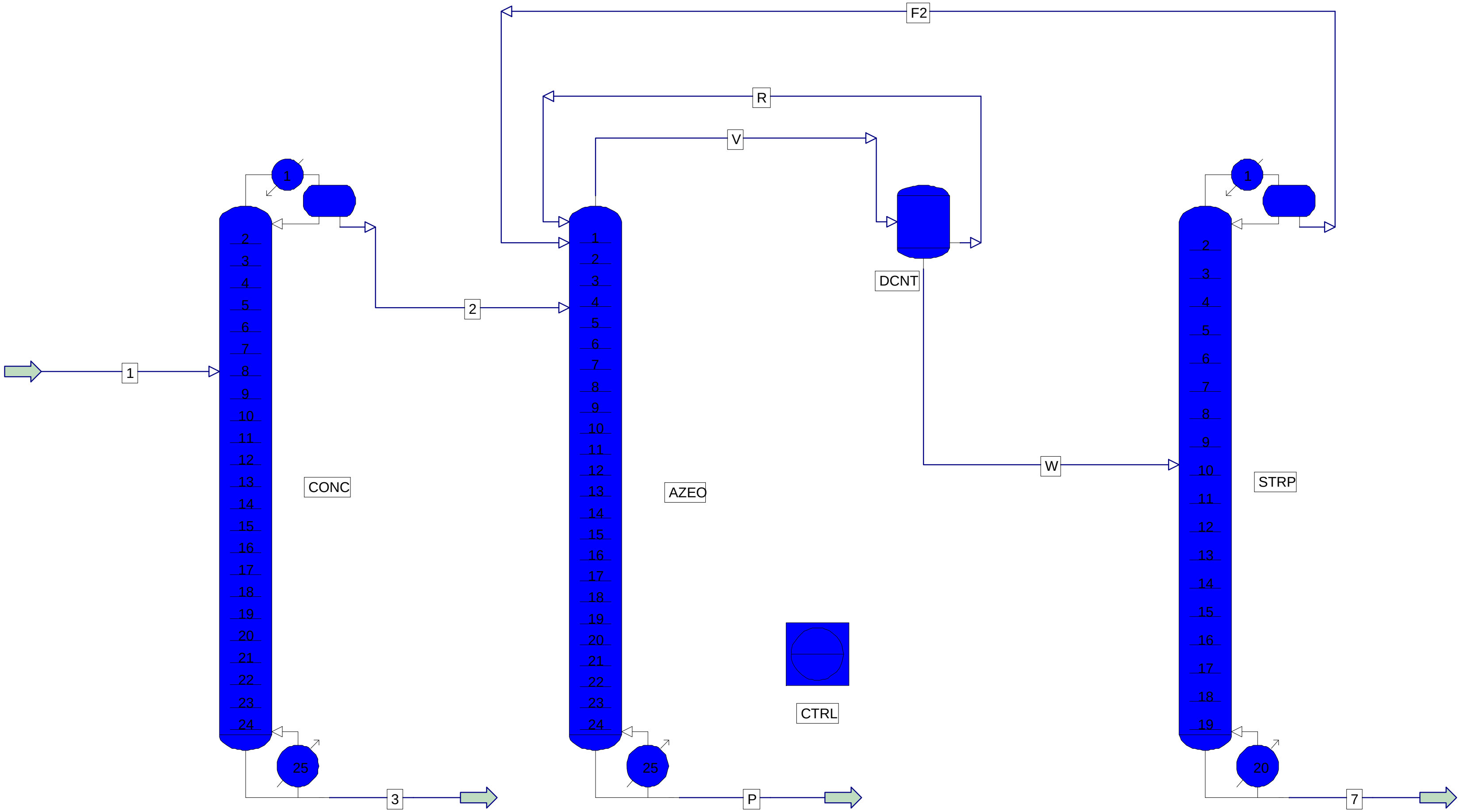
- Benzene flow from the decanter

$$= (127.4) \cdot (0.2895) \cdot (0.031511) = 1.162$$ K-mol/hr

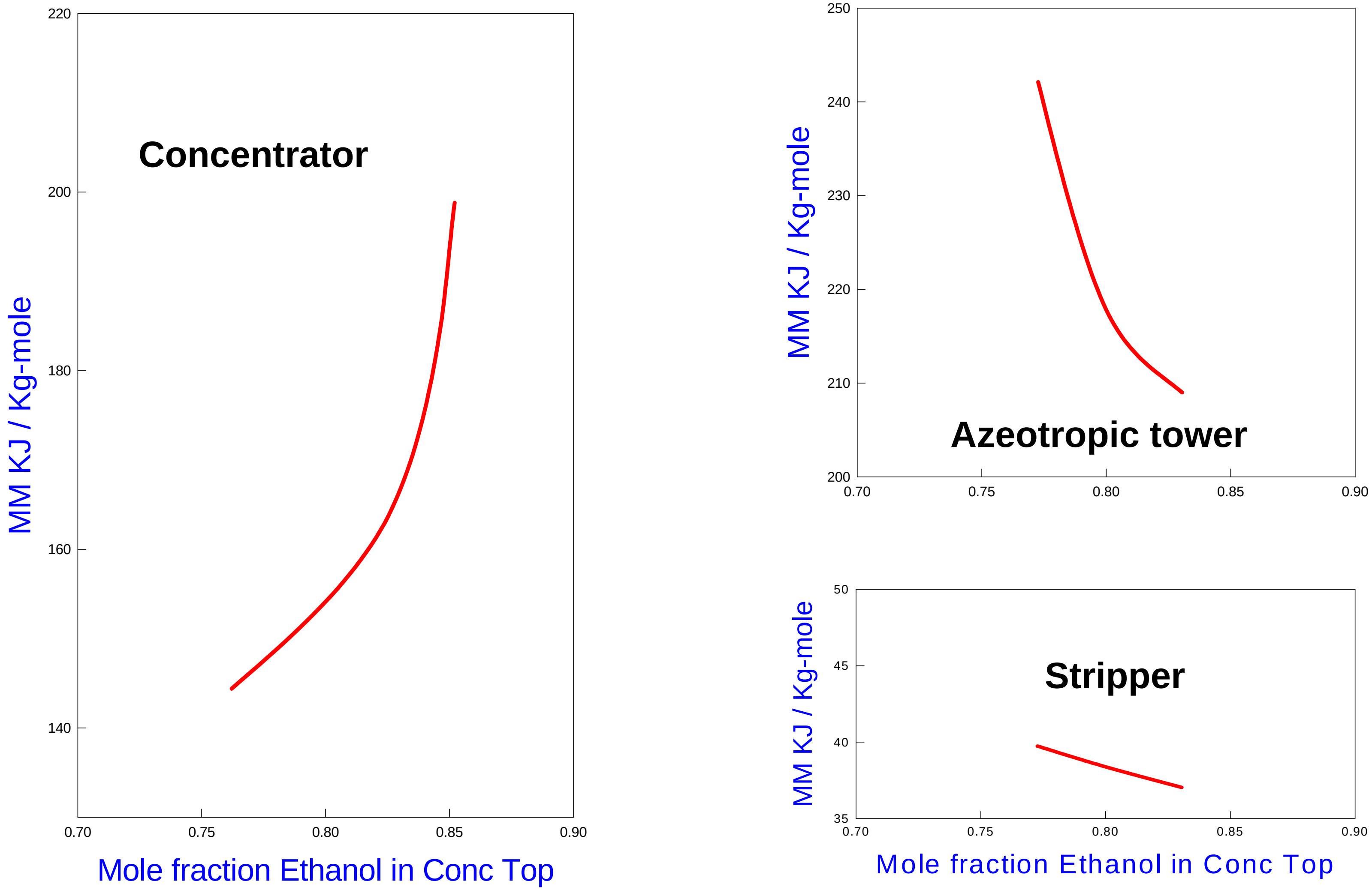
(1), (2)식을 연립하면 다음을 얻는다.

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

Step 7: 전체 공비증류공정의 모사

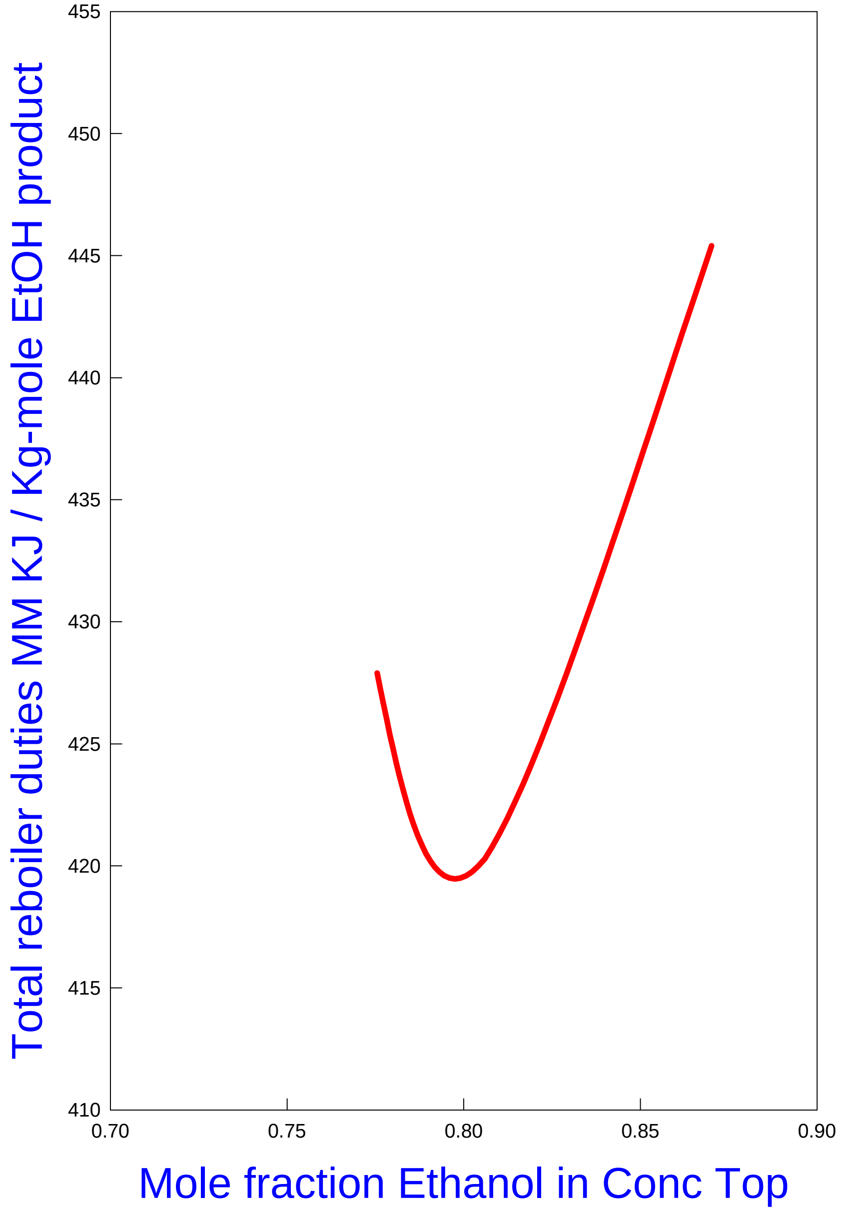


Step 8: Optimization of Overall Process

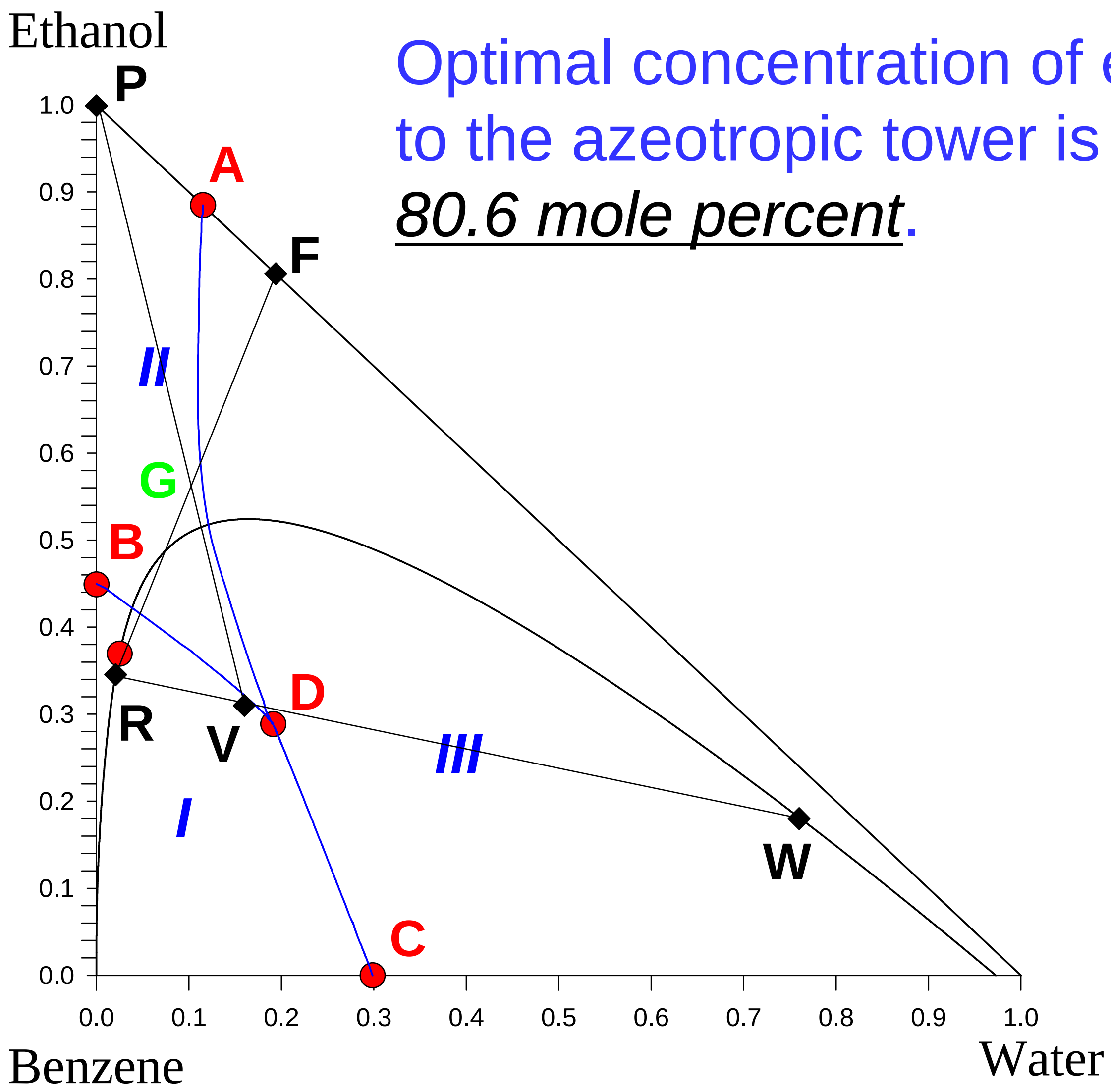


Concentrator, azeotropic tower and stripper reboiler duties vs. conc. EtOH in feed

Step 8: Objective Function



결 론



Optimal concentration of ethanol in the feed to the azeotropic tower is approximately *__80.6 mole percent__*.

끝....