



UNIVERSITY OF HOUSTON

CHEE 6322

Pressure Swing Distillation Analysis and Design

Authors:

Mate KOSOR
Brad STANLEY

For:

Dr. Peter STRASSER

02 December 2006

Abstract

The major goal of this paper is to present the findings of inquiries into the general nature of distillations and the specific inquiries into so-called “pressure swing distillations.” It aims to present a pressure swing distillation calculation for a two-column ethanol-benzene system which forms an azeotrope for some specified, fixed pressure. There is a wealth of literature on the subject of distillations, and as such, it is impossible for us to have covered them all; indeed, even to have covered a small percentage of them is beyond the scope of this report. However, drawing from an extensive knowledge of thermodynamics, balance equations, and external references, a rigorous treatment of pressure swing distillations is given here.

Contents

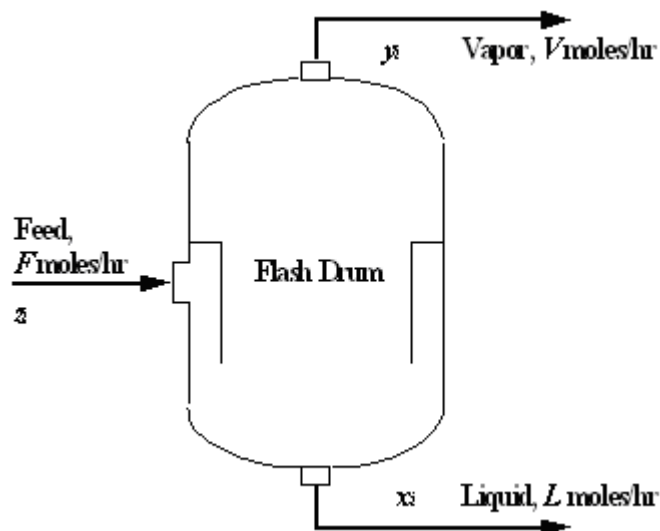
1	Theory of Distillations	2
1.1	Introduction	2
1.2	Distillation Techniques Involving Azeotropes	3
1.3	$\infty \backslash \infty$ Analysis	5
2	Pressure Swing Distillation	7
2.1	Problem Statement	7
2.2	Simplifying Assumptions and Justifications	7
2.3	Mass Balance Equations	10
2.4	Energy Balance	14
2.5	Procedure for Txy Diagrams	15
2.5.1	Bubble T Calculation	15
2.5.2	Dew T Calculation	18
2.5.3	Txy Diagrams	21
3	Conclusion	23
3.1	Results	23
3.2	Discussion of Application	26
A	Energy Balance	27
B	PSD Calculations	28
C	Alternative Solution	29

Chapter 1

Theory of Distillations

1.1 Introduction

We begin by considering the basic formulation of what it means to have a process which “distills” chemical substances. In the simplest terms, distillation is a separation process involving the heating of a liquid or vapor-liquid solution to collect a (theoretically) pure liquid in a container and condense a (theoretically) pure vapor. The simplest distillation process involving this is the case of Vapor-Liquid Equilibrium (also known as VLE).



In the above depicted Flash Drum, a feed of unknown composition is supplied to the drum, which then “distills” the pure liquid and vapor into a lower basin or container and an undefined upper level, respectively. In this sense, we should consider distillation as essentially a *mass transfer* process. By the differences in substances’ volatilities, it becomes possible for a distillation unit to separate those substances by phases by gradually altering either pressure or temperature over a given domain. That is to say, mass transport is fundamentally driven by a difference in concentrations—regions of high concentration flow to regions of low concentrations. Likewise, in distillation processes (an essential unit operation)

A highly idealized model for distillation is Raoult’s Law. Raoult’s Law holds only when the interactions occurring between the liquids are considered to be the same for the interactions occurring within the liquids; namely, that we have ideal liquids. Raoult’s Law is mathematically formalized as:

$$P = x_i P_i^{sat}$$

and it basically tells us that each individual species contributes some vapor pressure proportional to its concentration to the overall vapor pressure for the system. Thus, in Raoult’s Law, the more species there are, the less each contributes to the overall vapor pressure.

Unfortunately, Raoult’s Law is simply inadequate in the face of most standard separation processes. Distillations are often complicated by the existence of azeotropes, which generally involve oxygenated organic compounds such as ketones, ethers and alcohols. The underlying assumption in Raoult’s Law is that everything is ideal. In the case of azeotropic distillations, things are not so simple.

1.2 Distillation Techniques Involving Azeotropes

An azeotrope occurs when the ratio of compounds in the liquid phase to compounds in the vapor phase is one to one. Because of this distribution, we can not change the composition of the system through normal distillation (i.e. boiling). A class of distillation techniques, known as azeotropic distillations, has been used countless times to “break” the azeotropes, to enrich the substances beyond their azeotropic composition.

For instance, a mixture once commonly used for general anaesthesia consisted of diethyl ether and halothane. However, using regular distillation

methods, one can only achieve compositions of 66% diethyl ether and 33% halothane. This azeotrope caused the diethyl ether and halothane anaesthesia to be volatile and, in some cases, caused patients to suffer cardiac depression due to irritation of the catecholamine.

While this kind of volatility can only harm one person, if improper techniques are used in a chemical plant, many more lives could be put at risk. Hence the importance of developing an understanding and appreciation of how to break an azeotrope. The vast majority of azeotropes occur at maximum or minimum temperatures, and we can use this to our advantage. There are rare cases of saddle and double azeotropes where this claim may not hold, but we assume these cases are so rare as to not devote time to their peculiarities.

There are four major processes we will identify which one can use to work around azeotrope-forming compositions. These processes are all specialized insofar as one of them could not necessarily substitute for another. Each has its benefits and uses and should be considered in relation to the desired results; there is no one, set way to deal with azeotropic conditions.

- The first distillation method that deals with the presence of an azeotrope is pervaporation, in which a non-porous membrane is inserted into the system to separate the two substances. By partial vaporization of a liquid, the membrane is selectively used to let the desired liquid permeate through it. Modified Raoult's Law—which takes into account the fugacity and chemical potential of species—adequately models this distillation process.
- Another process is liquid-liquid extraction, solvent extraction, or partitioning. This involves separating two liquids based on their preference for two unique immiscible liquids. Liquid-liquid extraction is used in nuclear reprocessing, perfume production, and ore processing, to name a few of its applications. Questions regarding liquid-liquid extraction's effectiveness in batch distillations have received varied answers from different researchers and field engineers. The general consensus, however, is that one use discretion when doing liquid-liquid extraction and determine for him or herself the level of refinement needed.
- A third method, known as azeotropic distillation, requires that, given, for example, a binary composition, one should add a third substance to

the mix to catalyze the boiling point. In effect, this creates a lower boiling heterogeneous azeotrope. This lower boiling azeotrope can be dealt with by separating the two immiscible liquids based on their phases and decanting them.

- The last method we will discuss is called pressure swing distillation. It is mainly used when an azeotrope change composition at different pressures. Pressure swing distillation is accomplished by operating two different distillation columns at different pressures and recycling the material between these columns. The pressure “swing” between these two columns allows them to feed each other the azeotrope while distilling nearly pure chemical substances.

For now, let us simply consider the theory behind distillation processes.

1.3 $\infty \backslash \infty$ Analysis

$\infty \backslash \infty$ analysis was initially proposed to quantify multiple steady states (MSS) in ternary homogeneous azeotropic distillations. It has since been expanded to heterogeneous mixtures, column sequences and reactive distillation columns. We consider here a binary homogeneous distillation process involving an azeotrope.

Let us assume that there is an infinite number of stages and infinite reflux in a given distillation process. $\infty \backslash \infty$ analysis allows us to

- determine whether MSS exist for some feed composition, and
- locate the region of feed compositions that lead to the MSS

Consider a binary mixture of intermediate boiling components that form an azeotrope between the two intermediate components. Assuming we know the feed composition, and varying the distillate flow rate from zero to infinity, distillate and bottom product paths can be drawn along a residue curve. The bottom and distillate product paths are built consider the lever and compulsory presence of one pinch point in the column profile of an $\infty \backslash \infty$ column.

The bottom and distillate product paths may be represented in a bifurcation diagram. Generally speaking, a bifurcation diagram represents how the behavior of a system changes when parameters are varied. In distillation

columns, the parameter is usually the distillate flow rate or its dimensionless equivalent. Plotted against the distillate flow rate could be temperature, distillate composition, or whatever.

Besides the $\infty \backslash \infty$ analysis, a bifurcation diagram can be drawn for any system with finite columns and reflux using a software, AUTO. Given the dynamic model of the system, the software produces the complete diagram and the connected stability analysis. Because of the absolute completeness of information in a bifurcation diagram, they can be used heavily without worrying much about error.

For the binary system of ethanol and benzene, we create a residue curve assuming the ternary term has zero net effect on the forces. We analyze the liquid boiling envelope, and this analysis reveals that in this system, there does exist an azeotrope and it behaves as an unstable node. Being an unstable node means that the azeotrope will travel to the top of any distillation process, whereas the pure components are called stable nodes and always travel to the bottom of the distillation column. As the substances are mixing, the azeotrope is a saddle. That is to say, the residue curves run in towards the azeotrope for a little while before turning into a pure species component and moving away from the azeotrope. This is physically reasonable since compounds do mix under azeotropic conditions for a little while before reaching a limiting cycle. This is fully compliant with the existence of a Hopf bifurcation.

This indicates that the correct procedure for distillation of an ethanol and benzene system is pressure swing distillation. In pressure swing distillation, pure components are forced to the bottom and the azeotrope is exchanged from one column to the next through the vapor and the recycle streams. What pure component comes out at the bottom depends entirely on the setup of the distillation column (i.e. the pressure, temperature, coating (if any) on the walls, etc.). Setup should obviously improve the probability for a successful distillation of the desired compound while not sufficiently compromising operating costs.

A nulleline and stability analysis would be superfluous since the system is both binary and finite. We are already aware and have mentioned the behavior of this system at each plate in the distillation columns, and verifying these observations with calculations is not going to contribute in any meaningful way to the task at hand.

Chapter 2

Pressure Swing Distillation

2.1 Problem Statement

As newly hired engineers at Lube & Fuels Engineering, Inc., we have been assigned the task to design a distillation sequence for a benzene (1) and ethanol (2) system. We are given an initial feed for the system, 90 mol%, the feed ratio, two-thirds by mol ethanol and one-third by mol benzene at the bubble point at 101.3kPa, and that this system is to undergo distillation such that the compounds are separated into 99 mol% ethanol and 99 mol% benzene. We also know that we are allowed to choose the constant pressure of the first column, and that the pressure in the second column is set at 101.3kPa.

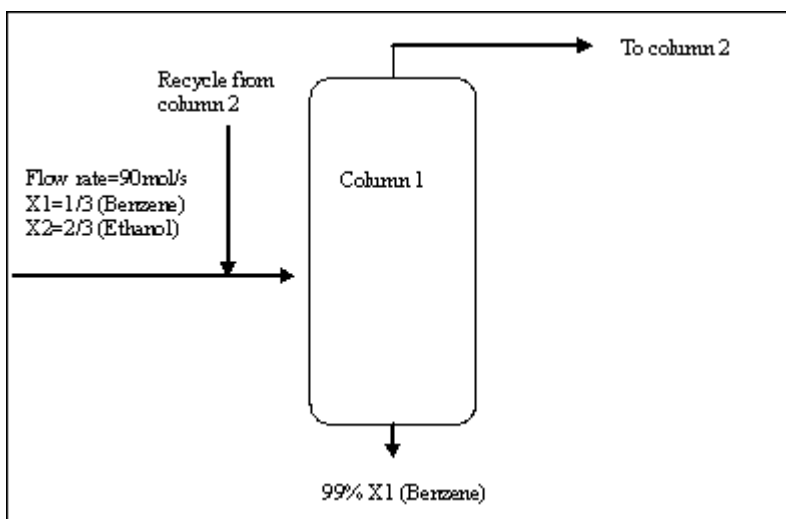
We are allowed to assume that the distillation process is highly idealized by 100% reflux and all separation stages are at equilibrium along the columns. Then, from section (1.3), we know that pressure swing distillation is the best technique for accomplishing our buyer's desired goal.

2.2 Simplifying Assumptions and Justifications

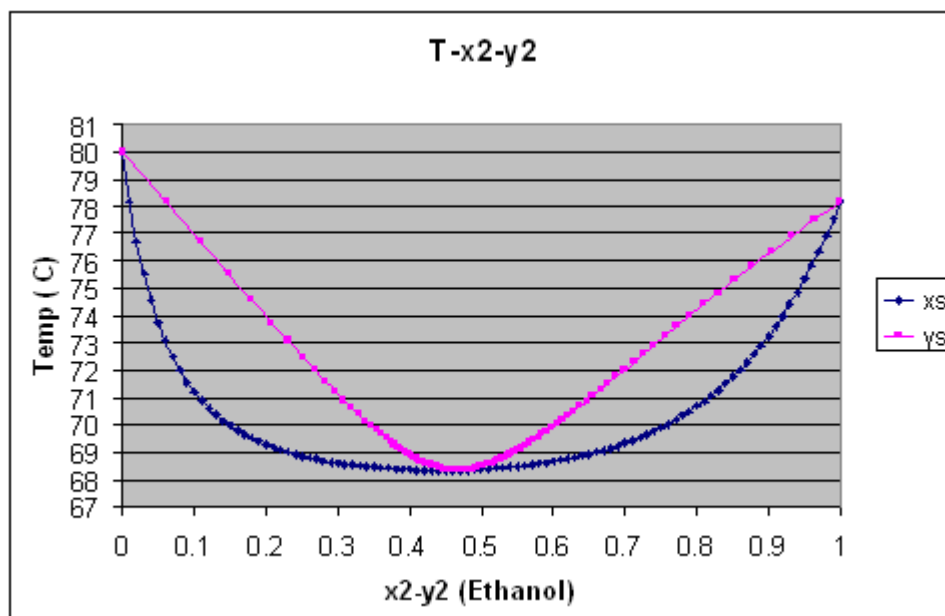
As with all engineering problems, simplifying assumptions have to be made. However, with a proper level of discretion, one can selectively choose the best assumptions that maximize the similarity between the theoretical calculations and what is “actually there” and minimize the amount of work on the engineers.

The project asks for the distillation of two chemical species: benzene and

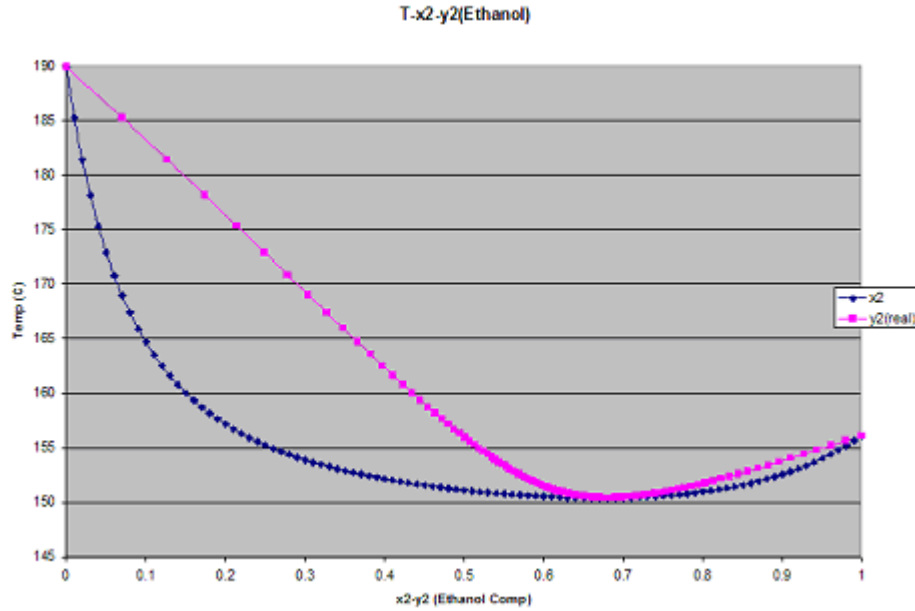
ethanol. The incoming composition into the first distillation column is .33 benzene and .67 ethanol with a flowrate of 90 mol/s at the bubble point. The given diagram shows that we wish to extract at least 99% liquid benzene at the bottom of the first column.



The process can be accomplished, but many problems will arise. If one simply considers ethanol as our working species, then the reason for abandoning this design is easy to see. The incoming composition of ethanol is $x_2 = .67$ and we wish to distill pure benzene. On a T - x_2 - y_2 diagram, one would have to move all the way to the left to reach pure x_1 . The problem arises due to the fact that the azeotrope at 101.3 kPa is situated at composition given by $x_2 = y_2 = .448$, as can be seen in the graph below.



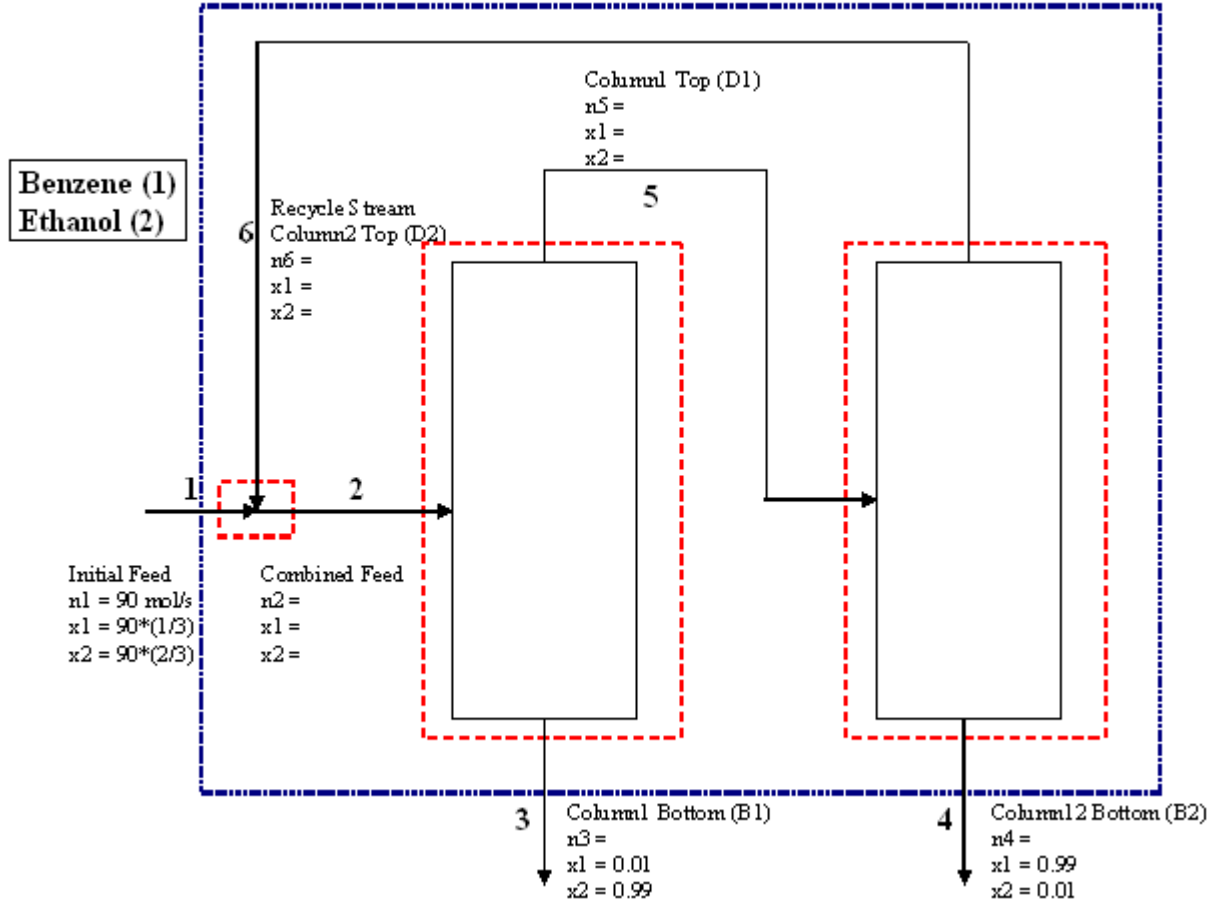
So in order to distill pure benzene, the azeotrope needs to be on the right side of the initial feed. If we try to distill pure benzene with the azeotrope on the left side of the initial composition, then the maximum concentration of benzene one could reach would be at the azeotrope ($x_1 = y_1 = .448$). Since the azeotrope is strongly pressure-dependent, an increase in pressure will shift the azeotrope to the right side of the graph. The pressure needs to be sufficiently high enough to be past the incoming composition. The closest pressure that allows for this is $P = 1200$ kPa. The diagram below shows the T- x_2 - y_2 at the pressure of 1200 kPa and has azeotrope past initial composition.



However, a pressure of 1200 kPa is very impractical due to its cost and the level of safety required to maintain stability. The same two pure species can be distilled in at least 99% purity if one chooses to distill ethanol from the first column (instead of benzene) and benzene from the second column. The azeotrope will not pose a problem since it will already be on the right side of the initial feed. The design now becomes to choose a correct number of plates to get close enough to the azeotrope to allow for the smallest pressure differential between the two columns. The pressure difference between the two will not be as great (and thus safer), and cost analysis shows it will be more beneficial to the customer.

2.3 Mass Balance Equations

Since we have chosen to put ethanol in the first column and benzene in the second, we propose a new schematic:



Now that we have stated our justifications, the next step in the process is to apply mass balance equations to determine the flow rates at the distillates (D1 and D2) and the bottom of the columns (B1 and B2). The mass balance is applied around the mixing point, column1, and column2, under the assumption that the process is at steady state.

Mass balance around the mixing point yields:

$$n_1 + n_6 - n_2 = 0$$

$$n_1 + n_6 = n_2, \text{ where } n_1 = 90 \text{ mol/s},$$

$$90 + n_6 = n_2$$

The mass balance around column1 is,

$$n_2 - n_3 - n_5 = 0$$

$$n_2 = n_3 + n_5$$

Mass balance around column2 is,

$$n_5 - n_4 - n_6 = 0$$

$$n_5 = n_4 + n_6$$

Combining these mass balance equations yields:

$$n_2 = n_3 + n_4 + n_6$$

$$90 + n_6 = n_3 + n_4 + n_6$$

$$90 = n_3 + n_4$$

Since the composition of ethanol and benzene at the initial feed and the bottom of each column are given by, $90x_1 = x_1n_3 + x_1n_4$ (Benzene) and $90x_2 = x_2n_3 + x_2n_4$ (Ethanol)

$$(1/3)90 = (0.01)n_3 + (0.99)n_4 \text{ Benzene}$$

$$(2/3)90 = (0.99)n_3 + (0.01)n_4 \text{ Ethanol}$$

Using equations above equations for benzene and ethanol, n_3 and n_4 may be calculated by solving the system of equations. This results in:

$$n_3 = 60.3061 \text{ mol/s}$$

$$n_4 = 29.6939 \text{ mol/s}$$

Composition of ethanol and benzene, at points 5 and 6, were previously calculated:

n5	y1 = 0.6185
	y2 = 0.3815
n6	y1 = 0.5307
	y2 = 0.4693

Therefore, given the composition of ethanol and benzene at points 5 and 6, flow rates at the distillates (D1 and D2) can be obtained by applying the mass balance around column2:

$$(0.6185)n_5 = (0.5307)n_6 + (0.99)n_3$$

$$(0.3815)n_5 = (0.4693)n_6 + (0.01)n_3$$

$$(0.6185)n_5 = (0.5307)n_6 + (0.99)(29.6939)$$

$$(0.3815)n_5 = (0.4693)n_6 + (0.01)(29.6939)$$

Setting up another system of equations, we solve n_5 and n_6 , which results in:

$$n_5 = 155.3 \text{ mol/s}$$

$$n_6 = 125.6 \text{ mol/s}$$

Therefore, the flow rates at the distillates (D1 and D2) and the bottom of the columns (B1 and B2) are:

Bottom Flow Rate 1 (B1)	60.3061 mol/s
Bottom Flow Rate 2 (B2)	29.6939 mol/s
Distillates Flow Rate 1 (D1)	155.3 mol/s
Distillates Flow Rate 2 (D2)	125.6 mol/s

By substituting n_3 and n_5 values into mass balance equation around column1, the flow rate of the recycled stream can be obtained:

$$n_2 = n_3 + n_5 = 60.3061 \text{ mol/s} + 155.3 \text{ mol/s}$$

$$n_2 = 215.6061 \text{ mol/s}$$

And the vapor composition of ethanol and benzene are:

$$x_1 n_2 = (0.01)n_3 + (0.6185)n_5$$

$$x_2 n_2 = (0.99)n_3 + (0.3815)n_5$$

$$(215.6061)x_1 = (0.01)(60.3061) + (0.6185)(155.3)$$

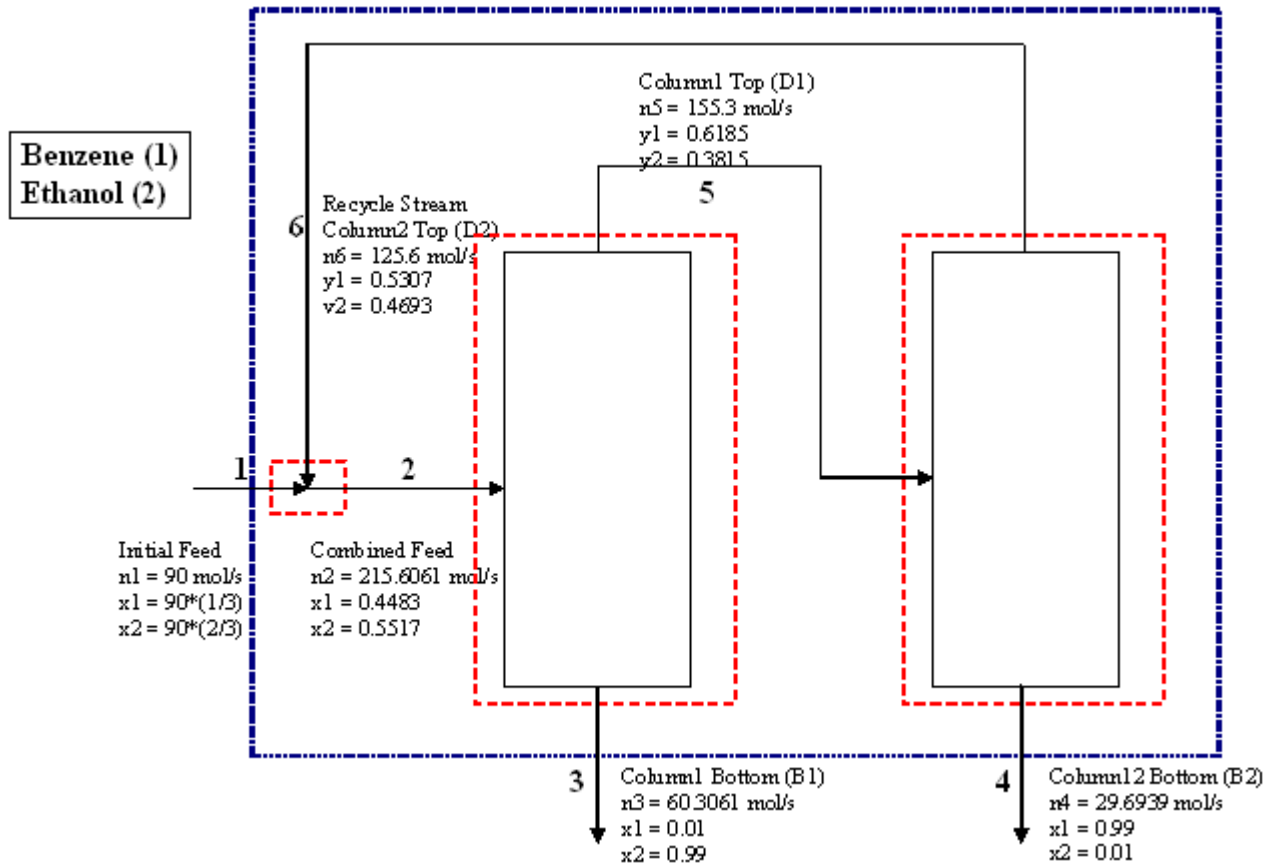
$$(215.6061)x_2 = (0.99)(60.3061) + (0.3815)(155.3)$$

Obviously,

$$x_1 = 0.4483$$

$$x_2 = 0.5517$$

Our completed mass balance schematic thus looks like



2.4 Energy Balance

The specifics of the energy balance equations used may be found in the appendix. The results of the energy balance showed us that:

$$Q_{column1} = 78.8028 \text{ kJ/s}$$

$$Q_{column2} = 104.913 \text{ kJ/s}$$

These results can be verified with the Energy Balance Excel Spreadsheet.

2.5 Procedure for Txy Diagrams

2.5.1 Bubble T Calculation

Starting with $P = 101.3 \text{ kPa}$ given in the problem description, and following the procedure for a Bubble T and a Dew T calculation in section 14.1 of our textbook, we received crucial information for our graphs and diagrams.

- 1) Set $P = 101.3 \text{ kPa}$. Set a range, R , for

$$R = \{x_1 : x_1 = .1, .2, .3, \dots\}$$

$$x_2 = 1 - x_1$$

where x_1 denotes the liquid composition of benzene and x_2 is ethanol. Set all the

$$\Phi_i = 1 \text{ for } i = 1, 2, \dots$$

- 2) Then using the reverse Antoine's equations, we calculated the saturation temperatures for the two components

$$T_1^{sat} = \frac{B_1}{A_1 - \ln P} - C_1 \text{ and } T_2^{sat} = \frac{B_2}{A_2 - \ln P} - C_2$$

- 3) Using both temperatures and the liquid compositions x_1, x_2 , the absolute T can be calculated by

$$T = \sum_i x_i T_i^{sat} \text{ for } i = 1, 2$$

- 4) Saturation pressures can then be evaluated with Antoine's equation

$$P_i^{sat} = \exp\left(A_i - \frac{B_i}{T + C_i}\right) \text{ for } i = 1, 2$$

- 5) The problem description asks for us to use Wilson's model to calculate the activity coefficients γ_i with the given values

$$\alpha_{12} = 131.47 \text{ cal/mol} = 550.07 \text{ J/mol}$$

$$\alpha_{21} = 1297.90\text{cal/mol} = 5430.41\text{J/mol}$$

Values for volume were found in table 12.5 in the book to be

$$V_1 = 89.41\text{cm}^3/\text{mol}$$

$$V_2 = 58.68\text{cm}^3/\text{mol}$$

Then, the following equations were used

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(\frac{-a_{12}}{RT}\right)$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(\frac{-a_{21}}{RT}\right)$$

and,

$$\ln \gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

$$\ln \gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) + x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right)$$

6) After this. values were obtained for the complete range of compositions where species 1 (benzene) was chosen to be the arbitrary species j . A new saturation pressure can be obtained by

$$P_j^{sat} = P_1^{newsat} = \frac{P}{\sum_i \left(\frac{x_i \gamma_i}{\Phi_i}\right) \left(\frac{P_1^{sat}}{P_i^{sat}}\right)} \text{ for } i = 1, 2$$

7) New absolute temperature and saturation pressures can be now calculated

$$T = \frac{B_1}{A_1 - \ln P_1^{newsat}} - C_1$$

$$P_i^{sat} = \exp\left(A_i - \frac{B_i}{T + C_i}\right) \text{ for } i = 1, 2$$

8) Now, the vapor compositions are obtained with Modified Raoult's Law,

$$y_i = \frac{x_i \gamma_i P_i^{sat}}{\Phi_i P} \text{ for } i = 1, 2$$

9) The new values for Φ_i are calculated by the virial equation of state coefficients obtained in table B.1:

$$Tr_i \equiv \frac{T}{Tc_i}$$

$$Pr_i \equiv \frac{P}{Pc_i}$$

$$B_i^0 = .083 - \frac{.422}{Tr_i^1 .6} \text{ for } i = 1, 2$$

$$B_i^1 = .139 - \frac{.172}{Tr_i^4 .2}$$

$$B_{ii} = B^0 + \omega B^1$$

This procedure also requires we calculate a mixture coefficient for the virial equation by the following equations

$$Vc_{12} = \left(\frac{Vc_1^{1/3} + Vc_2^{1/3}}{2} \right)^3$$

$$Tx_{12} = (Tc_1 Tc_2)^{(1/2)} (1 - K)_{12}^0$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2}$$

$$Z_{12} = \frac{Z_1 + Z_2}{2}$$

$$Pc_{12} = \frac{Z_{12} RTc_{12}}{Vc_{12}}$$

$$B_{12} = \frac{RTc_{12}}{P_{12}} (B_{12}^{\text{deg}} + \omega_{12} B_{12}^1)$$

$$\delta_{12} = 2B_{12} - B_1 - B_2$$

Finally,

$$\Phi_1 = \exp\left(\frac{B_{11}(P - P_1^{\text{sat}}) + Py_2^2 \delta_{12}}{RT}\right)$$

$$\Phi_2 = \exp\left(\frac{B_{22}(P - P_2^{\text{sat}}) + Py_1^2 \delta_{12}}{RT}\right)$$

10) Thus, a new value for the activity coefficient is now formulated with previous step 5 for the Wilson model. Also the new P_j^{sat} and T absolute are equally obtained from step 6.

11) The error is set to be $\epsilon \leq 0.001$ and is obtained by the difference, δT , between the latest T calculated and the one just before. If the $\delta T > \epsilon$, the iteration continues from step 7. When the error, $\delta T < \epsilon$, the iteration finishes.

2.5.2 Dew T Calculation

1) Set $P = 101.3$ kPa. Set a range, R , for

$$R = \{y_1 : y_1 = .1, .2, .3, \dots\}$$

$$y_2 = 1 - y_1$$

where y_1 denotes the vapor composition of benzene and y_2 is ethanol. Set all the

$$\Phi_i = 1 \text{ and } \gamma_i = 1 \text{ for } i = 1, 2$$

2) Then using the reverse Antoine's equations to calculate saturation temperatures for the two components

$$T_1^{sat} = \frac{B_1}{A_1 - \ln P} - C_1 \text{ and } T_2^{sat} = \frac{B_2}{A_2 - \ln P} - C_2$$

3) The absolute temperature is calculated using the to vapor compositions and saturation temperature

$$T = y_1 T_1^{sat} + y_2 T_2^{sat}$$

4) A new saturation pressure is calculated by setting an arbitrary species j as benzene(1) with the equation

$$P_j^{sat} = P_1^{newsat} = \frac{P}{\sum_i \left(\frac{x_i \gamma_i}{\Phi_i} \right) \left(\frac{P_1^{sat}}{P_i^{sat}} \right)} \text{ for } i = 1, 2$$

5) A new absolute temperature and saturation pressures can be now calculated

$$T = \frac{B_1}{A_1 - \ln P_1^{newsat}} - C_1$$

$$P_i^{sat} = \exp(A_i - \frac{B_i}{T + C_i}) \text{ for } i = 1, 2$$

6) The new values for Φ_i are calculated by the virial equation of state coefficients obtained in table B.1:

$$Tr_i \equiv \frac{T}{T_{c_i}}$$

$$Pr_i \equiv \frac{P}{P_{c_i}}$$

$$B_i^0 = .083 - \frac{.422}{Tr_i^{1.6}} \text{ for } i = 1, 2$$

$$B_i^1 = .139 - \frac{.172}{Tr_i^{4.2}}$$

$$B_{ii} = B^0 + \omega B^1$$

This procedure also requires to calculate a mixture coefficient for the virial equation by the following equations

$$V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2} \right)^3$$

$$Tx_{12} = (T_{c1}T_{c2})^{(1/2)}(1 - K)_{12}^0$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2}$$

$$Z_{12} = \frac{Z_1 + Z_2}{2}$$

$$P_{c12} = \frac{Z_{12}RT_{c12}}{V_{c12}}$$

$$B_{12} = \frac{RT_{c12}}{P_{12}}(B_{12}^{\text{deg}} + \omega_{12}B_{12}^1)$$

$$\delta_{12} = 2B_{12} - B_1 - B_2$$

Finally,

$$\Phi_1 = \exp\left(\frac{B_{11}(P - P_1^{sat}) + Py_2^2\delta_{12}}{RT}\right)$$

$$\Phi_2 = \exp\left(\frac{B_{22}(P - P_2^{sat}) + Py_1^2\delta_{12}}{RT}\right)$$

7) Now, the liquid compositions are obtained with modified Raoult's Law

$$x_i = \frac{y_i \gamma_i P}{\Phi_i P_i^{sat}} \text{ for } i = 1, 2$$

8) The problem description asks for us to use Wilson's model to calculate the activity coefficients γ_i with the given values

$$\alpha_{12} = 131.47 \text{ cal/mol} = 550.07 \text{ J/mol}$$

$$\alpha_{21} = 1297.90 \text{ cal/mol} = 5430.41 \text{ J/mol}$$

Values for volume were found in table 12.5 in the book to be

$$V_1 = 89.41 \text{ cm}^3/\text{mol}$$

$$V_2 = 58.68 \text{ cm}^3/\text{mol}$$

Then, the following equations were used

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(\frac{-a_{12}}{RT}\right)$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(\frac{-a_{21}}{RT}\right)$$

and,

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) + x_1 \left(\frac{\Lambda_{12}}{x_1 + x_2 \Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1 \Lambda_{21}} \right)$$

9) Then the process is repeated from step 4 to 6.

10) Do step 7 again to get the new liquid compositions.

11) The liquid compositions now need to be normalized by doing

$$x_i^{new} = \frac{x_i}{\sum_i x_i} \text{ for } i = 1, 2$$

12) Repeat step 8 and calculate the difference between the one calculated in step 8 and the new one and set it to be $\delta\gamma$. Set the error to be $\xi \leq 0.001$. If $\delta\gamma > \xi$, the process is repeated from step 10. If $\delta\gamma < \xi$, then the iteration can continue.

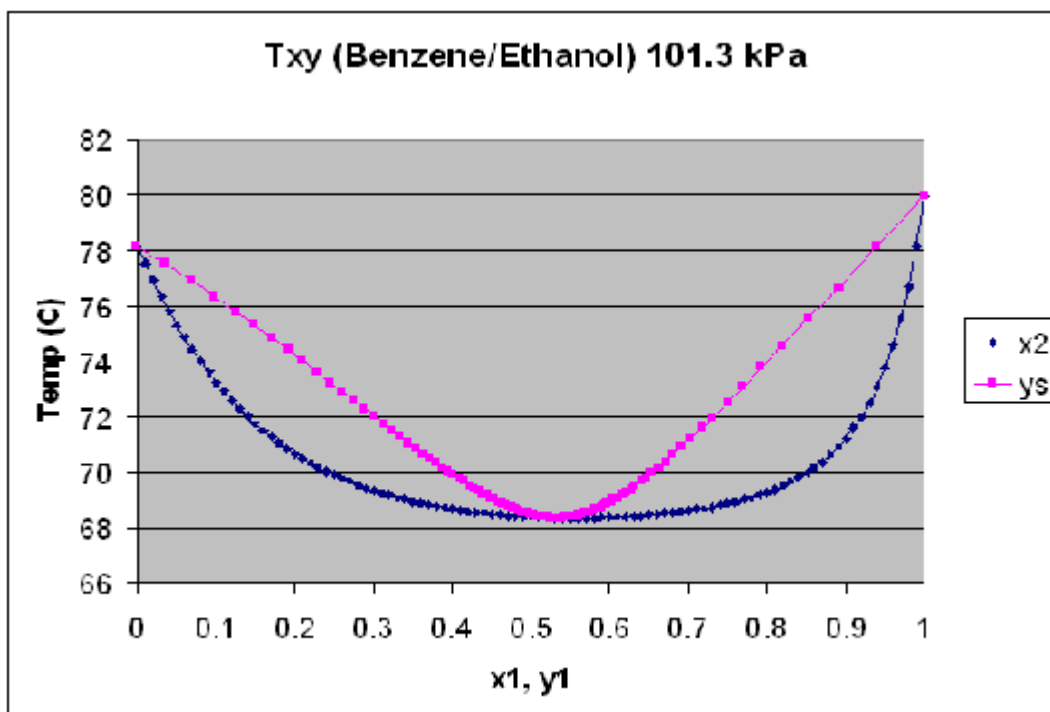
13) Do step 4 over again and calculate T like in step 5.

14) The error is set to be $\epsilon \leq 0.001$ and is obtained by the difference, δT , between the latest T calculated and the one just before. If the $\delta T > \epsilon$, the iteration continues from step 9. When the error, $\delta T < \epsilon$, the iteration finishes.

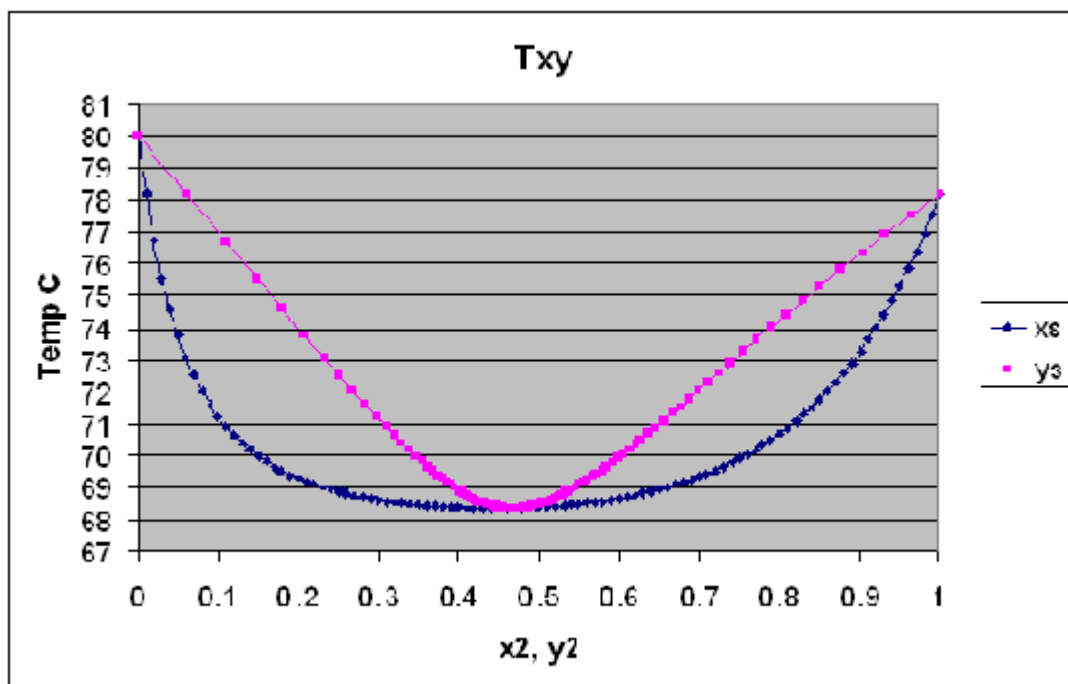
2.5.3 Txy Diagrams

After doing all these calculations (which may be checked in the Excel Spreadsheet), we received two graphs describing the azeotropic conditions.

This first one is the T - x_1 - y_1 diagram:



The second one shown here is the T - x_2 - y_2 diagram:



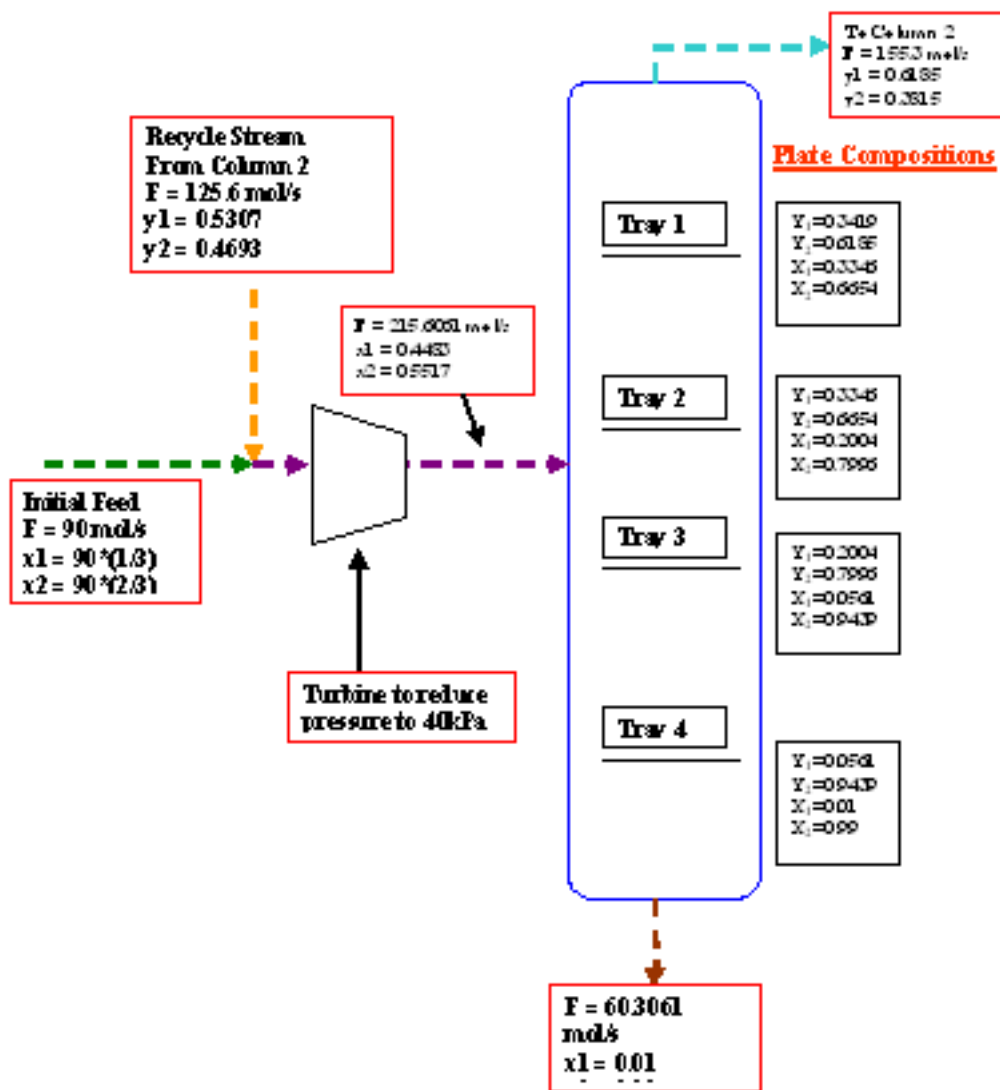
Chapter 3

Conclusion

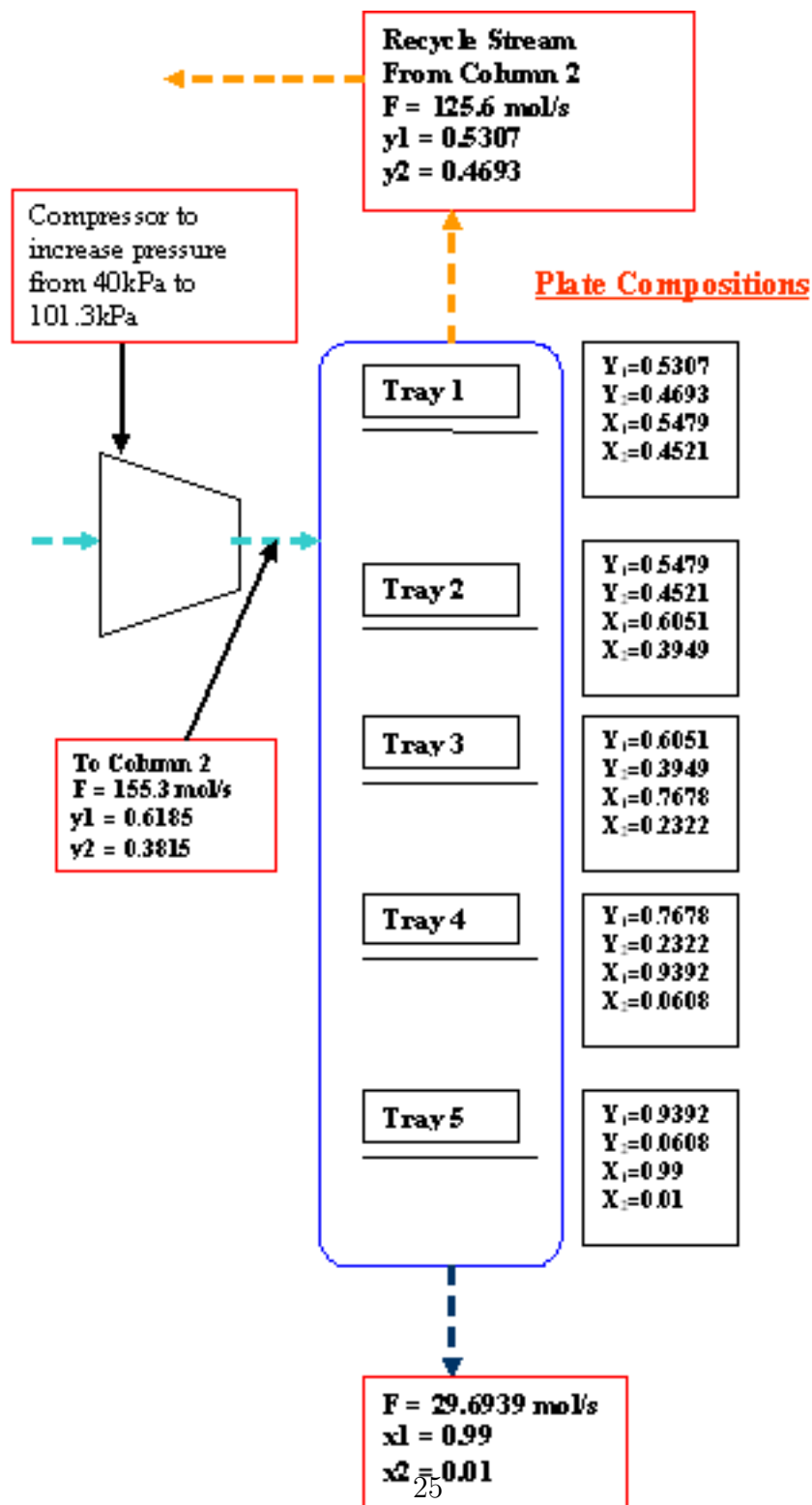
3.1 Results

In our study of the benzene-ethanol system, we found that using pressure swing distillation we could overcome the azeotrope that forms during regular distillation. We also discovered that different chemicals in different columns can require very different conditions for operation—sometimes these conditions are well over the budget of the customer, and it is important to keep this in mind when designing distillation columns and towers.

Ultimately, each of our distillation columns had four trays in it. This was sufficient for distilling the required concentrations. A completed schematic of Column 1 is given below,



The completed schematic of Column 2 is:



3.2 Discussion of Application

In chemical industry, the separation of a homogeneous azeotropic mixture is a common task. Batch distillation is especially a very popular unit operation in chemical engineering. The separation process is important for fine chemicals, seasonal demands of products and for pharmaceutical industries and food industry. For the separation of a binary homogeneous azeotropic mixture or closed boiling systems, using pressure swing distillation is one of the simplest solutions. Other, alternative processes, such as azeotropic distillation or extractive distillation, have a great industrial relevance, whereas the pressure swing distillation is only seldom applied. A similar process known as pressure swing adsorption is far more popular, since “swinging” the pressure results in much better adsorption. However, one of the main advantages of the pressure swing distillation process is that it totally removes the necessity of recycling an additional substance (entrainer), unlike the other alternatives, and thus has minimal pollution liability.

Much research has yet to be done on the differences in *all* distillation techniques for azeotropic-forming compounds. While there is plenty of experimental results for these distillation processes, theoretical calculations run sparse and are debated in the engineering and science communities. Hopefully within the near future these disputes will be resolved for more efficient production purposes.

Appendix A

Energy Balance

Appendix A includes the results of the energy balance equations.

Appendix B

PSD Calculations

Appendix B includes the results of the pressure swing distillation.

Appendix C

Alternative Solution

In this final Appendix C, we consider what would have happened if we had chosen benzene to be the chemical species in the first column.