REU 2004 Summer Program

Design of Solvent Recovery Systems Under Uncertainty

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Abstract

In the pharmaceutical and specialty chemical industry a small amount of product is produced to a large amount of waste. It is beneficial to these industries to find alternate schemes to process the wastes including solvent recovery. Thus, a greater understanding of continuous distillation schemes can be very advantageous. The schemes studied in this paper include systems with curved distillation boundaries, homogeneous azeotropic systems, and heterogeneous azeotropic systems.

The costs of separating these mixtures can be very high for these industries. Therefore a cost analysis and optimization process can help reduce the amount of energy that is consumed in this process and make the recycling of spent solvents an economically feasible process. There are two main costs in dealing with the addition of a unit operation, capital costs and operating cost. Capital costs change based on factors such as the height of the column, the diameter of the column, and the number of trays in the column. Operating costs are costs associated with the running of the column such as the entrainer recycle costs and reflux ratio. An effective distillation scheme will try to minimize these costs while still obtaining significant amounts of product.

The process of implementing a model to a real process needs to take into account the differences between the model and the actual system. Therefore a model needs to be able to handle a range of different parameters so that it can take into account these differences. This degree of uncertainty can arise from the thermodynamic model used to the actual numbers of the interaction coefficients. In industrial processes it is also necessary to be able to control the system to get a consistent product. Therefore it would be advantageous to study which parameters have the greatest effect on the process including reflux ratio, entrainer feed ratio, and the composition of the feed stream for the steady state cases.

Introduction

The pharmaceutical and specialty chemical industry often uses solvents that exhibit complex vapor liquid equilibrium. Devising a scheme that can separate these complex solvents can allow the plant to save money and lower pollution, since often the plant will burn the left over solvents. This can become a lot of waste especially in the pharmaceutical industry where the product is only a very small portion compared to the
large amount of leftover solvents and wastes, therefore, the old process of burning the waste solvents can cause a lot of pollution. Thus, an economically feasible separation scheme to recycle spent solvents would significantly lower costs for a pharmaceutical plant.

The Environmental Protection Agency, EPA, strictly regulates how much pollution a company can emit. The EPA puts monetary restrictions on the amount of pollution that a plant can release making it very worthwhile for a company to emit as little pollution as possible. Also since many chemicals often found in the pharmaceutical industry are hazardous to the environment, including many solvents used, a method to recycle the used streams or make an alternative product can be very beneficial to the company and the environment [1].

In order to greatly reduce the amount of pollution that a plant emits, a pharmaceutical plant could use the wastes from the process to create many other products. Therefore, a plant would not just make one product with many wastes as shown in Figure 1a, but instead, it would make many products using most of its left over materials as shown in Figure 1b. This would essentially eliminate waste and increase profits for the company. This type of product-only plant would also prevent the company from having to dispose of their wastes, thus decreasing the amount of pollution emitted.

The separation of components from a stream is a fundamental part of the chemical engineering industry. Distillation columns are a commonly used operation in industry to accomplish this task by using the differences in relative volatilities of each species. Sometimes there may not be a large difference in relative volatilities between components. This can occur when a mixture contains species with close boiling temperatures and systems that have azeotropes. An azeotrope exists at a specific composition when the compositions are constant between the vapor and liquid phases. This does not allow for higher compositions beyond the composition of the azeotrope. An azeotrope is a substance that retains the same composition between its liquid and vapor state when being boiled off. It is important to study azeotropic mixtures because they are found in many common industrial processes and many of these systems are difficult and costly to separate. Many times, these systems are also affected by model
uncertainty since they are very sensitive to changes in pressure, temperature, and feed compositions. It is these systems that a better understanding of distillation with azeotropes can make a difference in separating components in industry.

The purpose of this project is to develop a deeper understanding of complex distillation schemes and the uncertainty of the model, including those systems that contain azeotropes. The focus of the next sections in the introduction is to explain the basics of distillation columns as found in an introductory separation courses. The results and discussion has four sections. The first section in this report compares results from three case studies of ideal mixtures where the tray by tray model developed in Matlab and from Hysys are compared. The second section describes an azeotropic mixture which has a curved distillation boundary. The curved distillation boundary can be crossed by choosing suitable operating parameters. The third section shows distillation by the method of homogeneous azeotropic distillation. This section also includes cost analysis and model uncertainty analysis. The fourth section goes into some information of
heterogeneous azeotropic distillation and its advantages and disadvantages. The report closes with a conclusion, future work, and references.

**Background on Distillation Columns:**

In order to be able to model a distillation column, mass balances, energy balances, and vapor liquid equilibrium must be satisfied for the overall system and for all of the different species. A basic distillation column has four main parts: a stripping section, a rectifying section, a reboiler, and a condenser. As Figure 2 shows the stripping section is the bottom part of the column and consists of trays vertically aligned where vapor and liquid are in contact with each other to separate the heavier components from the lighter components. Whereas, the rectifying section is the top part of the column and is used to separate the lighter components from the heavier components by contacting the vapor and liquid. The distillate, D, comes out of the top part of the column and it contains the lighter components, whereas the bottom, B, comes out of the bottom part of the column and contains most of the heavier components. The reflux ratio, r, is the ratio between the liquid recycled back to the column and the liquid leaving as distillate. Likewise, the reboil ratio, s, is similar in that it is the ratio between the vapor being recycled to the column and the liquid leaving the column as the bottom. The theoretical tray is assumed to be in the column for this report.

For each tray in the column, the vapor and liquid will be in equilibrium. This can be modeled as Equation 1 for all of the species in the mixture.
where \( y \) is the vapor composition, \( x \) is the liquid composition, \( \gamma \) is the activity coefficient, and \( P_i^s \) is the vapor pressure of the pure component. This can be treated as an ideal gas if \( \gamma \) is equal to one. For most of the routine modeling in this paper the Wilson model will be used for the activity coefficient as shown in Equation 2.

\[
\ln \gamma_i = 1.0 - \ln \sum_{j=1}^{i=n} x_j A_{ij} - \sum_{i=1}^{k=n} \sum_{j=1}^{l=n} x_j A_{ij} \frac{x_i A_{ki}}{\sum_{j=1}^{l=n} x_j A_{kj}}
\]

where

- \( \gamma_i \) Activity coefficient for component \( i \)
- \( A_{ij} = \frac{V_j}{V_i} \exp\left(-\frac{a_{ij}}{RT}\right) \), Wilson constant
- \( x_i \) Mole fraction of component \( i \)
- \( T \) Temperature (K)
- \( n \) Total number of components
- \( a_{ij} \) Interaction coefficient
- \( V_i \) Molar volume of pure liquid component \( i \)

However, for complex systems with vapor-liquid-liquid, VLL, interactions the Wilson model is not an accurate model. In this case the Thermodynamic model of NRTL or UNIQUAC will be used because they better model these VLL interactions.

**Composition Profiles:**

With the previous balances it is possible to calculate the compositions at each of the trays. Starting with the overall mass balance and component balance, Equations 3 and 4 must be satisfied.

\[
F = D + B \tag{3}
\]

\[
F x_{i,f} = D x_{i,D} + B x_{i,B} \tag{4}
\]

where \( F \) is the feed flow, \( D \) is the distillate flow, \( B \) is the bottoms flow, and \( x \) is the composition of each of the components. Composition profiles for the stripping and rectifying sections show how the composition changes as the number of trays increase.
Calculating the profile for the rectifying section of the column is possible by starting at the distillate and calculating the compositions at each of the trays. Equation 5 is the equation that describes a calculation for each tray in the rectifying profile:

\[
x_{i,n+1} = \frac{r+1}{r} y_{i,n} + \frac{1}{r} x_{i,D}
\]  

(5)

The same calculation can be made for the stripping section starting from the bottom where for each tray the equilibrium between the vapor and liquid must be satisfied as shown in Equation 6,

\[
x_{i,n+1} = \frac{s}{s+1} y_{i,n} + \frac{1}{s+1} x_{i,B}
\]  

(6)

By using Equations 5 and 6, it is possible to calculate the compositions for any number of trays in both the rectifying and stripping section. This calculation can be shown in Figure 3, where the possible compositions are calculated. If a column is physically feasible then the stripping and rectifying profiles must intersect at the feed stage. The definition of this is represented in Equation 7.

\[
x^{\text{rectifying}} = x^{\text{stripping}}
\]  

(7)

![Figure 3 – Composition profile of a ternary mixture](image)

The composition of the bottom, feed, and distillate all lay on a straight line. This is a result of the mass balance as shown in Equations 3 and 4. Each point on the stripping
and rectifying profile represents a tray. The intersection of the stripping and rectifying profile represents the feed stage. Therefore a composition profile is an effective means of evaluating the design of a distillation column because it gives many of the critical parameters in relation to distillation columns.

Sometimes the rectifying and stripping profiles do not intersect. In this case, the distillation column is not physically possible. Figure 4a illustrates an example of compositional profiles for a feasible column because the profiles intersect, while 4b shows an example of an infeasible column because the stripping and rectifying profiles do not intersect.

![Figure 4 – Comparison between a feasible and infeasible column](image)

If a column is infeasible then some of the parameters have to be changed to make the column become feasible. This means either changing the reflux ratio, number of trays, or the desired compositions coming out of the distillate or the bottom. Sometimes, this is a sign of complex vapor liquid relationships such as systems with azeotropes or close boiling temperatures. If this is a case of more complex behavior then other distillation schemes must be looked at such as other ways of getting purer components such as changing the pressure or by adding an entrainer.

**Homogeneous and Heterogeneous Azeotropic Distillation**

There are two types of distillation involved when dealing with azeotropes, heterogeneous and homogeneous. When separating a binary mixture that contains an azeotrope an entrainer is added so that a higher level of purity can be achieved beyond the azeotrope. Heterogeneous azeotropic distillation deals with adding a partially immiscible entrainer that forms a ternary azeotrope with the two original components. One product is recovered as a pure product, and then the ternary azeotrope is then sent to
other separation processes where each of the components is separated. Homogeneous azeotropic distillation uses a miscible entrainer that does not form an azeotrope. The addition of an entrainer allows for the components in the mixture to be separated in two distillation columns into their pure forms [2].

The system of ethanol and water contains a binary azeotrope. In order to get higher purities an entrainer is added. Depending on the entrainer either homogeneous or heterogeneous azeotropic distillation can be used. A common entrainer used to create homogeneous azeotropic distillation is ethylene glycol which does not create a distillation boundary nor does it introduce any other azeotropes as seen in Figure 5a. Figure 5a is a residue curve map for the system and it does not contain any azeotropes nor distillation boundaries. This case is talked about later on in the paper. Some common entrainers used also are benzene and cyclohexane, both of which create more azeotropes but are not completely miscible within the ethanol and water as shown in Figure 5b. In contrast to the residue curve map in 5a, Figure 5b does contain distillation boundaries along with liquid liquid equilibrium constraints as shown in the shaded area. Therefore this creates the ideal situation for heterogeneous azeotropic distillation. Further information on this case is described in greater detail later on in the paper.

In systems that deal with homogenous azeotropic distillation the entrainer is normally added above the original feed stage. This is done so that the entrainer, usually the heaviest component, can remain in the liquid phase while having contact throughout
most of the column. By adding the entrainer above the feed then the composition profiles are changed for a system like this. Now instead of having only a rectifying and stripping section a middle profile is added. The middle profile is dependent on the feed ratio between the upper and lower feeds. The addition of the double feed column introduces a maximum reflux ratio along with a minimum reflux ratio for each entrainer feed ratio. There is also a minimum entrainer feed ratio to make the column feasible. All of these are a result of the behavior of the middle profile [3].

Heterogeneous azeotropic distillation has a wide range of advantages and disadvantages. Generally, heterogeneous azeotropic distillation requires less recycle of entrainer, fewer trays, and a smaller reflux ratio. All of these are good in minimizing the costs of running the distillation column. However, heterogeneous azeotropic distillation also has some disadvantages mainly that it is difficult to control. This process is difficult to control because it contains multiple steady states and large fluctuations in the temperature profile based mostly in the impurities in the bottoms concentration [4]. The existence of multiple steady states has been verified experimentally. Muller and Marquardt experimentally verified the existence of the multiple steady states and conclude that it results from the thermodynamic behavior of the system [5].

Methodology

The computer programs Distil, Matlab, and Hysys will be used to model the behavior of the compositions in the distillation column. Distil is the first program used in the task of designing distillation columns. Distil is used to get a tray by tray model of the compositions for each of the trays and can be used to determine if the desired distillation column is possible and the number of trays required. There is code written in Matlab that will calculate the composition profiles for the distillation columns to also determine the feasibility of a column. Hysys is a program that allows the user to model many processes often encountered in design problems. Hysys will be used as the last model of the desired process to determine the exact parameters that are needed to accomplish the desired tasks.

There are many thermodynamic packages that can be used to model the equilibrium between liquid and vapor. In this project, the Wilson model will be used
extensively, but in heterogeneous azeotropic distillation the NRTL and Uniquac thermodynamic models will be used to model the vapor-liquid-liquid equilibrium.

**Results and Discussion**

**Ideal Mixtures**

Before dealing with complicated distillation schemes, simple distillation columns were modeled in Hysys and Matlab to compare the results from both of the programs. For each of these examples the same specifications were used including the distillate compositions, bottom compositions, and reflux ratio. There were a few noticeable differences between the tray by tray models in Matlab and in Hysys especially in the number of trays required to carry out the separation. There are a specific number of parameters that need to be specified depending on the number of components in the system. For a three component system the feed compositions, the distillate compositions, one composition in the bottom stream, and the reflux ratio all need to be specified. However, in Hysys the number of trays must be designated as a design parameter instead. Therefore only the composition of either the distillate or bottom can be specified along with the reflux ratio. This extra stipulation makes it difficult to get exact results from both Matlab and Hysys. Therefore in doing these examples between Hysys and Matlab, a beginning approach was used in Distil which is a user friendly program that allows for design specifications to be inputted and then the composition profiles are given. With the column specifications in Distil, a model in Hysys was created with similar specifications. After the model in Hysys was created, it was checked with the tray by tray model in Matlab to make sure the column in Hysys is feasible.

To observe the similarities between Hysys and the tray by tray model created in Matlab a simple case study with the components of pentane, hexane and heptane was analyzed. This system does not contain any azeotropes or close boiling mixtures so the components can be separated in a routine fashion. The specifications used for this example are described in Table 1.

<table>
<thead>
<tr>
<th>Feed Conc.</th>
<th>Distillate Conc.</th>
<th>Bottom Conc.</th>
</tr>
</thead>
</table>

**Table 1 - Design specifications for pentane, hexane and heptane mixture**
As Figure 6 illustrates, the distillation in this case is feasible and does not require many trays to accomplish the distillation. The composition profiles given from both the Hysys and Matlab model are very similar. The data from both of these models was also validated using Distil with similar results [6].

Another case study used as an example of an ideal is system involves the components of methanol, ethanol, and 1-propanol. The specifications for the column are stated in Table 2 and the composition profiles are shown in Figure 7.

Table 2 – Specifications for methanol, ethanol, and 1-propanol system.

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Distillate</th>
<th>Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.3</td>
<td>0.963</td>
<td>0.02</td>
</tr>
</tbody>
</table>
The system containing hexane, heptane, and nonane was used to develop another case study to compare the differences in results between Hysys and Matlab. Table 3 shows the column specifications used in this case study. Figure 8, shows the composition profile for the system, which need a greater number of trays to separate due to overcoming the saddle point. The composition at the feed stage for both of the models is a little different but the compositions of the distillate and the bottom are the same and both of the columns are feasible. Thus the models in Matlab and Hysys give different compositions profiles but the compositions of both the distillate and bottom are the same for each of the models.

Table 3 – Column specifications for hexane, heptane, and nonane system
<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>0.3</td>
<td>0.988</td>
<td>0.02</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.3</td>
<td>0.012</td>
<td>0.42</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.4</td>
<td>0</td>
<td>0.56</td>
</tr>
<tr>
<td>Reflux</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These three case studies give confidence in the ability of Hysys to model systems of distillation column because the results from the Hysys model match the results from the tray by tray model developed in Matlab. It will then be possible, as described later, to use Hysys to model more complex behavior such as systems with homogeneous and heterogeneous azeotropes.

**Azeotropic Mixtures**

Azeotropic mixtures were modeled in Distil and Hysys to evaluate certain parameters on each of the systems including model uncertainty and optimization cases to determine the most efficient parameters for the system.

**Acetone, Chloroform, and Benzene Case Study**

The system of acetone, chloroform, and benzene contains a binary azeotrope between chloroform and acetone at 66 molar percentage chloroform and 34 molar...
percentage of acetone. This system demonstrates a distillation boundary as can be seen by the residue curve map as shown in Figure 9.

![Residue curve map for acetone, chloroform and benzene mixture](image)

Figure 9 – Residue curve map for acetone, chloroform and benzene mixture

The residue curve map depicts an azeotrope between acetone and chloroform. This creates a distillation boundary that is difficult to cross. Both pure acetone and chloroform are unstable nodes. The distillation boundary is created because there are two unstable nodes instead of one. The azeotrope in this case is a saddle point and benzene serves as the stable node. Each of the residue curves are depicted as the arrows, and these residue curves move towards higher temperatures. The azeotrope is the saddle point to both sides because it is the intermediate temperature between both acetone and benzene and chloroform and benzene. The existence of the distillation boundary causes this separation to its pure components to be very difficult because there are two distinct regions, I and II as shown in Figure 9 and it is usually not possible to cross distillation boundaries in distillation schemes. To separate this ternary mixture into its pure components two distillation columns are used as shown in Figure 10, the process flow diagram.
As long as both the distillate and bottom are in the same region then the column can be achieved. Therefore the first distillation column takes a feed in region I and separates it so that the top is pure acetone and the bottom is a mixture of benzene and chloroform close to the distillation boundary. The composition profile for the first column is shown in Figure 11.

As can be shown in Figure 11, the first column lies completely in region I. However the bottom composition is really close to the distillation boundary as seen by the bottom of the green line. This then can be the feed into the second column which operates in region II.

It is very difficult to cross the distillation boundary in most cases. In this case, the only reason that the distillation boundary can be crossed is because it is not linear but curved. This allows for the benzene/chloroform stream composition to be close to the
boundary line so that for the second column in the series it is possible to have the feed, distillate, and bottom composition both in region II of the composition profile as shown in Figure 12.

![Figure 12 – Composition profile for column 2 for acetone, benzene, and chloroform system](image)

The second column in the sequence takes the bottom from the first column and separates it into pure benzene and pure chloroform, in region two of the residue curve map. Table 4 gives the exact specifications for the benzene, chloroform, and benzene system as it relates to the flow sheet as shown in Figure 10[7].

<table>
<thead>
<tr>
<th></th>
<th>Acetone</th>
<th>Chloroform</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Azeotrope</td>
<td>0.338655082</td>
<td>0.661344918</td>
<td>0</td>
</tr>
<tr>
<td>Feed</td>
<td>0.1666667</td>
<td>0.16667</td>
<td>0.66667</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.999915</td>
<td>0</td>
<td>0.000085</td>
</tr>
<tr>
<td>Benzene/Chloroform</td>
<td>0.000157</td>
<td>0.200307</td>
<td>0.799536</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.000778</td>
<td>0.964103</td>
<td>0.035119</td>
</tr>
<tr>
<td>Benzene</td>
<td>0</td>
<td>0.007483</td>
<td>0.992517</td>
</tr>
</tbody>
</table>

This system is difficult to separate because the distillates and bottoms for both of the columns are close to the distillation boundary. If there is a little fluctuation in the compositions the system could move to the other side of the distillation boundary and therefore give products that are not desired.

There are some problems that have occurred with Hysys and the solver that it uses to find solutions to the different distillation columns. Many times if the parameters are gently eased to a solution the solver will handle it much better than if a large step is used. Therefore two different results can be obtained using the same parameters. This makes it difficult to get Hysys to reproduce earlier results.
Since this case study is very close to the distillation boundary it is very sensitive to the type of model used. First the thermodynamic packages were analyzed to see if different results would be obtained. As can be seen in Table 5, the system is very sensitive to the thermodynamic model.

Table 5 – Thermodynamic model uncertainty streams relate to those in the process flow diagram

<table>
<thead>
<tr>
<th></th>
<th>Acetone % in Acetone stream</th>
<th>Chloroform % in Chloroform stream</th>
<th>Benzene % in Benzene Recycle stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wilson</td>
<td>0.99989</td>
<td>0.99248</td>
<td>0.99804</td>
</tr>
<tr>
<td>General NRTL</td>
<td>0.99992</td>
<td>0.96292</td>
<td>0.99233</td>
</tr>
<tr>
<td>Antoine</td>
<td>0.70526</td>
<td>0.64658</td>
<td>0.99976</td>
</tr>
<tr>
<td>PRSV</td>
<td>0.76692</td>
<td>0.75222</td>
<td>0.99974</td>
</tr>
<tr>
<td>Peng-Robinson</td>
<td>0.74517</td>
<td>0.71640</td>
<td>0.99974</td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>Did Not Converge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Margules</td>
<td>Did Not Converge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>van Laar</td>
<td>Did Not Converge</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This result is to be expected since each model is designed for specific systems. The Wilson model is generally thought of as being the best to model the vapor-liquid equilibrium in many systems encountered in distillation columns.

Within the Wilson thermodynamic model there are binary interaction coefficients for each of the components in the system. Sometimes there can be fluctuations where the parameters are not completely accurate for the real system. In cases like these it is important to know how sensitive the system is to uncertainties such as fluctuations in the interaction coefficients. The system used to analyze this system has a reflux ratio of 6.5 with 125 trays for the first column and a reflux ratio of 10 with 60 stages for the second column. The default interaction parameters for the parameters in Hysys are shown in Table 6.

Table 6 – Default Hysys interaction coefficients

<table>
<thead>
<tr>
<th></th>
<th>Acetone</th>
<th>Chloroform</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0</td>
<td>-506.8518066</td>
<td>-243.9651031</td>
</tr>
<tr>
<td>Chloroform</td>
<td>116.1171036</td>
<td>0</td>
<td>-11.82310009</td>
</tr>
<tr>
<td>Benzene</td>
<td>682.4061279</td>
<td>-71.8108902</td>
<td>0</td>
</tr>
</tbody>
</table>
With these parameters the compositions for the each of the pure streams is shown in Table 7.

**Table 7 – Compositions for default Hysys parameters**

<table>
<thead>
<tr>
<th>Compositions</th>
<th>Acetone</th>
<th>Chloroform</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone Stream</td>
<td>0.99989</td>
<td>6.21E-09</td>
<td>1.06E-04</td>
</tr>
<tr>
<td>Chloroform Stream</td>
<td>7.79E-04</td>
<td>0.99248</td>
<td>6.73E-03</td>
</tr>
<tr>
<td>Benzene Recycle Stream</td>
<td>4.42E-20</td>
<td>1.96E-03</td>
<td>0.99804</td>
</tr>
</tbody>
</table>

This situation will be used as the default case for all of the other cases to be compared to and the composition profiles are shown in Figure 13a. By changing the interaction parameters the results do not change significantly because it only affects the compositional profiles therefore larger changes in interaction coefficients could require a greater amount of trays or a larger reflux ratio. The actual compositions of acetone in the acetone stream, the percentage of chloroform in the chloroform stream, and the percentage of benzene in the benzene recycle stream change very little. When the interaction coefficients are increased then the stripping profile increases in the length it extends as shown in Figure 13b. Likewise, when the interaction coefficients are decreased the length becomes smaller making the column less likely to be feasible as shown in Figure 13c. This decrease in the interaction coefficients might require an increase in the reflux ratio to counteract the difference.

![Figure 13 – Comparison of composition profiles with changes in the interaction coefficients](image)

<table>
<thead>
<tr>
<th>$a_{ij}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-506.8</td>
<td>-243.9</td>
<td></td>
</tr>
<tr>
<td>116.1</td>
<td>0</td>
<td>-11.8</td>
<td></td>
</tr>
<tr>
<td>682.4</td>
<td>-71.8</td>
<td>0</td>
<td>a) Default interaction coefficients</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$a_{ij}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-456.1</td>
<td>-219.5</td>
<td></td>
</tr>
<tr>
<td>127.7</td>
<td>0</td>
<td>-10.6</td>
<td>b) Interaction coefficients increased by 10%</td>
</tr>
<tr>
<td>750.6</td>
<td>-64.6</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$a_{ij}$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-557.5</td>
<td>-268.3</td>
<td></td>
</tr>
<tr>
<td>104.5</td>
<td>0</td>
<td>-13.0</td>
<td>c) Interaction coefficients decreased by 10%</td>
</tr>
<tr>
<td>614.1</td>
<td>-78.9</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
This system is also very sensitive to fluctuations in the feed composition due to its requirement that the bottom be very close to the distillation boundary. Therefore if a slight change in the feed to the first distillation column causes the composition of the bottom to change; then the feed into the second column will be in the other distillation region and the second column will be infeasible. This means that the control to this process must be carefully maintained to keep the process within the design restraints.

An industrial process that utilizes the curved nature of the distillation boundary to separate this mixture can be risky. Very little changes in the composition of the feed or impurities in the bottom or distillate can cause the distillation column to move into the other distillation region causing either distillation column to become infeasible. Therefore if there were any disturbances in the process then the distillation process as it was designed would not occur. This makes a distillation column similar to this very hard to control so the product from the distillation column can be consistent in its composition, temperature, and pressure.

**Ethanol Dehydration Case Study**

Extractive distillation deals with homogeneous azeotropic distillation. It allows for a mixture of two components to be completely separated into pure products with three distillation columns. In the case of adding a high boiling entrainer there is not a distillation boundary that exists on the residue curve map. This is because the azeotrope is the unstable node, ethylene glycol is the stable node, and both the water and ethanol serve as saddle points. Since there is only one stable node and one unstable node a distillation boundary is not formed and the distillation occurs only in one region.

A classic example of extractive distillation is the separation of ethanol from water by adding ethylene glycol as an entrainer. The mixture of ethanol and water exhibits an azeotrope at the concentration of 88 molar percentage of ethanol and 12 molar percent of water for a pressure of one atmosphere. However, pure ethanol can be very useful in many industries including the solvent industry and as a fuel additive. Therefore high purity ethanol is a very desirable product. A process flow diagram is shown in Figure 14 and the specifications for each of the columns are given in Table 8.
The first column in the process flow diagram is used to take the initial feed and bring it to the concentration of the azeotrope. The second column takes the feed from the first column and adds the entrainer, ethylene glycol. It is important that the ethylene glycol is added near the top of the column. This is because the entrainer should be a liquid in all of the trays to increase its ability to assist in breaking the azeotrope. The third column is used to separate the entrainer and water. The entrainer is then recycled back to the second column. Figure 15 shows the changes in concentration at the various feed locations. The entrainer, glycol, is added at stage 2 in order to have the maximum effect. The feed of water and ethanol is added at stage 25, and is the reason for the steps at stage 25 [8].
The temperature profile for the distillation column is shown in Figure 16. The x axis is the number of trays starting from the top while the y axis corresponds to the temperature. The temperature does not just increase in a smooth form but instead the temperature profile contains some irregularities where both of the feeds enter the column. In this column there are 33 stages, with the bottom feed coming into tray 23 and the entrainer or upper feed is coming into stage 1. The temperature generally decreases the higher up in the distillation column the measurement is taken. This occurs because the heavier components are present in higher concentrations closer to the bottom of the column and therefore a higher temperature is required to maintain the vapor phase. However in a two feed column the lower feed actually causes a dip in this trend because the feed is coming in at a cooler temperature.
In extractive distillation, there are three critical parameters that would be beneficial to minimize, the entrainer feed ratio, number of trays, and reflux ratio. Lowering each one reduces costs but also has an effect on the process. Lowering the entrainer feed ratio lowers the amount of pure ethanol recovered as distillate. Instead more ethanol is lost as part of the bottom product. Lowering the number of trays in the distillation column requires a larger reflux ratio for the column to be feasible. Likewise, lowering the reflux ratio requires more trays in the column for the column to be feasible. Since these three critical parameters are interconnected, it is important to find the parameters that give the best product for the least amount of cost. The Hysys simulation allows for quick simulations of the process to determine the results from manipulating the operating parameters of the distillation column. Therefore many cases were run to determine the minimum costs for running the simulation by a trial and error approach. The results to this problem are shown in Table 9.

### Table 9 – Simulation to find best parameters for ethanol case

<table>
<thead>
<tr>
<th>Reflux Ratio</th>
<th>Entrainer Molar Flow</th>
<th>Number of Trays</th>
<th>Azeotrope Molar Flow</th>
<th>Molar flow of 95% ethanol</th>
<th>Molar Flow of Bottom</th>
<th>% of ethanol in bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>100</td>
<td>33</td>
<td>45.34</td>
<td>41.94</td>
<td>103.4</td>
<td>0.000089</td>
</tr>
<tr>
<td>3.2</td>
<td>100</td>
<td>33</td>
<td>45.34</td>
<td>41.95</td>
<td>103.4</td>
<td>0.000004</td>
</tr>
</tbody>
</table>

Figure 16 – Temperature profile of ethanol dual feed column
<table>
<thead>
<tr>
<th>Re reflux</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>50</td>
<td>33</td>
<td>45.34</td>
<td>41.47</td>
<td>53.87</td>
</tr>
<tr>
<td>3.1</td>
<td>50</td>
<td>33</td>
<td>45.34</td>
<td>40.81</td>
<td>54.53</td>
</tr>
<tr>
<td>3.1</td>
<td>50</td>
<td>30</td>
<td>45.34</td>
<td>39.58</td>
<td>55.75</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>33</td>
<td>45.34</td>
<td>40</td>
<td>55.33</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>30</td>
<td>45.34</td>
<td>38.4</td>
<td>56.93</td>
</tr>
<tr>
<td>2.9</td>
<td>50</td>
<td>30</td>
<td>45.34</td>
<td>37.42</td>
<td>57.92</td>
</tr>
<tr>
<td>2.9</td>
<td>50</td>
<td>27</td>
<td>45.34</td>
<td>35.39</td>
<td>59.95</td>
</tr>
<tr>
<td>2.8</td>
<td>50</td>
<td>27</td>
<td>45.34</td>
<td>17.63</td>
<td>77.7</td>
</tr>
</tbody>
</table>

As seen from the chart the most efficient scheme from the trial and error method is a reflux ratio of 2.9, Entrainer/Feed ratio of 1.1, and 27 trays based on an eyeball estimate.

The Hysys optimizer was used to try to find the minimum costs. It tried to minimize either the reflux ratio or entrainer/feed ratio by manipulating either the reflux ratio or the entrainer molar flow. However, many problems were encountered when dealing with the optimizer. For example, many times the solver would say it had reached an optimum solution. When this occurred the column spreadsheet was not converged, therefore the solution that the optimizer got as the answer was for a scenario that did not converge. When using the optimizer there are different kinds of optimizers that are built into the program. The customizable optimizer was never able to get to work because of problems within the program.

In order to get a more accurate optimized case an objective function needs to be created. A cost analysis can be performed to find the best answer to the posed problem. Equation 8 illustrates the formula to calculate the total cost in yearly terms.

\[
TotalCost/\text{yr} = \frac{CapitalCost/\text{yr}}{\text{yr}} + \frac{OperatingCost/\text{yr}}{\text{yr}} \quad (8)
\]

This equation does not take into account administration cost because it would be constant for all of the case studies performed in the Hysys flowsheet. The capital costs describe all of the costs that come from building a column. The capital cost includes all resources such as space, labor, piping, pumping, labor, etc. In this model the only portion of capital cost changing from each scenario is the number of trays. The operating costs deals with the costs incurred from operating the distillation column. In this case there are two operating cost parameters that are changing from case to case, entrainer/feed ratio and
reflux ratio. A formula for calculating the revenue based on the amount of ethanol recovered in the column can be used. The final objective function would try to maximize the costs subtracted from the profits to find the best case scenario.

It is commonly discussed in the literature that the entrainer feed ratio is the most important factor in increasing the costs of the process. Therefore in deriving an objective function it was given the most weight. The reflux ratio was weighted to be less than that of the entrainer feed ratio, but to be higher than that of the number of trays. Likewise, the number of trays was the least important in the amount of weighing. The objective function took into account the molar flow rate of 95% ethanol leaving the process while subtracting from that the costs as shown in Equation 9.

\[
Obj = 0.95 \cdot M_E - (10 \cdot F_r + 2 \cdot R + \frac{N_T}{10})
\]

Where:
- \( M_E \): Molar flow of ethanol in the process flow diagram
- \( F_r \): Molar flow of entrainer/ molar flow of feed
- \( R \): Reflux Ratio
- \( N_T \): Number of trays in the column

Using this equation many case studies were run to find the maximum value for the equation. The results to these simulations are given in Figure 17. This Figure shows that the smallest entrainer feed ratio that gave significant amounts of ethanol product is the best solution.
Figure 17 – Optimization graph based on changes in reflux ratio and feed ratio

In this graph the x axis is the reflux ratio, the y axis is the value of the objective function whereas the differences in each of the series represents a different feed ratio. The maximum value in this graph is with a feed ratio of 1.1 and a reflux ratio of 3.2. Figure 17 also illustrates the effects of the minimum reflux ratio and the maximum reflux ratio. For the feed ratio of 1.1 the minimum reflux ratio is close to the reflux ratio that gives the small output to the objective function. Likewise, the maximum reflux ratio is close to the reflux ratio that gives a similar result for a higher reflux ratio. As the feed ratio increases the range between the maximum and minimum reflux ratio also increases.

**Acetone, Water, and Methanol Case Study**

Another system that contains a homogeneous azeotrope is the system of acetone, water, and methanol. In this case there is an azeotrope between acetone and methanol at approximately 80 molar percentage of acetone and 20 molar percentage of methanol. In order to break this azeotrope water is added as an entrainer in a similar manner that ethylene glycol is added to the ethanol water system. This system is accomplished in two columns, because in this case a column is not need to concentrate the acetone and
methanol to the azeotropic concentrations. The process flow diagram is shown in Figure 18.

![Figure 18 – Process flow diagram for acetone, methanol, water system](image)

The first column uses the water as an entrainer which is added to tray 38, and the feed of 50% methanol and 50% acetone, added to tray 61. The column has a total of 71 trays with a reflux ratio of 5. The distillate is consists of 95% acetone. The bottom stream is water and methanol which is then separated in the second column. The second column has 15 trays with a reflux ratio of 5. The water is then recycled where it is reused as the entrainer.

The composition profile, Figure 19, for this system illustrates the differences between a single feed and a double feed column. Instead of just having a stripping and rectifying section like a single feed column, a double feed column also contains a middle profile which is between the top and bottom feed. The rectifying section is from the upper feed to the condenser; likewise, the stripping section is from the lower feed to the reboiler. It is the effect of the middle profile that allows for greater purities beyond the azeotrope. The curl at the end of the rectifying profile always seems to occur for this system. If the number of trays is reduced then the curl occurs at a lower composition, therefore a less pure distillate is formed.
The temperature profile for the first column, shown in Figure 20, also demonstrates the irregularities of adding an entrainer above the feed. In the temperature profile it is possible to see the steep increase in temperature when the water entrainer is added and the slight decrease in temperature in the column when the acetone methanol feed is added to the distillation column. The x axis is the tray number starting from the top and the y axis is the temperature.
Like the ethanol and water system it is desirable to find an optimum solution so that the profits from running a similar column can be maximized. A similar method was used to find a better solution. The first column is the focus of the minimization because the second column is not does not demonstrate any complex behavior. The first method imposed was a trial and error method. The results from this method are shown in Table 10.

Table 10 – Optimization data for acetone water methanol system

<table>
<thead>
<tr>
<th>Reflux Ratio</th>
<th>Molar Flow of Entrainer</th>
<th>Molar flow of feed</th>
<th>Number of Trays</th>
<th>% Acetone</th>
<th>Molar Flow of Acetone</th>
<th>% Water in Bottom</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.950</td>
<td>52.610</td>
<td>0.000</td>
</tr>
<tr>
<td>4.9</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.950</td>
<td>52.607</td>
<td>0.000</td>
</tr>
<tr>
<td>4.8</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.951</td>
<td>52.566</td>
<td>0.000</td>
</tr>
<tr>
<td>4.7</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.951</td>
<td>52.573</td>
<td>0.000</td>
</tr>
<tr>
<td>4.6</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.952</td>
<td>52.543</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.951</td>
<td>52.561</td>
<td>0.000</td>
</tr>
<tr>
<td>4.4</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.952</td>
<td>52.536</td>
<td>0.000</td>
</tr>
<tr>
<td>4.3</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.951</td>
<td>52.564</td>
<td>0.000</td>
</tr>
<tr>
<td>4</td>
<td>55</td>
<td>100</td>
<td>71</td>
<td>0.950</td>
<td>52.614</td>
<td>0.000</td>
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<tr>
<td>3.8</td>
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<td>100</td>
<td>71</td>
<td>0.948</td>
<td>52.723</td>
<td>0.000</td>
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<td>3.6</td>
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<td>71</td>
<td>0.944</td>
<td>52.948</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>65</td>
<td>100</td>
<td>71</td>
<td>0.966</td>
<td>51.774</td>
<td>0.000</td>
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<tr>
<td>4.5</td>
<td>75</td>
<td>100</td>
<td>71</td>
<td>0.975</td>
<td>51.266</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>85</td>
<td>100</td>
<td>71</td>
<td>0.982</td>
<td>50.908</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
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<td>0.987</td>
<td>50.648</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>100</td>
<td>100</td>
<td>71</td>
<td>0.989</td>
<td>50.554</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>75</td>
<td>100</td>
<td>71</td>
<td>0.975</td>
<td>51.264</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>75</td>
<td>100</td>
<td>65</td>
<td>0.950</td>
<td>52.617</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>75</td>
<td>100</td>
<td>60</td>
<td>0.740</td>
<td>67.564</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>75</td>
<td>100</td>
<td>71</td>
<td>0.975</td>
<td>51.264</td>
<td>0.000</td>
</tr>
<tr>
<td>4.5</td>
<td>75</td>
<td>100</td>
<td>50</td>
<td>0.970</td>
<td>51.554</td>
<td>0.000</td>
</tr>
</tbody>
</table>

As can be seen from the Table the optimum solution from the trial and error method is an entrainer/ feed ratio of .75, 50 trays, and a reflux ratio of 4.5.

Many different parameters can have effects on the system. Some of these changes have a greater impact on how the system behaves then others. It is then important to
study these changes to have a greater feel for how each of these variables affect the process in case one changes when the system is operating and how the controls will be able to handle it. Three variables were studied in order to understand their effect on the system. The first one was the affect the reflux ratio has on the number of trays. The results from these calculations can be seen in Figure 21.

This graph is taken with a entrainer feed ratio of .55 in compositions similar to the case described previously. As can be seen from Figure 19 the process contains a minimum reflux ratio along with a maximum reflux ratio. As the reflux ratio increases from 3.3 to about 6.25 the number of trays decreases but as the reflux ratio increases from 6.25 the number of trays increases until the maximum reflux ratio is reached at 16.25. There is a trade off between the reflux ratio and the number of trays required for the distillation column. As the reflux ratio decreases from the optimum value the number of trays required increases significantly. This decreases the operating costs but the capital costs increases significantly. As the reflux ratio increases from the optimum value the number of trays increases therefore increasing both the operating and capital costs, which is not desirable.
The process is also sensitive to the amount of entrainer that is added to determine the quality of acetone leaving the distillation column. Figure 22 shows the effect the molar flow rate of entrainer has on the process.

![Figure 22 – Purity of Acetone leaving the column in relation to changes in molar feed of entrainer](image)

In this graph the feed rate of 50% acetone and 50% methanol is 100 moles. Therefore there is a threshold to the amount of entrainer used and the purity of acetone where there is a sharp change in the compositions at a little greater than 50 moles. At molar flow rates greater than 150 there is no change in the purities of acetone leaving the column therefore there is less need to increase the number. As the molar flow of the entrainer decreases from 150 to 50 the purity of acetone decreases, although this decrease in purity is not a very large drop.

Fluctuations in the feed compositions can also play an impact on the system. In an industrial process it is not always guaranteed that compositions being fed into the distillation column will be exactly the desired compositions. These disturbances can play a role in the control that the distillation column uses. To see the effects of fluctuations in the control of these processes different compositions were inputted to see the steady state values and how the purity of the acetone leaving the column changes with respect to the composition of the acetone being fed into the column. The results to these simulations are shown in Figure 23.
As can be seen from this chart there are two limits to the process. The purity of acetone leaving the column increases as the composition of acetone in the feed up to 40%, but after reaching 40% as the composition increases the purity of the composition of acetone leaving the column begins to decrease.

A change in the percentage of the interaction coefficients does still affects the feasibility of the distillation column, but it does not demonstrate a visible pattern to the increasing or the decreasing of the interaction coefficients.
Figure 24 – Effects of changes in interaction coefficients on the acetone, methanol, and water system

The process of extractive distillation is able to withstand fluctuations in the model in a better manner than that the systems which utilize a curved distillation boundary. This is important to implementing these systems in a real process because they are able to handle disturbances and can take into account the uncertainties that the differences in the model and the system. By studying the impact of these uncertainties and the costs of the system it is possible to understand the behavior of the distillation columns and how to implement the distillation column in a physical plant.

Ethanol, Water, and Cyclohexane Case Study

Another method of separating ethanol and water can be accomplished by adding cyclohexane. This creates a heterogeneous azeotropic mixture with a ternary azeotrope that acts as the unstable node. There are three regions in this system as shown in Figure 25 which is modeled using the NRTL thermodynamic model.

Figure 25 – Residue curve map for ethanol, water, and cyclohexane system

The key to this separation is the liquid-liquid interactions. The liquids in the shaded region are not completely miscible therefore; it is possible to use a decanter to separate the differences in the liquids. This is the way that the distillation boundary can be crossed in order to get greater purities beyond those of the azeotrope between ethanol and water.

Another entrainer that can be used to separate ethanol and water is benzene. Benzene creates a similar situation as that found in the ethanol, water, and cyclohexane case study.
system. A typical schematic for a series to separate a mixture like this is shown in Figure 26.

![Process flow diagram for heterogeneous distillation of ethanol, water, and benzene](image)

Figure 26 – Process flow diagram for heterogeneous distillation of ethanol, water, and benzene

The first column in this process concentrates the feed of the ethanol and water to the concentration of the azeotrope. The second column is where the critical separation is done where the distillation boundaries are crossed by using the decanter. The third column is used to recycle the entrainer and get more water. The specifics of the column were devised in Distil. The composition profiles for the system are shown in Figure 27. The exact specifications for this system are given in Table 11.

![Composition profile for ethanol, water, and benzene system](image)

Figure 27 – Composition profile for ethanol, water, and benzene system
The composition profiles contain the stripping and rectifying profiles. In addition to the basic stripping and rectifying profiles the column also contains the decanter line represented as the blue line. It shows the differences in the liquid compositions in the decanter. The reflux and distillate are made up of a mixture of both of the liquids to get its composition. With these different compositions the distillation has crossed the distillation boundary which allows for greater purities.

The third column is used as a recovery column where greater amounts of water are removed from the process but the ethanol and entrainer are recycled back to the second column along with some additional entrainer that might have been lost in other streams. The advantage of this process is that the amount of entrainer is far less than that of the homogeneous case. The reflux ratio is greatly reduced along with the number of trays. However, this process is very difficult to model and understand because of the role the liquid-liquid interactions play within the system and the distillation column along with the decanter.

Heterogeneous azeotropic distillation is also dependent on the effects of reflux ratio on the number of trays that are required for the distillation column. As Figure 28 illustrates the heterogeneous azeotropic distillation only has a minimum reflux ratio. After a certain reflux ratio is reached the number of trays does not decrease. The
heterogeneous system is affected less by the change in the reflux ratio than that of the homogeneous azeotropic system.

![Figure 28 – Trade off between reflux ratio and number of trays for heterogeneous azeotropic system](image)

Heterogeneous azeotropic distillation is an effective way of achieving purities beyond the compositions of the azeotrope by utilizing the partial miscibility the entrainer introduces to the system to gain compositions on different sides of the distillation boundaries. Heterogeneous azeotropic distillation also is not affected by the reflux ratio in terms of the number of trays and has lower costs.

**Conclusions**

There are three schemes to separating complex mixtures. These methods include mixtures with curved distillation boundaries, homogeneous azeotropic systems, and heterogeneous azeotropic systems. Each of these systems has advantages and disadvantages for both costs and model uncertainty. The curved distillation boundary systems are effective in that not many distillation columns are needed. Also with systems like these no new component is needed to be added to the system for the separation. However, this system is very sensitive to changes in the model parameters. These parameters range from changes in the model uncertainty as shown in Figure 13 to changes in the operation parameters, such as feed compositions and reflux ratio. These parameters cause the distillation to become infeasible because the distillation region cannot be crossed. Because of this reason a process that utilizes the curved nature of the
The second method of separating complex mixtures is to introduce an entrainer that does not cause a distillation boundary to form. The entrainer is added above the feed so that it can have the greatest effect on the vapor by remaining a liquid on most of the trays in the column. The homogeneous azeotropic system introduces significant costs because it requires the recycling of a significant amount of entrainer back into the system. This recycle cost is a very significant part of the process and it is advantageous to minimize this cost first. Often in systems of homogeneous azeotropic distillation the entrainer represents a significant amount compared to the amount of feed that is introduced into the column. The reflux ratio is also dependent on the ratio of the feed and entrainer feed. In a mixture like this there exists a minimum entrainer feed rate, a minimum reflux ratio, and a maximum reflux ratio. The closer the feed ratio is to the minimum feed ratio the smaller the range between the maximum and minimum reflux ratio. Homogeneous azeotropic mixtures are less affected by changes in the model uncertainty than systems that rely on curved distillation boundaries. Changes in the model and changes in the operating parameters such as the entrainer flow rate or reflux ratio have a smaller impact on the system.

Heterogeneous azeotropic systems provide another scheme to separating complex mixtures. These systems generally involve fewer costs than those of homogeneous azeotropic systems and more reliability than that of the curved distillation boundaries. However there are complications to these systems involving the immiscibility of the two liquid phases. The column behavior to these systems is not completely known. There are large fluctuations in the temperature profile based on the compositions of the bottom stream. However these systems generally involve less entrainer flow rate and recycle rate and the reflux ratio is less dependent on this ratio. These systems are also more robust than that of the curved distillation boundary and can better handle changes in the model parameters.

**Future Work**

- Devise a working model of a heterogeneous azeotropic distillation column in Hysys
- Evaluate effects pressure can have on the separation schemes
- A more in depth cost analysis comparing all separation schemes for the ethanol water dehydration system
- Further analyze and compare the effect uncertainty has on the all of the separation schemes
- Move into characterizing the dynamic behavior of the distillation columns
- Devise effective control schemes to control each of the various distillation schemes

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