Simulation of Ethanol Dehydration Using Cyclohexane as an Entrainer

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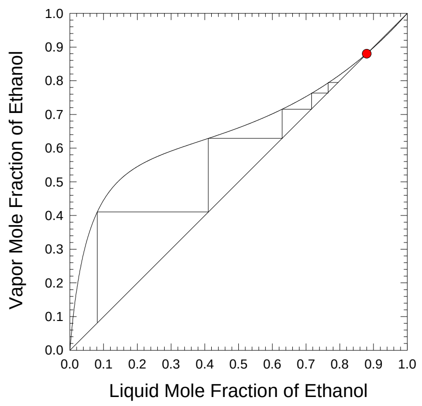
조정호

Limit of Distillation by Azeotrope

Ethanol / Water System



- 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

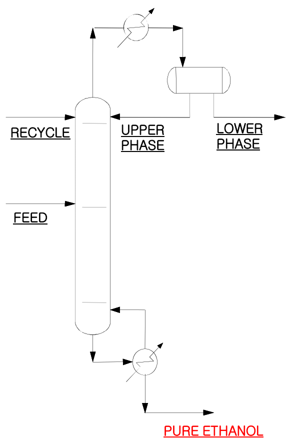
Separation of Azeotropic Mixture

- Shift the Azeotropic Point by Changing Pressure.
- 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)

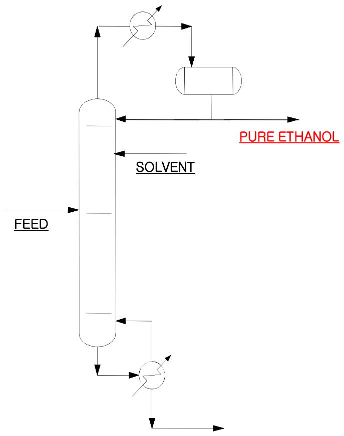
Azeotropic vs. Extractive Distillation (1)

- 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.

Azeotropic vs. Extractive Distillation (1)

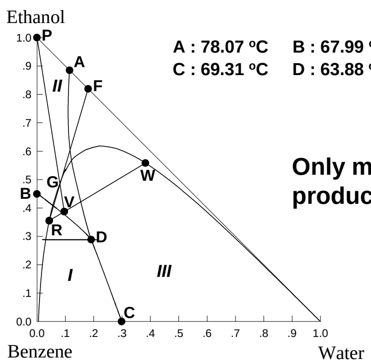


Azeotropic Distillation



Extractive Distillation

Principles of Azeotropic Distillation

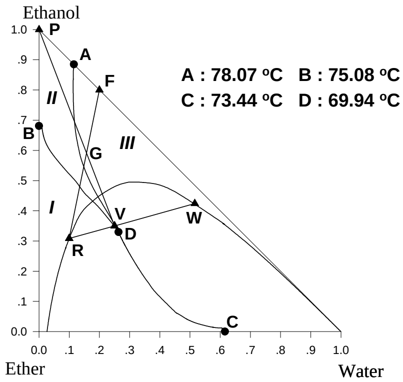


A : 78.07 ºC B : 67.99 ºC
C : 69.31 ºC D : 63.88 ºC

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

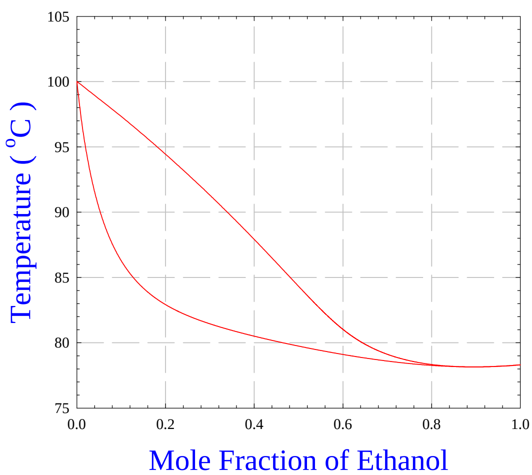
Aqueous ethanol can be separated into their pure components by distillation by the addition of a third component, so called the entrainer, which forms a ternary heterogeneous azeotrope with a lower than any other binary azeotropes.

How to Select an Entrainer

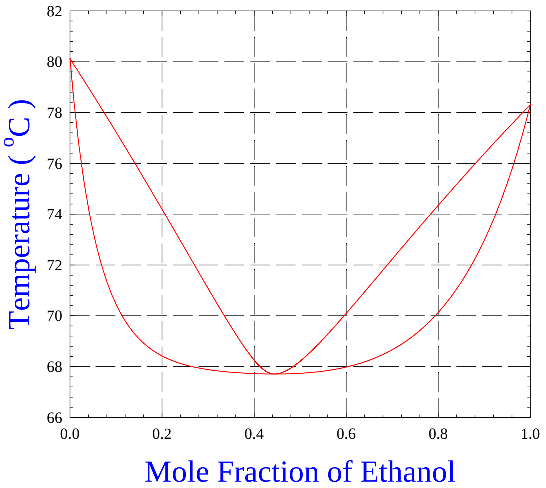


In this case, pure ethanol cannot be obtained since *G* is in region *III*.

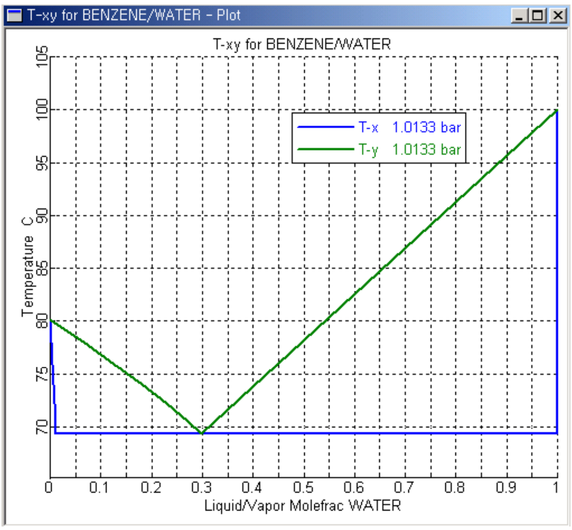
Homogeneous Azeotrope (1): Ethanol-Water



Homogeneous Azeotrope (2): Ethanol-Benzene

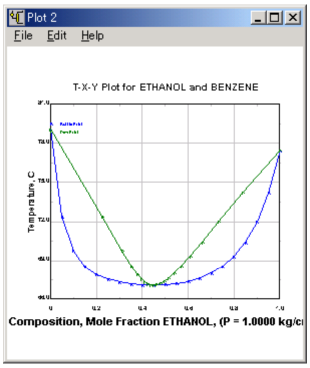


Heterogeneous Azeotrope (3): Benzene-Water

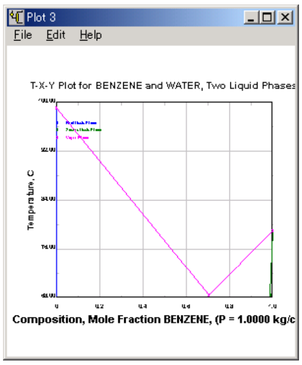


Theory of Azeotropic Distillation (I)

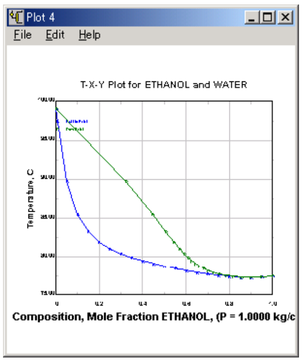
Ethanol / Benzene



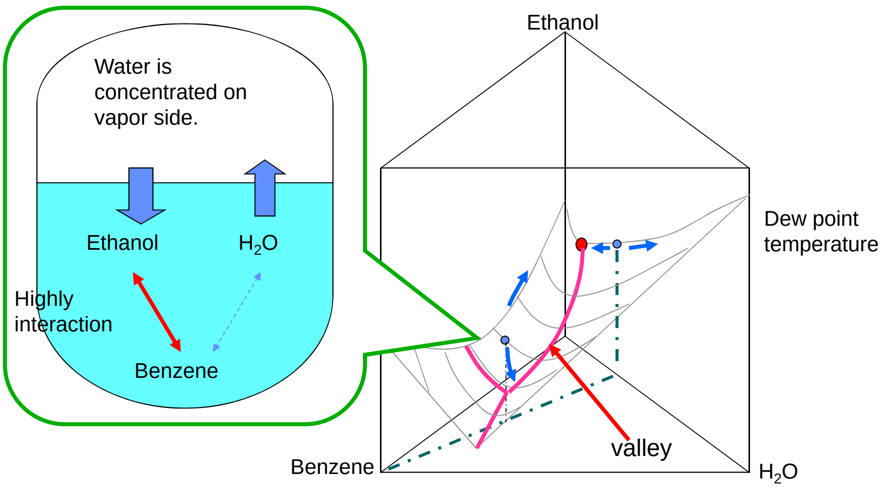
Benzene / Water



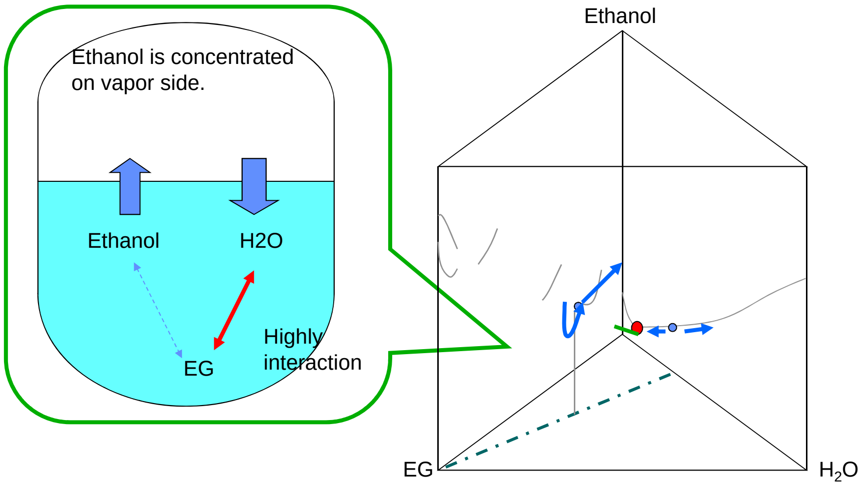
Ethanol / Water



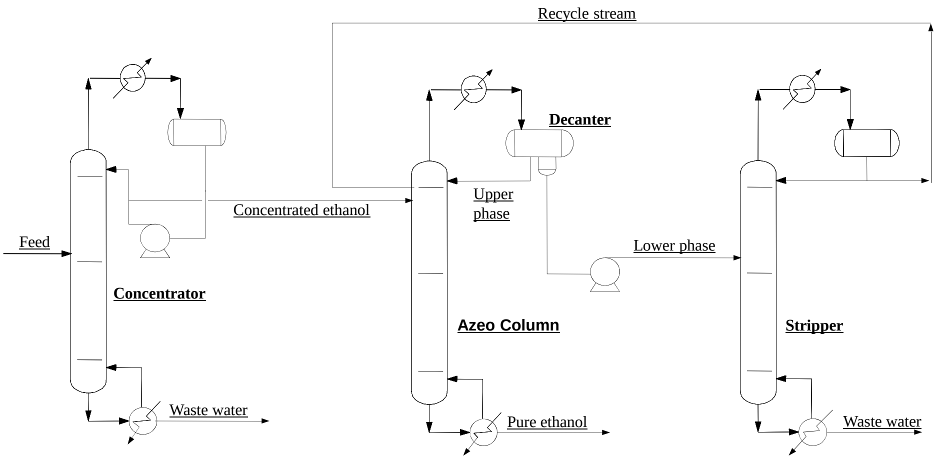
Theory of Azeotropic Distillation (II)



Theory of Extractive Distillation



Configuration of Azeotropic Distillation



Problem: Ethanol Dehydration

- Feedstock information
  - Feed Composition
    1) Ethanol : 10mole%
    2) Water : 90mole%
  - Feed Condition
    1) Inlet Temperature : 25°C
    2) Inlet Pressure : 200 kPa
  - Flow Rate
    1) 100 Kg-mole/hr
- Entrainer: Cyclohexane
- Cooling Medium: Cooling water
  1) In/Out Temperature : 32°C /40°C
  2) Decanter Operating Temperature : 45°C

Simulation Procedure

- Step 1: Selection of Proper Thermo Model & Construction of Binodal Curve
- Step 2: Finding Binary & Ternary Azeotropic Points
- Step 3: Construction of Binary & Ternary Residual Curves
- Step 4: Concentrator Simulation
- Step 5: Azeotropic Column Simulation
- Step 6: Azeo + Dryer(Stripper) Column Simulation
- Step 7: Simulation of Overall Azeotropic Distillation Unit
- Step 8: Optimization of Ethanol Dehydration Process

Step 1a: Selection of Proper Thermo. Model

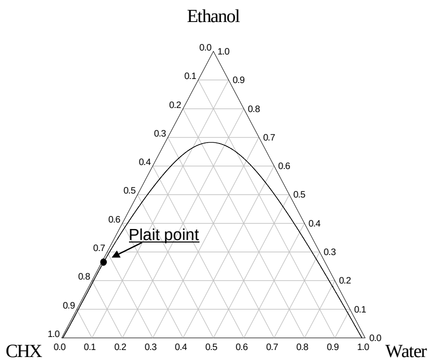
- NRTL. This model has up to 8 adjustable binary parameters that can be fitted to data.

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

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

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

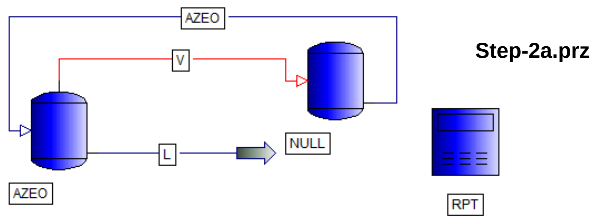
Step 1b: Construction of Binodal Curve



- Binodal Curve Construction using NRTL
  1) Water
  2) Ethanol
  3) Cyclohexane
- Temperature = 45°C
- Binary Interaction Parameters

Comp I	Comp J	A(I,J)	A(J,I)	α(I,J)
1	2	721.10	437.83	0.4685
1	3	1,225.89	2,807.80	0.1600
2	3	-60.00	660.00	0.3000

Step 2a: Finding Azeotropes (Ethanol+Water)



Stream Name Stream Description		AZEO	L	V
Phase		Liquid	Liquid	Vapor
Temperature Pressure	C KG/CM2	78.105 1.033	78.105 1.033	78.105 1.033
Flowrate	KG-MOL/HR	1.000	1.000	1.000
Composition ETHANOL H2O CH		 0.884 0.116 0.000	 0.884 0.116 0.000	 0.884 0.116 0.000

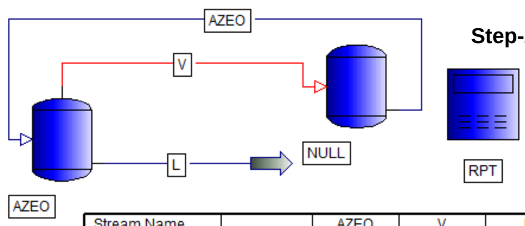
Ethanol=0.8839 mole fraction

Step 2a: Finding Azeotropes (Ethanol+Water)

STREAM ID	AZEO	L	V
NAME			
PHASE	LIQUID	LIQUID	VAPOR
THERMO ID	NRTL01	NRTL01	NRTL01
FLUID MOLAR FRACTIONS			
1 ETHANOL	**0.8839**	**0.8839**	**0.8839**
2 H2O	0.1161	0.1161	0.1161
3 CH	0.0000	0.0000	0.0000
TOTAL RATE, KG-MOL/HR	1.0000	1.0000	1.0000
TEMPERATURE, C	**78.1046**	**78.1047**	**78.1047**
PRESSURE, KG/CM2	1.0330	1.0330	1.0330
ENTHALPY, M*KCAL/HR	2.1269E-03	2.1269E-03	0.0114
MOLECULAR WEIGHT	42.8113	42.8113	42.8113
MOLE FRAC VAPOR	0.0000	0.0000	1.0000
MOLE FRAC LIQUID	1.0000	1.0000	0.0000

Step 2b: Finding Azeotropes (Ethanol+CHX)

Step-2b.prz



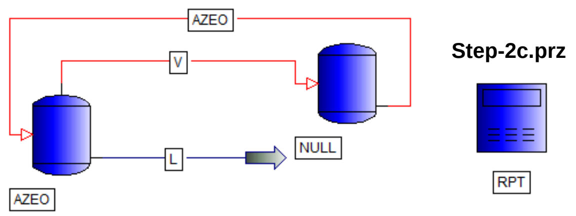
Stream Name Stream Description		AZEO	V	L
Phase		Liquid	Vapor	Liquid
Temperature	C	64.729	64.729	64.729
Pressure	KG/CM2	1.033	1.033	1.033
Flowrate	KG-MOL/HR	1.000	1.000	1.000
Composition				
ETHANOL		0.451	0.451	0.451
H2O		0.000	0.000	0.000
CH		0.549	0.549	0.549

Ethanol=0.4515 mole fraction

Step 2b: Finding Azeotropes (Ethanol+CHX)

STREAM ID	AZEO	L	V
NAME			
PHASE	LIQUID	LIQUID	VAPOR
THERMO ID	NRTL01	NRTL01	NRTL01
FLUID MOLAR FRACTIONS			
1 ETHANOL	**0.4515**	**0.4515**	**0.4515**
2 H2O	0.0000	0.0000	0.0000
3 CH	0.5485	0.5485	0.5485
TOTAL RATE, KG-MOL/HR	1.0000	0.9999	1.0000
TEMPERATURE, C	**64.7286**	**64.7286**	**64.7286**
PRESSURE, KG/CM2	1.0330	1.0330	1.0330
ENTHALPY, M*KCAL/HR	2.1454E-03	2.1451E-03	0.0105
MOLECULAR WEIGHT	66.9635	66.9635	66.9636
MOLE FRAC VAPOR	0.0000	0.0000	1.0000
MOLE FRAC LIQUID	1.0000	1.0000	0.0000

Step 2c: Finding Azeotropes (Water+CHX)



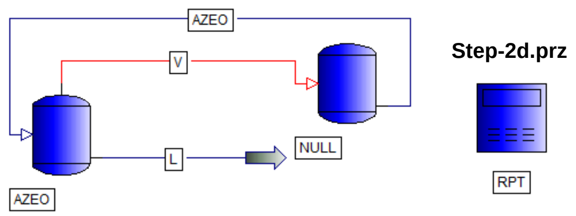
Stream Name Stream Description		AZEO	V	L
Phase		Liquid	Vapor	Liquid
Temperature Pressure	C KG/CM2	69.277 1.033	69.277 1.033	69.277 1.033
Flowrate	KG-MOL/HR	1.000	1.000	1.000
Composition ETHANOL H2O CH		 0.000 0.298 0.702	 0.000 0.298 0.702	 0.000 0.298 0.702

Cyclohexane=0.7017 mole fraction

Step 2c: Finding Azeotropes (Water+CHX)

STREAM ID	AZEO	L	V
NAME			
PHASE	LIQUID	LIQUID	VAPOR
THERMO ID	ALCO01	ALCO01	ALCO01
FLUID MOLAR FRACTIONS			
1 ETHANOL	0.0000	0.0000	0.0000
2 H2O	0.2983	0.2983	0.2983
3 CH	**0.7017**	**0.7017**	**0.7017**
TOTAL RATE, KG-MOL/HR	1.0000	1.0000	1.0000
TEMPERATURE, C	**69.2771**	**69.2771**	**69.2771**
PRESSURE, KG/CM2	1.0330	1.0330	1.0330
ENTHALPY, M*KCAL/HR	2.2118E-03	2.2118E-03	0.0104
MOLECULAR WEIGHT	64.4300	64.4300	64.4300
MOLE FRAC VAPOR	0.0000	0.0000	1.0000
MOLE FRAC TOTAL LIQUID	1.0000	1.0000	0.0000
MOLE FRAC LIQUID1	0.7025	0.7025	N/A
MOLE FRAC LIQUID2	0.2975	0.2975	N/A

Step 2d: Finding Azeotropes (Ethanol+Water+CHX)



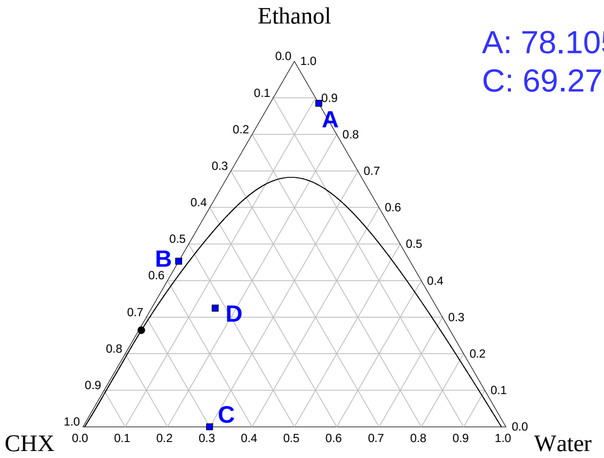
Stream Name Stream Description		AZEO	V	L
Phase		Liquid	Vapor	Liquid
Temperature Pressure	C KG/CM2	62.296 1.033	62.296 1.033	62.296 1.033
Flowrate	KG-MOL/HR	1.000	1.000	1.000
Composition ETHANOL H2O CH		 0.324 0.149 0.527	 0.324 0.149 0.527	 0.324 0.149 0.527

Ethanol=0.3239, Water=0.1495 mole fraction

Step 2d: Finding Azeotropes (Ethanol+Water+CHX)

STREAM ID	AZEO	L	V
NAME			
PHASE	LIQUID	LIQUID	VAPOR
THERMO ID	ALCO01	ALCO01	ALCO01
FLUID MOLAR FRACTIONS			
1 ETHANOL	**0.3239**	**0.3239**	**0.3239**
2 H2O	**0.1495**	**0.1495**	**0.1495**
3 CH	0.5266	0.5266	0.5266
TOTAL RATE, KG-MOL/HR	1.0000	1.0000	1.0000
TEMPERATURE, C	**62.2956**	**62.2955**	**62.2955**
PRESSURE, KG/CM2	1.0330	1.0330	1.0330
ENTHALPY, M*KCAL/HR	1.9549E-03	1.9549E-03	0.0105
MOLECULAR WEIGHT	61.9354	61.9354	61.9354
MOLE FRAC VAPOR	0.0000	0.0000	1.0000
MOLE FRAC TOTAL LIQUID	1.0000	1.0000	0.0000
MOLE FRAC LIQUID1	0.5551	0.5551	N/A
MOLE FRAC LIQUID2	0.4449	0.4449	N/A

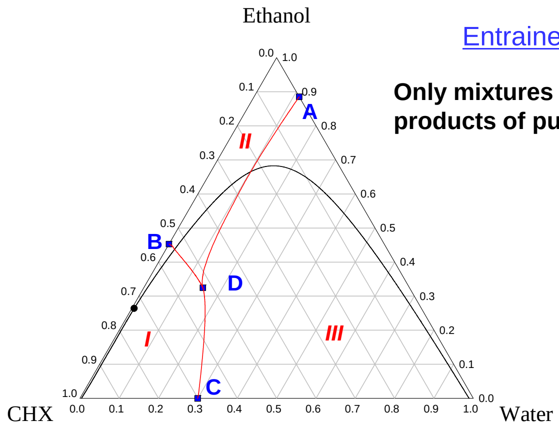
Results for Step 2



A: 78.105°C, B: 64.729°C
C: 69.277°C, *D: 62.296°C*

Entrainer Selection Criteria 1

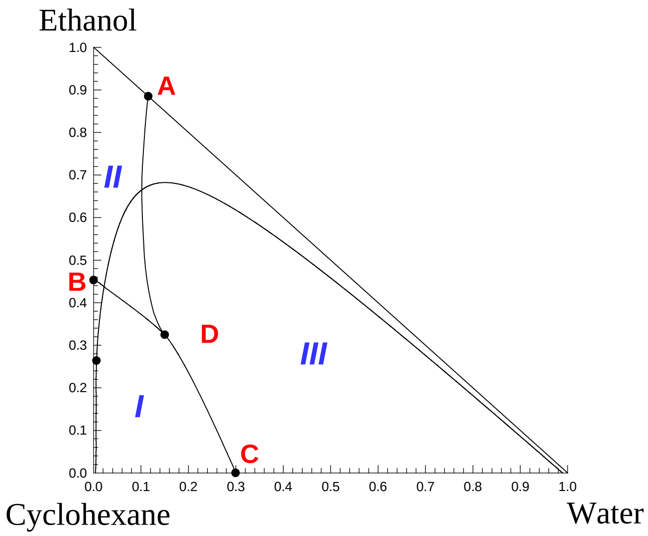
Step 3: Construction of Residual Curves



Entrainer Selection Criteria 2

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

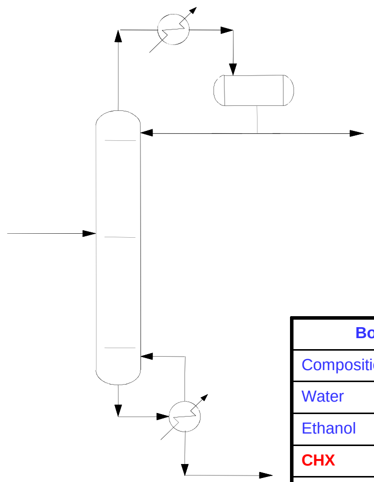
Step 3: Construction of Residual Curves



Step 3a: Feed having composition in region *I*

Region 01.prz

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



Top Product	
Composition	Mole %
Water	16.06
Ethanol	33.47
CHX	50.46
Total Flow	59.75

Bottom Product	
Composition	Mole %
Water	1.00
Ethanol	-
CHX	**99.00**
Total Flow	40.25

Step 3a: Stream Summary

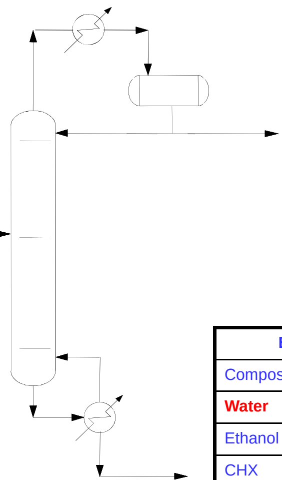
Composition	Mole fraction
Water	0.1495
Ethanol	0.3239
CHX	0.5266

STREAM ID	1	2	3
NAME			
PHASE	LIQUID	LIQUID	LIQUID
THERMO ID	NRTL01	NRTL01	NRTL01
FLUID MOLAR FRACTIONS			
1 WATER	0.1000	0.1606	1.0000E-02
2 ETHANOL	0.2000	0.3347	0.0000
3 CH	0.7000	0.5046	**0.9900**
TOTAL RATE, KG-MOL/HR	100.0001	59.7473	40.2528
TEMPERATURE, C	25.0000	44.0000	82.4224
PRESSURE, BAR	2.5000	1.0340	1.5890
ENTHALPY, M*KJ/HR	0.3362	0.3340	0.5312
MOLECULAR WEIGHT	69.9282	60.7848	83.4998
MOLE FRAC VAPOR	0.0000	0.0000	0.0000
MOLE FRAC TOTAL LIQUID	1.0000	1.0000	1.0000
MOLE FRAC LIQUID1	0.7323	0.5207	0.9913
MOLE FRAC LIQUID2	0.2677	0.4793	8.7310E-03

Step 3b: Feed having composition in region *III*

Region 03.prz

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



Top Product	
Composition	Mole %
Water	16.00
Ethanol	33.55
CHX	50.45
Total Flow	59.04

Bottom Product	
Composition	Mole %
Water	**99.00**
Ethanol	0.33
CHX	0.67
Total Flow	40.96

Step 3b: Stream Summary

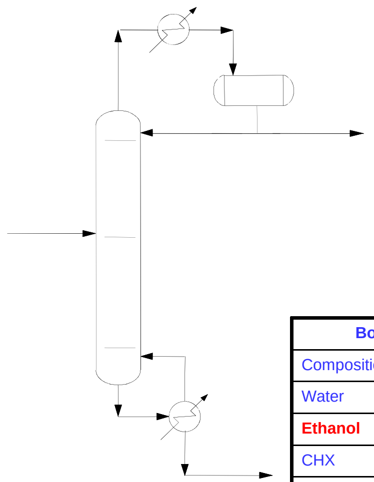
Composition	Mole fraction
Water	0.1495
Ethanol	0.3239
CHX	0.5266

STREAM ID	1	2	3
NAME			
PHASE	LIQUID	LIQUID	LIQUID
THERMO ID	NRTL01	NRTL01	NRTL01
FLUID MOLAR FRACTIONS			
1 WATER	0.5000	0.1600	**0.9900**
2 ETHANOL	0.2000	0.3355	4.7329E-03
3 CH	0.3000	0.5045	5.2671E-03
TOTAL RATE, KG-MOL/HR	100.0001	59.0365	40.9636
TEMPERATURE, C	25.0000	44.0000	81.9645
PRESSURE, BAR	2.5000	1.0340	1.5890
ENTHALPY, M*KJ/HR	0.2614	0.3301	0.2556
MOLECULAR WEIGHT	43.4698	60.7981	18.4965
MOLE FRAC VAPOR	0.0000	0.0000	0.0000
MOLE FRAC TOTAL LIQUID	1.0000	1.0000	1.0000
MOLE FRAC LIQUID1	0.3095	0.5204	5.2241E-03
MOLE FRAC LIQUID2	0.6905	0.4796	0.9948

Step 3c: Feed having composition in region *II*

Region 02.prz

Feedstock	
Composition	Mole %
Water	5.00
Ethanol	70.00
CHX	25.00
Total Flow	100.00



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

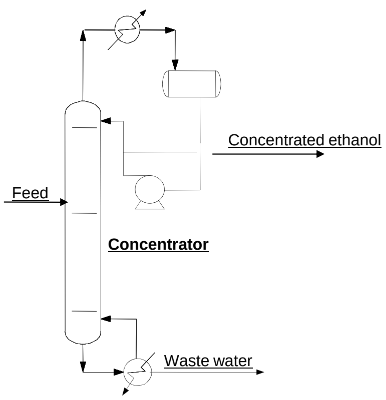
Bottom Product	
Composition	Mole %
Water	0.00
Ethanol	**99.00**
CHX	1.00
Total Flow	59.59

Step 3c: Stream Summary

Composition	Mole fraction
Water	0.1495
Ethanol	0.3239
CHX	0.5266

STREAM ID	1	2	3
NAME			
PHASE	LIQUID	LIQUID	LIQUID
THERMO ID	NRTL01	NRTL01	NRTL01
FLUID MOLAR FRACTIONS			
1 WATER	0.1000	0.1606	0.0100
2 ETHANOL	0.6000	0.3373	**0.9900**
3 CH	0.3000	0.5021	9.3357E-11
TOTAL RATE, KG-MOL/HR	100.0001	59.7492	40.2509
TEMPERATURE, C	25.0000	59.1697	90.1506
PRESSURE, BAR	2.5000	1.0340	1.5890
ENTHALPY, M*KJ/HR	0.2936	0.4575	0.4415
MOLECULAR WEIGHT	54.6913	60.6889	45.7885
MOLE FRAC VAPOR	0.0000	0.0000	0.0000
MOLE FRAC LIQUID	1.0000	1.0000	1.0000

Step 4: Concentrator Simulation



Basis: Feed = 100 Kg-mole/hr

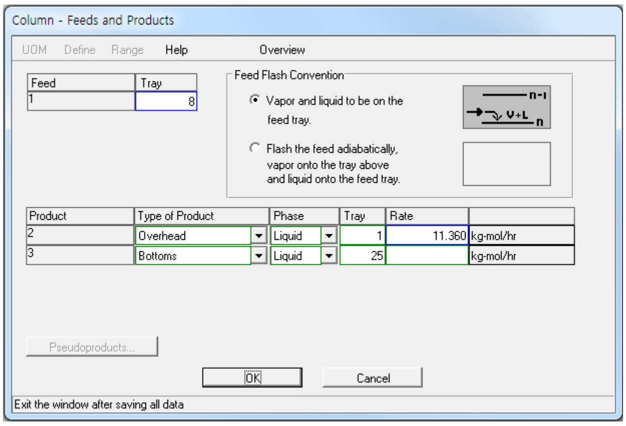
$x_F = 0.10$

Ethanol Mole Balance

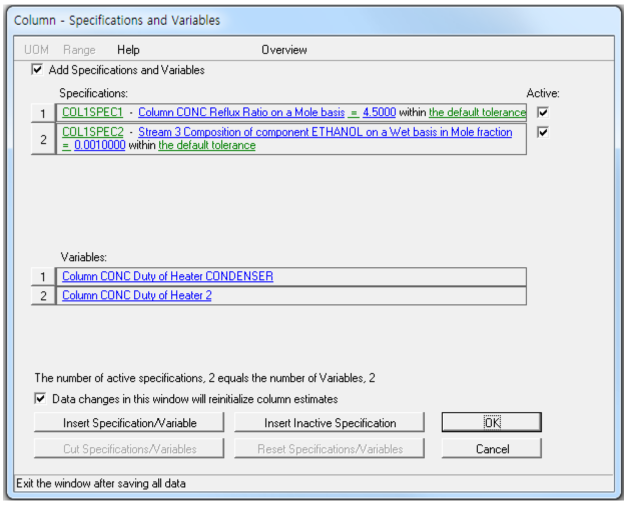
$F\,x_F = D\,x_D$ (Nearly Pure Water at Column Bottom)

$$D = \frac{F \cdot x_F}{x_D} = \frac{F \cdot x_F}{x_{azeo}} = \frac{(100)\cdot(0.1)}{(0.88)} = 11.36$$

Initial Estimates for Concentrator



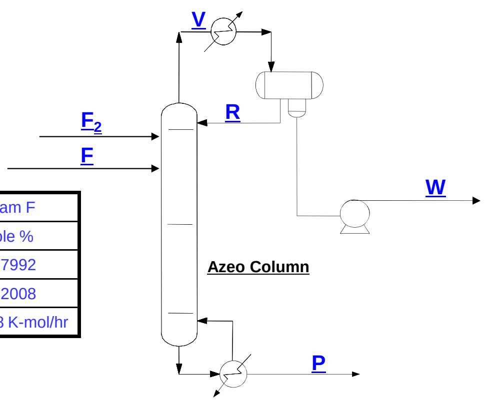
Product Specifications & Variables



Stream Summary Around Concentrator

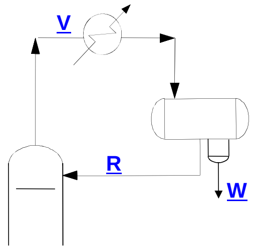
STREAM ID	1	2	3
NAME			
PHASE	LIQUID	LIQUID	LIQUID
THERMO ID	NRTL01	NRTL01	NRTL01
FLUID MOLAR PERCENTS			
1 ETHANOL	10.0000	80.7992	0.1000
2 WATER	90.0000	19.2008	**99.9000**
TOTAL RATE, KG-MOL/HR	100.0001	12.2678	87.7323
TEMPERATURE, C	25.0000	45.0000	112.2049
PRESSURE, KG/CM2	2.5000	1.0330	1.5890
ENTHALPY, M*KCAL/HR	0.0470	0.0139	0.1777
MOLECULAR WEIGHT	20.8205	40.6832	18.0431
MOLE FRAC VAPOR	0.0000	0.0000	0.0000
MOLE FRAC LIQUID	1.0000	1.0000	1.0000

Step 5a: Azeotropic Column Simulation



Composition of Stream F	
Component	Mole %
Ethanol	80.7992
Water	19.2008
Flow Rate	72.2608 K-mol/hr

Step 5b: Decanter Simulation



Assume OVHD Vapor Composition, V around ternary azeotrope

	Mole %
CHX	53.00
Ethanol	31.00
Water	16.00

Step 5b: Decanter Simulation *(Continued)*

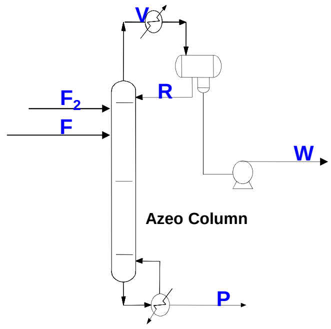
```
TITLE PROJ=AZEOTROPE, PROB=FLASH,USER=J.H.CHO
  PRINT INPUT=ALL, RATE=M, FRACTION=M, PERCENT=M
  DIMENSION METRIC
COMPONENT DATA
  LIBID 1,CH/2,ETHANOL/3,WATER
THERMODYNAMIC DATA
  METHOD SYSTEM(VLLE)=NRTL, SET=NRTL01
STREAM DATA
  PROP STRM=V, TEMP=45, PRES=1.033, RATE(M)=100, & COMPOSITION(M)=1,53/2,31/3,16
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 %)
CHX	53.00	92.5560	4.2709
Ethanol	31.00	7.2189	60.2960
Water	16.00	0.2251	35.4331
Flow Rate	100 %	55.20 %	44.80 %

Step 5c: Component Mass Balance Around Azeo Column

- Water balance around Azeotropic Column

$$Azeo\_feed = 12.2678 \times (1-0.808) + F_2 \times (1-0.808)$$
$$= 2.35542 + 0.192F_2$$
$$W = V \times (0.4880) \times (0.354331)$$
$$= 0.15874 \cdot V$$
$$0.15874 \cdot V = 2.35542 + 0.192 \cdot F_2 \quad \text{- (1)}$$



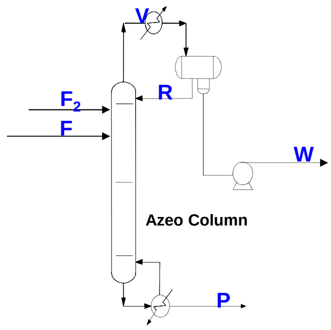
Step 5c: Component Mass Balance Around Azeo Column

- Ethanol balance around Azeotropic Column

$$V \times (0.4480) \times (0.60296) = (0.808) \times F_2$$
$$0.27013V = 0.808F_2$$
$$F_2 = 0.33432 \cdot V \quad \text{- (2)}$$

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

$V = 25.15131$ K-mol/hr, $F_2 = 8.40859$ K-mol/hr

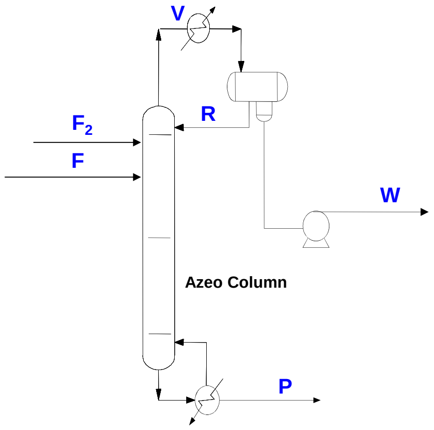


에탄올에 대해서는 Aqueous phase로 나간 모든 에탄올이 Stripper에서 회수되어 F_2로 돌아온다고 가정한다.

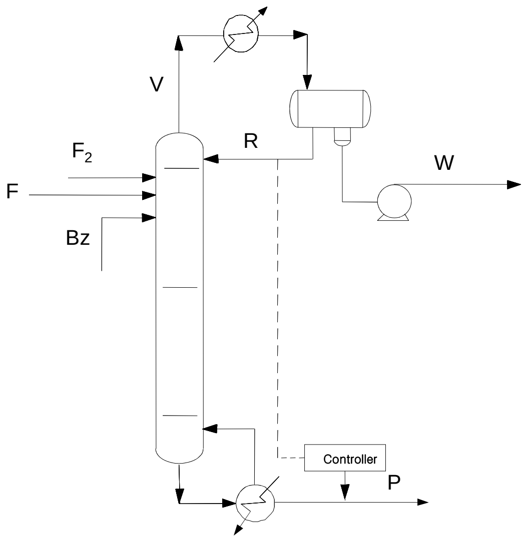
Step 5c: Component Mass Balance Around Azeo Column

- CHX flow from the decanter

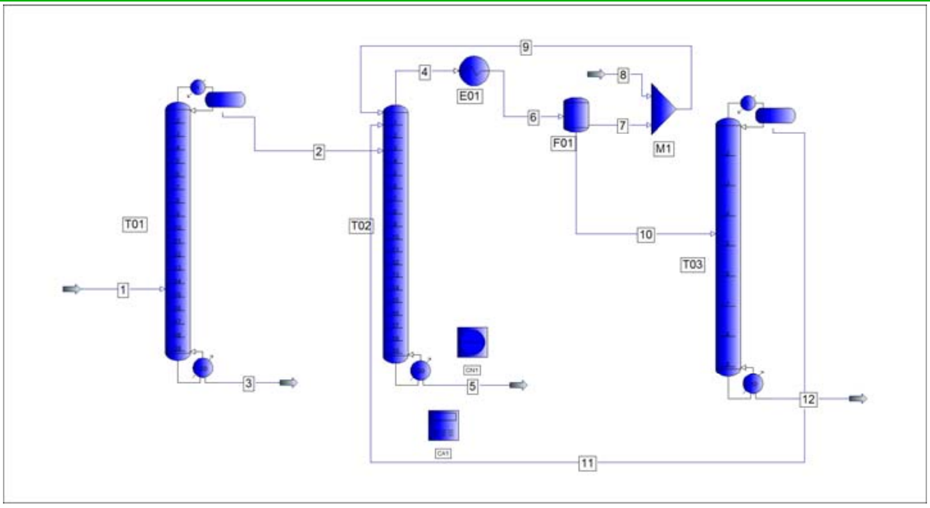
$= (25.15131) \cdot (0.4480) \cdot (0.042709) = 0.48806$ K-mol/hr



Step 5: Azeotropic Distillation Column Simulation



Step 7: Simulation of an Overall Azeotropic Unit



Overall Process.prz

Future Works

- Minimization of overall reboiler heat duties by varying the top concentration of ethanol at concentrator top for three-columns configuration
- Comparison of three-columns and two-columns configuration in ethanol dehydration using several entrainers
- Application of an environmentally-friendly entrainer, NC5 to obtain an absolute ethanol in azeotropic distillation
- Experimental works for ternary LLE rather than each binary VLE's & LLE
- Comparison of an extractive distillation process using solvent with an azeotropic distillation process using entrainer

The End….