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#### MEASUREMENT AND PREDICTION OF THE COMPOSITION OF FRUIT DISTILLATES

presented by

**Michael Joseph Claus** 

has been accepted towards fulfillment of the requirements for the

Ph.D

degree in

Biosystems Engineering

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#### MEASUREMENT AND PREDICTION OF THE COMPOSITION OF FRUIT DISTILLATES

By

Michael Joseph Claus

#### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Agricultural Engineering

### ABSTRACT

#### MEASUREMENT AND PREDICTION OF THE COMPOSITION OF FRUIT DISTILLATES

By

Michael Joseph Claus

The production of high quality fruit spirits has always been and continues to be heavily dependent upon the sensory evaluation of the distillate by the distiller. Sensory fatigue can be a problem for distillers during production. A simple method for prediction of the distillation characteristics of the important flavor compounds present in these spirits can increase the yield and quality of these spirits and reduce the dependence of the distillation process on the distiller's senses. This distillation process is difficult to model because of the number of components present in the spirits as well as the constantly changing thermodynamic interactions present on each tray due to its batch nature. The Chemstations CHEMCAD<sup>™</sup> modeling software program with a batch distillation model was utilized to predict the concentrations of the important flavor components present in distilled fruit spirits as a function of distillate volume. This modeling process utilized the analysis of the composition of the fermentation mash as a starting point. This approach permits a distiller to predict which volume fractions of the distillate should be retained as product, increasing yield and quality. Additionally this approach can be used to analyze the effects of flaws in the fermentation process that might lead to distilled products not fit for consumption.

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## **KEY TO SYMBOLS**

С	Number of components (Gibb's Equation)
D	Total distillate
F	Total feed
F	Number of degrees of freedom (Gibb's Equation)
H	Vapor enthalpy
$h_D$	Enthalpy of liquid in the distillate
hj	Enthalpy of the liquid stream leaving plate j
$\tilde{L_j}$	Liquid stream leaving plate j
$L_{j+1}$	Liquid stream entering plate j
P	Number of Phases (Gibb's Equation)
Q <sub>R</sub>	Total heat supply to bottoms (reboiler)
Qc	Heat load on condenser
R	Reflux Ratio
Τ	Total batch time
t	User defined time
<i>x</i> <sub>D</sub>	Distillate composition of component 1 in mixture
x <sub>Dav</sub>	Average distillate composition of component 1 in mixture
<i>x<sub>F</sub></i>	Feed composition of component 1 in mixture
$x_j$	Liquid composition of component 1 in mixture leaving plate j
<i>x<sub>j+1</sub></i>	Liquid composition of component 1 in mixture entering plate j
XW	Liquid composition of component 1 in bottoms
V	Vapor molal flow rate
$V_{j}$	Vapor stream leaving plate j
$V_{j+1}$	Vapor stream entering plate j
Уj	Vapor composition of component 1 in mixture leaving plate j
<i>Y</i> <sub><i>j</i>+1</sub>	Vapor composition of component 1 in mixture entering plate $j$

### 1. INTRODUCTION

#### 1.1 Michigan Brandy Industry

The growing distillation industry in Michigan is the result of recent changes to the state laws regarding the licensing of fruit distilleries. The number of stills has increased from zero in 1996 to nine in 2003. Michigan is ideal for the production of fruit spirits due to the variety of fruit that grow in the state. Michigan's brandy industry primarily follows the traditional German process for fruit spirits<sup>1</sup>. This batch distillation process with reflux utilizes a multistage still to preserve the flavors and essences in the distillate. Research at Michigan State University has been focused on enhancing the efficiency of the traditional European style of fruit spirits production, and improving the quality of the distilled spirits.

#### **1.2 Fruit Brandy Production**

Distillation is one of the oldest separation processes and is the most widely used unit operation<sup>2</sup>. There are two competing styles for producing fruit spirits in Europe. Alambic distillation is used for producing spirits similar to cognac, and batch distillation produces eau-de-vie or schnapps. The alambic style involves distillation through a simple pot still, collecting the distillate and repeating the distillation multiple times to achieve high proofs<sup>3</sup>. The German style of batch distillation involves a single distillation utilizing a column with reflux on the batch still to obtain high proof spirits. These spirits are traditionally stored in glass and served as water clear brandies<sup>1</sup>.

Fruit brandies are produced by fermentation and distillation of the whole fruit to enhance the flavor and quality of the spirits. The fruit utilized for the production of fruit spirits should be unblemished; however, overripe fruit is preferred for fruit spirits as there is more sugar to ferment. The fruit is mashed and yeast is added for fermentation. Upon completion of the fermentation the fruit mash is distilled resulting in high proof water clear spirits. Finally after storage at high proof (aging) for one month to several years, the distillate is diluted to drinking strength (>40% Alcohol By Volume (A.B.V)) and bottled<sup>4</sup>. Figure 1.1 shows the process involved in the production of fruit spirits, from the fresh fruit to the bottled product.

#### **1.3** Congener Formation and the Need for Control

The number and concentrations of compounds present in the fruit spirits are much greater than other types of distilled spirits due to the use of whole fruit mashes. Figure 1.2 compares the congeners present in distilled fruit spirits with other types of spirits such as gin, vodka, and whiskey<sup>5</sup>. The skins and flesh of the fruit contribute to the increased number of flavor compounds present in these spirits. The distillation process also attempts to maximize the flavor compounds for fruit spirits, where vodka and gin types of spirits attempt to reduce the concentration of the flavor constituents<sup>5</sup>.



Figure 1.1 The process involved in making distilled fruit spirits. Fresh fruit is mashed, fermented and then distilled. The distillate collected is aged and then diluted to drinking strength and bottled.



Figure 1.2 Volatiles in distilled spirits. The concentration of volatile congeners in the distilled spirits (mg/100 mL of alcohol). Fruit spirits have higher concentrations of volatiles than other distilled beverages<sup>5</sup>.

After water and ethanol, methanol is present in the next highest concentration of the flavor components found in these distilled spirits. Methanol is regulated by the Alcohol and Tobacco Tax and Trade Bureau (TTB) and the Food and Drug Administration (FDA), to prevent distillers from producing a product which can be a health hazard<sup>6</sup>. Methanol is present in these spirits because naturally occurring enzymes present in fruit induce the breakdown of pectin, which in turn releases methanol into the mash. This increased methanol in the mash is directly related to the concentration of methanol present in the final distilled product.

Fusel alcohols such as 1-propanol, *t*-butanol, and isoamyl alcohol, and carbonyl compounds such as acetaldehyde, acetone, and benzaldehyde are present in the mash of fruit fermentations at higher concentrations than in wines or grain mashes<sup>7, 8, 9</sup>. The concentration of the fusel alcohols in the final distilled spirits must be carefully controlled by the distiller because of the negative aromatic characteristic associated with the higher concentration of these higher chain alcohols. Acetone and acetaldehyde also have negative aroma characteristics.

Fruit fermentations vary widely in chemical makeup. Each fruit and variety in each fruit will have unique characteristics. Furthermore, within each variety of fruit exists variations caused by growing conditions (e.g. soil), seasonal variation, and regional climate. A batch of cherries harvested on one day can have a very different makeup than a batch of cherries harvested a week later. Additionally, the yeast involved in the fermentation process can affect the flavor profile of the fruit mash. In general, the effects of wild strains of yeasts and molds are mitigated by over-inoculation of the mash with the

desired yeast; however, it is possible for some wild microbes to be present in the mash and alter the composition of the congener compounds.

Variation in fruit mash composition directly leads to changes in distillate composition. Predictive control of the distillation based upon the composition of the fruit mash will increase the overall quality of the spirits.

#### **1.4 Chemstations CHEMCAD™ Program**

Chemstations Inc. CHEMCAD<sup>™</sup> process simulation software possesses a batch distillation module capable of modeling the distillation process involved in the manufacture of fruit spirits. The CHEMCAD<sup>™</sup> program can provide simulation of a number of industrial functions/unit operations including: batch distillation (with reflux as required by the present work), reactions, extraction, continuous distillation, electrolytic processes, vapor/liquid/liquid equilibrium calculations, equipment sizing, environmental calculations, cost estimates, heat exchanger networks, and safety analyses<sup>10, 11</sup>.

The CHEMCAD<sup>™</sup> program is designed to be user friendly, which is one of the primary reasons for its choice for the current work. Use of the program involves entering the flow rates involved in the distillation, analysis step size (time), and composition of the pot charge. The CHEMCAD<sup>™</sup> program is designed to produce data that can be easily interfaced with other computer programs such as Microsoft Office programs<sup>10</sup>. The ability to transfer the data to a spreadsheet program makes analysis of the data easier than other programs which do not interface well with other programs<sup>10</sup>.

#### 1.5 **Objective**

This project involves predicting the concentration of congener compounds common to fruit spirits by utilizing simple distillation methods of the mash, and the CHEMCAD<sup>TM</sup> computer program. If the quality of the resulting fruit spirits could be predicted based on the makeup of the mash content, the distillation process could be controlled to increase the quality and yield of the final product. Use of CHEMCAD<sup>TM</sup> as a predictive model with actual fruit spirit distillations is aimed at determination of the usefulness of this approach.

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### 2. DISTILLATION PRINCIPLES

#### 2.1 Degrees of Freedom

Gibb's phase rule states that the number of degrees of freedom associated with a mixture is based on the equation below,

$$F = C - P + 2$$

where *F* is the number of degrees of freedom, *C* is the number of components, and *P* is the number of phases<sup>1</sup>. A two component mixture would then have F = 4 - P degrees of freedom. If temperature is kept constant the remaining degrees of freedom F' = 3 - P, which has a maximum value of two. These two degrees of freedom are pressure and composition of one component (mole fraction  $X_A$ ). When increasing to a three component mixture there are F = 5 - P degrees of freedom. As the number of components present in the mixture increases, the degrees of freedom increase, which in turn makes modeling the process more difficult<sup>1, 2</sup>.

#### 2.2 Batch Distillation of Fruit Spirits

There are two competing styles for producing fruit spirits in Europe. Simple pot style, alambic, distillation is used for producing spirits similar to cognac and column still distillation is used to produce eau-de-vie (French) or schnapps (German). The alambic style involves distillation through a simple pot still, collecting the distillate, and repeating the procedure multiple times to obtain high proof distillate products. This style utilizes high temperatures at the heat transfer surface and the resulting spirits are often harsh. To

overcome the dour flavor of these spirits, they are often stored in oak casks to extract the flavors from the wood. Figure 2.1 is an illustration of an alambic style still.

The German style of batch distillation involves a single pass through a reflux column on a batch still to obtain high proof spirits. This approach utilizes lower temperatures and the resulting spirits are traditionally stored in glass and served as water clear brandies<sup>3</sup>. Figure 2.2 is an illustration of the multistage batch still used for this type of distillation.

Fruit brandy distillation is different from traditional brandies which are distilled from grape wines. Fruit spirits are produced by the crushing, fermentation, and distillation of the mash of the whole fruit. Using the whole fruit in the process increases the essences and improves the sensory experience of consuming distilled spirits<sup>3, 4</sup>. The fruit flesh, skins and seeds presence in the fermentation mash and distillation process increase the concentrations of congener compounds (compounds other than ethanol and water) present in the fruit spirits. Fruit spirits have higher concentrations of nearly all types of congener compounds when compared to other types of distilled spirits<sup>4</sup>.

Distillation is the process of concentrating or separating compounds based on their volatility. Traditionally three fractions of fruit spirits are collected. The first fraction, the heads, will have higher concentrations of the lower boiling point compounds. The middle fraction, the hearts, is the fraction which will eventually become the potable product. The final fraction, the tails, will have a higher concentration of the higher boiling point compounds.



# Alambic Still

One stage distillation •Multiple distillations required to increase separation •High amount of product loss

A. Fire or Steam Heat Supply

- B. Copper Pot
- C. Alambic Hat
- D. Swans Neck
- E. Condenser
- F. Distillate Spout

Figure 2.1 Alambic style still. This still utilizes only one stage requiring the distillate to be redistilled to obtain a good product. The alambic still is recognized from the alambic (onion shaped) hat and swans neck transfer tube.



# **Batch Still**

## Multiple stage distillation

- Each stage acts as one alambic distillation
  Higher separation with multiple trays
- •Higher purity of product
- •Greater yield

- A. Steam Heat Supply
- B. Copper Pot
- C. Distillation Column
  - 1. Tray
  - 2. Downcomer
- D. Condenser
- E. Distillate Spout

**Tray Operation** 



Figure 2.2 Multistage batch still. This apparatus used multiple stages to increase the separation of the components. The trays force the vapor phase to pass through the condensed liquid allowing reflux and better separation of the components.

#### 2.3 Rayleigh Distillation

The most basic type of distillation is a simple binary distillation also known as a Rayleigh distillation. Two compounds with different boiling points can be distilled under simple distillation conditions. A simple distillation involves no trays, the pot for boiling the mixture is connected to the condenser. When the liquid in the pot is boiled, the vapor is removed in each time interval and condensed in the condenser. The vapor becomes richer in the more volatile component than the liquid remaining in the pot, thus reducing the concentration of the more volatile component present in the pot. The vapor condensed in the condenser increases in the concentration of the more volatile components are separated into two separate vessels, the more volatile in the distillate and the less volatile in the pot<sup>2, 5</sup>. Figure 2.3 shows a schematic diagram of the Rayleigh distillation apparatus<sup>2</sup>.

The mass balance around the entire system for the entire operating time is:

$$F = W_{final} + D_{total}$$
$$Fx_F = x_{W,final}W_{final} + D_{total}x_{D,avg}$$

where F represents the feed, D represents the distillate W represents the bottoms, and  $x_f$  represents the mole fraction of the feed<sup>2</sup>.

The variables F,  $x_F$  and the desired value of either  $x_{W,final}$  or  $x_{D,avg}$  are specified requireing an additional equation to solve for the three unknown variables  $D_{total}$ ,  $W_{final}$ , and the unspecified variable above. The Rayleigh equation is derived from a differential mass balance. The assumption is made that the holdup in the accumulator and column are negligible<sup>2</sup>. The differential amount of material -dW of concentration  $x_D$  is removed from the system, resulting in the differential mass balance:

$$-x_D dW = -d(Wx_W) = -Wdx_W - x_W dW$$

Rearranging and integrating gives:

$$\int_{W=F}^{W_{final}} \frac{dW}{W} = \int_{x_F}^{x_{W,final}} \frac{dx_W}{x_D - x_W} \quad \text{or} \quad \ln\left[\frac{W_{final}}{F}\right] = -\int_{x_{W,final}}^{x_F} \frac{dx_W}{x_D - x_W}$$

The vapor product is in equilibrium in simple batch distillations. Because a total condenser is used, the substitution of  $y = x_D$  can be made<sup>2</sup>. Then:

$$\ln\left[\frac{W_{final}}{F}\right] = -\int_{x_{W,final}}^{x_F} \frac{dx}{y-x} = -\int_{x_{W,final}}^{x_F} \frac{dx}{f(x)-x}$$

where x and y are in equilibrium which can be expressed as y = f(x,p)

By integrating the above equations it is now possible to find a solution for the unknown variables  $D_{total}$ ,  $W_{final}$ , and  $x_{W,final}$  or  $x_{D,avg}$ . Time is implicitly present in these equations because W,  $x_W$ , and  $x_D$  are time dependent<sup>2</sup>.



W	Bottoms
D	Distillate
X <sub>D</sub>	Mole Fraction of Distillate
X <sub>w</sub>	Mole Fraction of Bottoms
Q <sub>R</sub>	Reboiler Heat Load

Figure 2.3 Simple batch distillation schematic<sup>2</sup>.

#### 2.4 Multistage Batch Distillation

For multistage systems  $x_D$  and  $x_W$  are no longer in equilibrium, and the Rayleigh equation can not be integrated until a relationship between  $x_D$  and  $x_W$  are found<sup>2</sup>. Stage by stage calculations must be made to obtain the relationship between  $x_D$  and  $x_W$ . By assuming that the holdup is negligible at each tray, the condenser, and the accumulator, mass and energy balances around any stage *j* and the top of the column can be performed as shown in figure 2.4. At any time *t* these balances become:

$$V_{j+1} = L_{j+1} + D$$
  

$$V_{j+1}y_{j+1} = L_jx_j + Dx_D$$
  

$$Q_C + V_{j+1}H_{j+1} = L_jh_j + Dh_D$$

The molal flow rates are expressed in these equations by V, L, and D. The energy balance is not needed if constant molal overflow is assumed, because the vapor and liquid flow rates will be constant. The equation for constant molal overflow then becomes<sup>2</sup>:

$$y_{j+1} = \frac{L}{V} x_j + \left(1 - \frac{L}{V}\right) x_D$$

This represents a straight line on a y-x diagram. The slope will be L/V and the intercept with the y = x line will be  $x_D$ . Either  $x_D$  or L/V will need to vary during the batch distillation, and the operating line will be constantly changing<sup>2</sup>. The 150 L Christian Carl still is based on a varying reflux ratio, attempting to keep the concentration of  $x_D$  at a maximum.

For variable reflux ratio operation of a batch distillation, the equation for constant molal flow rate holds, with the slope varying, and the intersection with the y = x line at a

constant  $x_D$ . Figure 2.5 shows the McCabe-Thiele diagram for multistage batch distillation with variable reflux. The McCabe-Thiele diagram relates  $x_W$  and  $x_D$  allowing integration of the Rayleigh equation<sup>2</sup>.

The feed concentration  $x_F$  is found by identifying the initial value of L/V is found by trial and error, and specifying the number of stages and the distillate composition  $x_D$ . The final value  $x_{W,final}$  occurs when L/V is in total reflux, or L/V = (L/V)<sub>max</sub>. Once  $x_{W,final}$ is found,  $W_{final}$  is determined from integration by the equation<sup>2</sup>:

$$W_{final} = F \exp\left(-\int_{x_{W,final}}^{x_F} \frac{dx}{y-x}\right)$$

•



Figure 2.4 Schematic of a multistage batch distillation apparatus<sup>2</sup>.


Figure 2.5 McCabe-Theile diagram for multistage batch distillation with variable reflux<sup>2</sup>.

#### 2.5 Multicomponent Batch Distillation

The additional degrees of freedom associated with the addition of more compounds to the mash make the modeling of multicomponent batch distillations difficult. By increasing the number of components from two to three the number of degrees of freedom increases to account for the composition of the feed. Each additional compound included in the feed will in turn increase the complexity of the interactions of the components. Each interaction between each component must be taken into account for modeling these types of distillations. The variety in compound interactions (e.g. polar and non-polar, size, hydrogen bonding, etc.) require many different types of models to explain the behavior of the components present in the multicomponent distillations. These models rely upon large sets of coupled, nonlinear ordinary differential equations. The models available in CHEMCAD<sup>™</sup>, and the formulas used for this work are included in the appendix of this work.

In multicomponent distillation, neither the distillate composition nor the bottoms composition is completely specified because there are not enough variables to allow complete specification<sup>2</sup>. The calculation procedure is greatly affected by the inability to completely specify the distillate and bottoms composition. It is possible to identify components in four classifications. Those components for which the fractional recoveries in the bottoms or distillate are known as key components, the most volatile of which is known as the light key (LK) and the least volatile of which is known as the heavy key (HK). The other compounds are known as the non-key components. Those non-key components that are more volatile than the LK component are known as light non-key

(LNK) and the compounds less volatile than the LK compound are the heavy non-key compounds (HNK).

The overall balance equation is:

$$F = B + D$$

The component balance equations become:

$$Fz_i = Bx_{i,bot} + Dx_{i,dist}$$

and the mole fractions must sum to 1.

$$\sum_{i}^{C} x_{i,dist} = 1.0$$
$$\sum_{i}^{C} x_{i,bot} = 1.0$$

For a three component mixture the component balance equation is written three times, and must then sum to meet the overall balance equation.

The problem of solving for the external mass balances arise. The unknowns are B, D,  $x_{2,dist}$ ,  $x_{3,dist}$ ,  $x_{2,bot}$ , and  $x_{3,bot}$ . This leaves six unknowns with five independent equations. The additional equations of energy balances or equilibrium expressions always add additional variables<sup>2</sup>. Internal stage-by-stage calculations for tertiary systems rely on the compositions of the components at one end of the column, and these as mentioned earlier are unknown. By assuming one of them is known, the problem becomes a trial-and-error exercise<sup>2</sup>.

Many formulae for these trial-and-error calculations have been developed for mixtures of three or more components. Additional variability to the molal flow rate of each component and chemical interactions further complicate the problem resulting in the need for a software suite like CHEMCAD<sup>TM</sup> to perform these calculations using a variety of these distillation models<sup>6</sup>. A description of the models used in this work can be found in the appendix.

#### 2.6 Trays and Usage

Distillation trays rely on the principle of reflux for increasing the separation of the compounds present. Reflux is the partial condensation of vapor and the return of the liquid down the column. At every interface between the liquid layer and the condensed layer, contact is occurring causing greater separation of the compounds present<sup>1, 2, 3, 7</sup>.

As the name implies, sieve trays have numerous small holes in the plate of the tray which, for the Christian Carl still used in this experiment, are capped by a plate as illustrated in Figure 2.6. These holes are small enough that the pressure of the vapor from the tray below causes only the upward flow of vapor and liquid does not flow downward. The liquid phase flows across the top of the tray until it reaches the downcomer (the opening for the liquid to flow downward) and the vapor from the tray below is forced to pass through the holes and the liquid, and then onto the next tray. This configuration leads to excellent contacting between the two phases and makes the composition approach vapor-liquid equilibrium.

The 10 L Holstein still uses bubble cap trays. Bubble cap trays use the same idea of passing the vapor from the tray below through the condensed layer on the tray above. As seen in figure 2.7 a bubble cap tray has a cap over a tube from the lower tray. The vapor must pass through the condensed liquid in order to get through to the next tray. Both types of trays can be modeled by the CHEMCAD<sup>™</sup> software program.



Figure 2.6 Christian Carl style sieve trays. The sieve tray has a number of holes along the tray through which the vapor from the tray below must pass. This action forces the vapor to pass through the condensed liquid on the tray, increasing the separation of the components present.



Figure 2.7 Bubble cap tray. Used by Holstein stills, this tray design traps the condensed liquid on the surface of the tray without allowing it to flow through to the tray below. The design also forces the vapor from the tray below to pass through the condensed liquid layer, increasing the separation of the components present.

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#### **3. BRANDY FLAVOR COMPONENTS**

#### 3.1 Overview

Organic acids, esters, and fusel alcohols form the main body of the congener compounds (all compounds other than ethanol and water) in the distilled spirits<sup>1</sup>. Some other compounds are also present in the distillate, but the above organic compounds account for the majority of congeners present. The formation of most of the congeners in the distillation occurs in the fermentation of the mash in the presence of yeast<sup>1</sup>. The fermentation process is controlled to prevent an excess of undesired compounds, and increase the yield of ethanol. Control of the fermentation includes temperature control, fermentation duration, and mixing. High temperature fermentations have reduced ethanol yield and increased congener concentrations. If the temperature of the fermentation is too low, the yeast activity decreases, requiring a longer duration of fermentation. Common fermentation time. Stirring the fermentation can decrease the time required for complete fermentation, and decrease the mash viscosity<sup>2, 3</sup>.

Any wild strains of yeast, molds, or other microbes may cause increased concentrations of undesired compounds. Over-inoculation of the mash with the desired strain of yeast is the best method for preventing other microbes from producing undesired compounds. Over-inoculation requires adding an amount of yeast greater than the minimum amount required to ferment the mash. The desired yeast will out-compete the wild microbes for the nutrients needed for growth and reproduction. This method reduces the production of undesired flavors at a cost of more yeast.

#### 3.2 Ethanol

The distillation of fruit spirits relies on the conversion of fruit sugars to ethanol by yeast. The Embden-Meyerhoff-Parnas Pathway (EMP) is the well know process for the conversion of sugars to ethanol by yeast. This pathway proceeds by degrading the sugar to acetaldehyde where it is then reduced to ethanol. Figure 3.1 shows the EMP pathway common to yeast fermentation of ethanol<sup>4</sup>. The yield of ethanol is dependant upon the initial concentration of the total sugar present in the fruit which is measured as total dissolved sugar present in the liquid mash. The total dissolved solids (brix), however, also includes unfermentable compounds such as sorbitol, and must only be used as a guide to determine the approximate concentration of the sugars present in the mash. The EMP process yields two moles of ethanol for every one mole of glucose present in the fruit. Other sugars present in the fruit include fructose, maltose and sucrose<sup>2</sup>.

#### 3.3 Methanol

Methanol is a very important compound in the production of fruit brandies. The United States Food and Drug Administration (FDA) and Alcohol and Tobacco Tax, and Trade Bureau (TTB) regulate the methanol concentration in distilled spirits at 0.35% v/v (2.765 g/L)<sup>5</sup>. Methanol is a positive flavor component of brandies; therefore, its complete elimination from brandies is not the aim of the regulations. Methanol is similar to ethanol in taste and smell; however, it is toxic and potentially dangerous if present in high concentrations. These regulations are primarily a consequence of the use of methanol by unlicensed distillers to adulterate beverages by addition of methanol to increase the alcohol concentration.



Figure 3.1 The Embden-Meyerhoff-Parnas pathway for the fermentation of glucose by yeast. One mole of glucose produces 2 moles of CO<sub>2</sub> and 2 moles of ethanol. This pathway also produces energy for the yeast cells<sup>4</sup>.

The regulation of methanol is based on associated health hazards. Methanol is a poison that interrupts nerve impulses. Methanol causes headache, nausea, and can attack the optic nerve blurring vision or even causing blindness<sup>6, 7</sup>. Chronic exposure to methanol can cause kidney and liver dysfunction. Methanol is metabolized in the body to formaldehyde, which is also poisonous to humans<sup>6</sup>. Interestingly, the antidote for acute methanol poisoning is administration of ethanol; therefore, the low regulated levels of methanol in high proof fruit brandies pose little or no health hazard.

Methanol is a side product of the fermentation process along the EMP process. However, a larger concentration of the methanol comes from an enzymatic interaction of pectinesterase with the pectin of the fruit<sup>3</sup>. The structure of pectin and the enzymatic reaction of pectinesterase on pectin can be seen in figures 3.2 and 3.3 respectively<sup>3</sup>. This is part of the natural decomposition process of the fruit, which is designed by nature to prevent animals from removing the seed from the nutrients of the fruit because of the poisonous methanol that is present. The whole fruit is used in the fermentation of fruit spirits which increases the amount of pectin and pectinesterase in the mash and consequently increases the concentration of methanol in fruit spirits when compared with other distilled spirits<sup>2.3</sup>.



Figure 3.2 The structure of pectin. The arrows point to sites where the pectinesterase enzyme cleaves methanol from the pectin in the reaction seen in figure 4.3<sup>3</sup>.



Figure 3.3 The reaction of the pectinesterase enzyme with pectin. Only the active site on pectin for the enzyme is shown. This reaction is the primary source of methanol in distilled fruit spirits<sup>3</sup>.

#### 3.4 Fusel Alcohols

Fusel alcohols are defined as those alcohols larger than ethanol (e.g. C>2) and compose the largest group of aroma compounds in alcoholic beverages<sup>1, 8</sup>. The most common fusel alcohols in distilled spirits include 1-propanol (*n*-propanol), 2-methyl-2-propanol (isobutyl alcohol), and 3-methyl-1-butanol (isoamyl alcohol). Isoamyl alcohol is the main fusel alcohol synthesized during fermentation by yeast accounting for 40 to 70% of the total fusel alcohol concentration in distilled spirits depending upon the type of mash<sup>1</sup>. Formation of these fusel alcohols is thought to be independent of the raw materials used in the mash in that the formation of these longer chain alcohols can occur in whiskeys as easily as in tequila, gin, or fruit spirits<sup>1, 8</sup>. N-propanol, and branched C<sub>4</sub> and C<sub>6</sub> alcohols are formed from valine, leucine, and isoleucine in the presence of yeast.  $\alpha$ -keto acids are first decarboxylated to aldehydes and then reduced to the corresponding alcohol. Fusel alcohols are thought to form in fermentation under both anaerobic conditions from amino acids and aerobic conditions from sugars<sup>8</sup>.

#### 3.5 Carbonyl Compounds

#### 3.5.1 Aldehydes

Aldehydes are the intermediates in the production of alcohols by yeast. The aldehyde concentration in the distilled spirits is due to the inefficiency of the yeast in reducing the aldehydes to their corresponding alcohol<sup>9</sup>. The yeasts are making the

aldehydes as well as reducing them to alcohols; however, the reduction of the aldehyde to alcohol is not as efficient as the production of the aldehydes<sup>9</sup>.

The most common aldehyde present in the distilled fruit spirits is acetaldehyde. Acetaldehyde is an intermediary in the EMP pathway and is present in all distilled spirits. Acetaldehyde has a low boiling point and is soluble in both water and ethanol, and is at its highest concentration in the early (heads) portion of the distillation<sup>10</sup>.

Benzaldehyde, sometimes referred to as bitter almond oil, is another important aldehyde present in stone fruits. Benzaldehyde comes from the amygdalin present in the pit of stone fruit. The hydrolysis of one mole of amygdalin yields two moles of glucose one mole of cyanide and one mole of benzaldehyde<sup>10, 11</sup>. Benzaldehyde is considered a positive aroma characteristic in stone fruit brandies<sup>2, 10, 12</sup>. It is present in the late hearts and tails of the distillate due to the relatively high boiling point.

#### 3.5.2 Ketones

Ketones are produced in the yeast cells as an oxidation product of alcohols and excreted as an unwanted side product. The most common keytone present in the distilled spirits is acetone, which has a negative aroma associated with it in fruit spirits<sup>2, 10</sup>. Acetone may be produced from oxidation of 2-propanol as well as other microbes present in the fermentation media. *Clostridium acetobutylicum* for example, is used in the industrial fermentation of acetone, butanol, and ethanol<sup>13</sup>.

#### 3.5.3 Esters

Esters are formed during the distillation and storage of the spirits and generally add positive flavor aromatic qualities to the distilled fruit spirits. The highest

concentration esters present are ethyl formate and ethyl acetate. Ester formation is due to the esterification of alcohols with organic acids. The formation of ethyl acetate and ethyl formate involve the reaction of acetic acid with ethanol and methanol respectfully<sup>14</sup>. These two esters are present in the highest concentration in the distilled spirits because they are derived from the two highest concentration alcohols.

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#### 4. MATERIALS AND METHODS

#### 4.1 **Overview**

Description of batch column distillation by computer modeling involves many steps. First, a distillation medium must be designed to test the methodology. Two types of batches were used and compared for testing the methodology of this procedure. Standard batches based on the congener components, and fruit fermentation batches were the feed for the distillations. The distillation of standard batches allowed for material balances on the process, where fermentation of fruit allowed for a better understanding of the process as implemented in the fruit spirits production process. Analysis of the concentration of the compounds studied was completed using gas chromatography (GC).

A simple bench-top distillation was used to determine the concentrations of the compounds in the mash to input as the feed to the distillation modeling program CHEMCAD<sup>TM</sup>. This distillation was run to completion to achieve complete recovery of the congener compounds. Analysis of the distillate provided values to enter for the feed for the simulation program. Comparison of the modeling program with actual distillation can allow the distiller to predict where to make cuts and therefore improve the quality and yield of spirits produced. Figure 4.1 illustrates the procedure used in comparison of the computer modeling prediction approach with distillation results.



Figure 4.1 Procedure of comparing CHEMCAD<sup>™</sup> predicted concentrations against the experimental concentrations during distillation. The simple distillation of the mash provides the concentrations of each component for input into the CHEMCAD<sup>™</sup> program.

#### 4.2 Fermentation

The fermentation of fruit mash followed procedures common to industrial practices. Fruit used in this process was crushed using either a rolling mill or a mortar and pestle. The whole fruit was used in the fermentation mash to provide increased flavor components. Care was taken to prevent seeds from being crushed in the mashing process, as this can lead to undesired products in the distillate. After mashing the fruit, the mash was fermented in temperature controlled fermenters equipped with stirrers. These fermentation conditions increase the ethanol yield when compared to uncontrolled fermentations<sup>1</sup>. Fermentation is a controlled form of the natural rotting process experienced by all fruit. By controlling the fruit, temperature, atmosphere, and stirring the mash a higher quality is expected than an uncontrolled fermentation.

Pries de mousse yeast (Lalvin, EC-1118, Lallemand Inc.) was used for fermenting the mash. This strain of *saccharomyces cerevisiae* is used in whole fruit fermentations because of its robust nature and ability to survive in a wide range of conditions. The mash was held between 13 and 15°C allowing the yeast to be active, while also producing ethanol rather than other compounds. Fermentations were allowed to continue for between ten days and three weeks based on the extent of fermentation that was monitored using refractive index measurements of the liquid mash. A portable refractometer available from Fisher (Catalog Number 13-946-21) was used to measure the dissolved solids (Brix) present in the liquid portion of the mash. This analysis allowed for the monitoring of the sugar in the fermentation, which is consumed by the yeast to produce ethanol<sup>1, 2</sup>.

Two scales of fermentations were used in this study; a 200 gallon (750 L) fermenter and 30 gallon (115 L) fermenter. Each batch fermentation produced multiple distillations to attempt to eliminate error associated with different fermentations. In previous work it was determined that the fermentation mash composition varied from one fermentation to the next due to differences in sugar content, yeast activity, and temperature variations. By fermenting large batches and distilling multiple samples of the fermentation batch the error associated with fermentation variation is lessened.

#### 4.3 Standard Solutions

A solution was prepared to simulate the composition of the liquid phase of a fruit mash after fermentation. An aqueous solution of the ten highest composition components present in the solution was prepared. These solutions did not have solid particles from the fruit flesh, yeast, unfermented sugar or other components common to fermentations of fruits. The concentration of each component was based upon simple distillations of fruit mash to attempt to mimic the concentrations of these mashes as best as possible. The standard batches were used to reduce the dependence of this research on fruit, and attempt to reduce errors caused by working with fermentation mixtures with unknown concentrations. The standard batches allowed for material balances to be performed on the process as well.

Two sizes of batches were created, one for use with the 150 L still and one for use with the 10 L still, respectively. A 30 L standard batch allowed three distillations in the 10 L still and a 750 L batch allowed five distillations on the larger scale still. The composition of the standard batches can be seen in tables 4.1 and 4.2. Each batch had an

ethanol concentration of 8%, similar to that found in fruit fermentations before distillation. Each batch was well mixed before use.

Standard batches were treated in a similar manner as the fruit mashes. Three samples from each batch were taken for simple distillation and analysis via gas chromatography. These results were first checked to verify that the concentration of each component was similar to that of the standard batch, and these values were entered into the computer simulation program. Distillations were run in the appropriate still (10 and 150 L) and the distillate was analyzed using GC. A comparison was made between the distilled samples and the computer programs predictions. Table 4.3 list the manufacturer and lot numbers for the chemicals used in making these standard batches.

## Table 4.1Standard batch composition for the 10 L distillations. Thecomposition of the 30 L mixture used for distillation in the 10 L still.

Compound	Volume (mL)	Concentration (% v/v)
1-Propanol	24	0.08
Acetaldehyde	15	0.05
Acetone	15	0.05
Benzaldehyde	2	0.0067
Ethnaol	2400	8.00
Ethyl Acetate	6	0.02
Ethyl Formate	6	0.02
Isoamyl Alcohol	24	0.08
Methanol	24	0.08
t-Butyl Alcohol	24	0.08
Water	27460	91.53
Total	30000	

### Table 4.2Standard batch composition for the 150 L distillations. The

composition of the 750 L mixture used for distillation in the 150 L  $\,$ 

#### still.

Compound	Volume (L)	Concentration (% v/v)
1-Propanol	0.90	0.12
Acetaldehyde	0.45	0.06
Acetone	0.30	0.04
Benzaldehyde	0.15	0.02
Ethnaol	60.00	8.0
Ethyl Acetate	0.15	0.02
Ethyl Formate	0.20	0.0267
Isoamyl Alcohol	0.75	0.10
Methanol	1.00	0.133
t-Butyl Alcohol	0.50	0.067
Water	685.60	91.41
Total	750.00	

#### Table 4.3 Manufacturer and Lot Numbers for compounds used in standard

#### batches prepared.

Compound	Manufacturer	Lot Number	Notes
1-Propanol	Spectrum	OA0142 and KI389	
Acetaldehyde	Sigma	HO 00550 HO	99.5% +
Acetone	J. T. Baker	T 38B21	
Benzaldehyde	Aldrich	09323LA	99% +
Ethanol	Pharmco	209184	Absolute Anhydous 200 proof
Ethyl Acetate	Columbus Chemical Industries.	200019824	ACS Grade
Ethyl Formate	Sigma	10511DA	97%
Isoamyl Alcohol	Sigma	012K1320	98%
Methanol	Spectrum	QR0243	Spectroscopic Grade
t-Butyl Alcohol	Spectrum	PL0883	2-methyl-2-propanol
Water			Distilled and Deionized on Campus

#### 4.4 **Rayleigh Distillation**

A bench-top Rayleigh distillation was used to determine the concentration of the congener components in the fermentation mash. A 250 to 300 mL sample of the fermentation mash was distilled in a simple distillation apparatus similar to the one shown in figure 4.2. The mash was heated using a silicon oil bath and cold tap water was used to cool the condenser. The mash was distilled five minutes after the temperature reached 98°C to achieve complete recovery of the congener components present in the mash. This process required an average of 65 minutes. Longer distillations where the mash was heated to 100°C for ten minutes, 110 minutes total runtime, produced results where congeners present in smaller concentrations were reduced below their detection level by GC due to the increased water content of the distillate. In addition, these longer distillations produced congener concentrations similar to those of the 65 minute run.

These Rayleigh distillations were run in triplicate and the distillate of each was analyzed using gas chromatography. Triplicate GC analyses were performed on each distillate yielding nine total data points for each congener for each fermentation mash. The concentrations of the compounds present in the distillate were determined from a standard curve for each compound using ethanol as an internal standard. The compound concentrations were then averaged and normalized to the concentration of ethanol present in the fermentation mash. These values were used in subsequent modeling attempts as the starting concentration for each compound present in the fermentation mash.



Silicon Oil Bath

Figure 4.2 Batch bench top distillation apparatus. The procedure was carried out using 250-300 mL of mash. The distillation was held at 98° C for 5 minutes to achieve complete collection of the congeners. The distillate ranged between 25 and 55 mL recovered<sup>3</sup>.

#### 4.5 Computer Modeling

#### 4.5.1 Using the CHEMCAD<sup>™</sup> Computer Program

The Chemstations Inc. CHEMCAD<sup>TM</sup> program using batch distillation mode is used for modeling the distillation process. The computer program can predict the composition of the compounds present in distillate and bottoms at time intervals set by the user. The program requires many steps to reach the final solution; however, the steps for producing results are not overly complicated<sup>4</sup>.

Using CHEMCAD<sup>TM</sup> involves first beginning a job which includes choosing a file name and the operating units included in the flowsheet. The flowsheet comprises the input and output streams and the application equipment that is to be used. The default units are based on the English system of units; however, a wide range of units are available. For the present work, the units chosen were based on the metric system. Table 4.4 lists the units for these experiments<sup>4</sup>.

# Table 4.4Units used in CHEMCAD™ program. These units allow for easier<br/>comparison of the CHEMCAD™ predicted values with the values<br/>acquired from actual distillations<sup>5</sup>.

<u>CHEMCAD TM Unit Selections</u>					
Total Com Strea	Flow ponent Flow m Edit	StdL L/h Liquid Volume Fraction Automatic Conversion			
Time Mass/Mole Temperature Pressure Enthalpy Work Liquid Volume Liq. Vol. Rate Crude Flow Rate Vapor Volume Vapor Vol. Rate	h kg C atm kJ kW <sup>·</sup> h Liter Liter BPSD m <sup>3</sup> m <sup>3</sup> /h	Viscosity Surface Tension Solubility Par. Dipole Moment Cake Resistance Packing DP Currency Currency Factor	Pa-sec N/m (J/m <sup>3</sup> ) <sup>xx</sup> 0.5 C <sup>·</sup> m m/kg mm Water/m \$ 1		
Liquid Density Vapor Density Thickness Diameter Length Velocity Area Heat Capacity Specific Heat Heat Trans. Coeff. Therm. Conduct.	kg/L kg/m <sup>3</sup> m m m/sec. m <sup>2</sup> kJ/kmole K kJ/kmole KW/m <sup>2</sup> K W/m K				

After selecting the appropriate units, the chemical components are chosen. The list of chemical components in CHEMCAD<sup>TM</sup> allow for identification via chemical formula, chemical name, or numerical identifier. Ethanol, for example can be identified by name (ethyl alcohol, ethanol) chemical formula ( $C_2H_6O$ ) and numerical identifier internal to the computer program (134). The list of chemical compounds includes both organic and inorganic compounds and numbers about 1,8000 components<sup>4</sup>. Those compounds not present in the list can be added if some chemical information is included as well. For the purposes of these experiments, all the compounds of interest were included in the list in CHEMCAD<sup>TM</sup>.

After entering the chemical compounds of interest, the thermodynamic model and K-values are chosen. CHEMCAD<sup>TM</sup> will suggest the best thermodynamic and K-value options for the compounds that were entered in the previous step using the *Thermo Wizard* option; however, the user can modify the thermodynamic and physical properties at any time in the simulation process. The concentration and volume of the components in the pot of the still (input stream) are then input into the program<sup>4</sup>.

The next step in setting up the simulation program involves specifying the details on the unit operations. For example, in this work the number of trays on the still, the number of operations, the reflux ratio, the volumetric flow rate of the distillate, the step size, record frequency and stop criteria were all specified. The number of trays refers to the number of physical trays used by the still; however, the size and type of tray are included later in the process. The number of operations refers to the different operating conditions used in the process. For example if the distillate flow rate, or reflux ratio were changed, a new operation would need to be included. These operations run sequentially,

and should not be confused with trays or analysis steps. The time step size refers to the timeframe in between analysis, for example, a setting of 0.05 hours will allow for the numerical integration once every three minutes<sup>4</sup>. The record frequency refers to the number of time steps where the data is recorded. The default is once every third time step<sup>5</sup>. Stopping the operation can be completed via many methods. Time, volume of the distillate, composition of the distillate and temperature are all options for stopping the distillation. For these experiments a stop time was utilized, to correspond with the average distillate collection time associated with the distillation process<sup>4</sup>.

After specifying the unit operations, the physical properties of the equipment can be included in the simulation process. Tray type (bubble cap or sieve) and the size of the components can be included. The help function of the CHEMCAD<sup>TM</sup> program clearly describes the individual measurements needed for this portion of the process<sup>4, 5</sup>.

Finally running the simulation and plotting the results complete the simulation process. The software calculates and plots the results in these experiments as liquid volume fractions (concentration) against time. The time frame can be converted to cumulative distillate volume using the distillate flow rate. The raw data at each point can be transferred to Microsoft Excel<sup>™</sup> in using the plot batch column history function of the software and processed as desired<sup>4, 5</sup>.

#### 4.5.2 CHEMCAD<sup>™</sup> as a Predictive Model

The compounds used in the modeling of the fruit spirits by the CHEMCAD<sup>™</sup> program are given in table 4.5 with the chemical formula, name and internal CHEMCAD<sup>™</sup> numbers<sup>5</sup>. The concentration of these compounds were entered based on the results of the GC analysis of the simple batch distillation. The thermodynamic model chosen by the *ThemoWizard* was the NRTL method for its ability to model non-ideal solutions. The six thermodynamic models selected as best for the alcohol distillations included; NRTL, ESD, UNIFAC, Modified UNIFAC, UNIFAC LLE, and UNIQUAC. All six of these models were used for these experiments

The appendices give an overview of the thermodynamic models and the methodology for determining the best thermodynamic model to use for analysis. The timeframe, distillate flow rate, and analysis time were all based on a distillate volume consistent with the volumes collected during the actual distillation of these fruit spirits which were 750 ml for large still distillations and 75 ml for 10 L still distillations. The data were analyzed in Microsoft Excel<sup>™</sup> to plot concentration against cumulative-distillate-volume.

# Table 4.5 Compound name, formula and internal CHEMCAD<sup>™</sup> number for identification. These compounds were analyzed in the distillate. The chemical name common to CHEMCAD<sup>™</sup> were given as well as alternative names<sup>5</sup>.

Compound/Alt. Name	Formula	CHEMCAD <sup>™</sup> Number
Ethanol Ethyl alcohol	C <sub>2</sub> H <sub>6</sub> O	134
Methyl alcohol	CH₄O	117
Acetone	C <sub>3</sub> H <sub>6</sub> O	140
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	128
<i>Tert</i> -butyl alcohol	$C_4H_{10}O$	161
1-Propanol	C <sub>3</sub> H <sub>8</sub> O	146
3-Methyl-1-butanol Iso amyl alcohol	C <sub>5</sub> H <sub>12</sub> O	315
Ethyl formate	$C_3H_6O_2$	141
Ethyl acetate	$C_4H_8O_2$	155
Benzaldehyde	C7H6O	342
Water	H <sub>2</sub> O	62

#### 4.5.3 CHEMCAD<sup>™</sup> Calibration

Designing the operation of the CHEMCAD<sup>™</sup> program around a variable reflux still required a calibration method to produce approximations for the reflux ratio at the different operation steps of the distillation. As the flow rate of the cooling water into the condenser varied, the reflux ratio and distillate flow rate also varied. This is not a set of conditions that is directly possible with the simulation software which uses a single reflux ratio throughout the distillation. To mimic the results of a commercial batch distillation, it was necessary to divide the distillate flow rate to produce a matching distillation profile by CHEMCAD<sup>™</sup>. To approximate the reflux ratio and distillate flow rate for each operation step, a distillation of 8% ethanol in water was used. Volume fractions were collected in the same manner as the actual batch distillation, however, the time for each fraction was also recorded, and each fraction was analyzed using the GC. The time for each volume fraction was calculated and the total distillation was broken up into the appropriate number of operation steps.

The flow rate data were entered into each of these operation steps and the data were plotted using CHEMCAD<sup>™</sup>. By comparing the ethanol concentration against distillate volume for the CHEMCAD<sup>™</sup> results and the actual concentration data obtained from the GC analysis of the distillate, the reflux ratio for each operation step was varied until the CHEMCAD<sup>™</sup> prediction matched that of the distillation. These operation steps which included parameters (e.g. reflux ratio, distillate flow rate, analysis time, end conditions) at each time interval were used as the basis for the CHEMCAD predictive modeling of these fruit spirits distillations. It is assumed that by modeling the distillation reflux ratio on the experimental results of an 8% ethanol/water binary mixture, the error in reflux ratio and flow rate will be minimized as the bulk concentration of the fruit mash is an 8% ethanol in water solution.

#### 4.6 Experimental Multistage Batch Distillation

The distillation of fruit spirits was performed at two scales. A 10 L still and a 150 L still were used in this study. Both stills are of German manufacture and made of copper. The 10 L Holstein still uses electrically heated water to produce steam, and the 150 L Christian Carl still uses direct injected plant steam for the heating of the pot. The 10 L still uses bubble cap trays where the 150 L still uses sieve trays. Other than these few exceptions, the stills use the same principles for operation. Figures 4.3 and 4.4 are schematic diagrams of the 10 L and 150 L stills used in these experiments, respectively.

The distillation of fruit spirits uses the variable reflux mode of operation to attempt to keep the concentration of alcohol constant throughout the distillation. The temperature at the top of the condenser was kept at 72°C for the duration of the distillation<sup>2.6</sup>. The sensor at the top of the condenser regulated the flow of the cooling water into the system which in turn varied the reflux ratio of the distillation process. This process improves ethanol yield when compared to fixed reflux ratio systems<sup>7</sup>.

The distillation process was begun by filling the pot with fermented mash and filling the condenser and partial condensers with water. A silicon based antifoam agent (Dow Corning, AF Emulsion, Food Grade, Lot # HH077895) was added to the mash to reduce the frothing that occurs in these types of distillations. Next the stirrer was turned on for mashes that are heavy in solid material to prevent baking and also to prevent

foaming. The steam was then injected into the steam jacket and heating begins. Slow heating works best and increases the yield of ethanol produced. As the heating of the mash continues, the evolution of lower boiling compounds increases and the vapor passes onto the trays. As the vapor comes in contact with the cool metal surface, the vapor condenses. Vapor then has to pass through this condensed layer increasing the separation of the compounds. Finally after passing through all the trays the vapor was condensed in the condenser. The liquid distillate was water clear and came out from the distillate tube at the end of the still.

Three collection fractions are commonly recovered in fruit spirit production. The first fraction is the heads which contains the highest concentration of lower boiling point (relative to ethanol) compounds. The concentration of ethanol is at its greatest in this fraction, but the heads are not potable and blending with other fractions is not practiced due to the high concentrations of acetaldehyde, acetone, and methanol. The next fraction of distillate is the hearts which will become the potable product. The hearts has an average ethanol concentration of approximately 72-77% alcohol by volume. Also, the hearts, has relatively low concentrations of low and high boiling compounds and methanol. Often more than one heart cut is taken and blended together after aging. Finally the tails cut is collected. The ethanol concentration is usually below 55% A.B.V., but the presence of relatively high concentrations of fusel alcohols and terpenes reduce the clarity and overall aroma of the distillate. Tails cuts are often collected and redistilled to increase the overall yield of ethanol from the process; however, the resulting distillate from this re-distillation is inferior when compared to a hearts cut from a distilled fruit spirit. After collecting the tails, the steam is turned off and the cooling water is turned on

to maximum. The pot is emptied and cooled and cool water is used to clean the trays.

The distillate is aged in glass before dilution and bottling.


Figure 4.3 Schematic of 10L Holstein Still. The electric heater is used to generate steam from an internal water source.



Figure 4.4 Schematic diagram of 150L Christian-Carl Still<sup>2</sup>.

### 4.7 Comparison

### 4.7.1 Predictive Comparison of CHEMCAD™

The concentrations of the components in the distillate were compared with the predicted CHEMCAD<sup>TM</sup> values. The cumulative distillate volume was used as the independent variable instead of time because in the laboratory it is easier to plan an experiment around a constant volume fractionation procedure than a constant time fractionation procedure. The volume fraction concentration used in the dependent variable is in terms of % v/v, a common concentration unit in the distilled beverage industry.

### 4.7.2 Standard and Fruit Batch Distillations

The standard batch distillations were compared with fruit spirits distillations by comparing congener concentration (% v/v) against cumulative distillate volume (mL). These comparisons were made to increase the reproducibility of the results as fruit spirits distillations are often not reproducible on a batch basis due to varying concentration of the fermentation fed.

### 4.8 Gas Chromatography Methods

A Shimadzu GC-17A gas chromatograph with flame ionization detector (FID), and an AOC-20i autosampler (12 vial capacity) was used for analysis of the distillates. The column used for the analysis is a 30 meter long 0.25 mm i.d. Stabilwax 30 column obtained from Restek. A 0.2  $\mu$ L injection volume was used for all samples to avoid overloading the column. The injector and detector temperature were set at 240°C and 255°C respectively. Separation of the compounds was achieved using a ramp program for the column. The initial temperature of the oven was set at 38°C and a heating rate of 1.2°C/min was used until 80°C was reached. A 30°C/min heating rate was used from 80°C to 170°C and the final temperature was held for 2 minutes. The total cycle time of the analysis was 42 minutes which includes the sample preparation, injection of the sample, and cooling of the GC oven. Each sample was run in triplicate and average values were used in all results. Figures 4.5 and 4.6 show sample chromatographs taken from the distillate of one fruit batch.



Figure 4.5 Sample chromatograph. This sample chromatograph is from a heart cut of an apple spirits distillation. The peaks of the compounds with longer retention times are identified.



Figure 4.6 Sample chromatograph. Enlarged view of the chromatograph shown in figure 4.5. The peaks identified represent the compounds that elute in the first ten minutes of the chromatography run.

### 4.9 Retention Time and Reproducibility Validation

The Shimadzu GC-17A equipped with an AOC-i Autosampler and the temperature program outlined above was able to produce reliable, reproducible results. Each distillation fraction was analyzed in triplicate via this chromatographic method. In addition, because there were multiple distillations from each fermentation batch or standard fermentation batch, the results from each set of conditions were able to be analyzed for instrumental errors. The use of the autosampler system allowed for reproducible retention times throughout the duration of these experiments. Table 4.6 lists the compounds analyzed, their average retention time, and the error found in the retention time. These results are complied from two sets of procedures. One large still batch fermentation, with the analysis of the simple distillate (n = 9), three distillations with 16 fractions (n = 144) and one small still batch fermentation, with simple distillation analysis (n = 9) and three batch distillations (n = 81). The retention times were constant throughout these experiments as shown by the small percent error over the large sample size (n = 243). While this is just a fraction of the total data collected, this reliability in reproducing the retention time of these components was present throughout the whole experimental procedure.

## Table 4.6Mean retention time, and error associated with the compoundsanalyzed in these experiments. The small error is due to reproducibleinjection conditions because of the autosampler.

Compound	Mean Retention Time	Standard Deviation	% Error
Acetaldehyde	1.450	0.006	0.42
Acetone	1.996	0.010	0.52
Ethyl formate	2.058	0.017	0.81
Ethyl acetate	2.196	0.016	0.75
2-Methyl-2-propanol	2.657	0.015	0.55
Methanol	2.814	0.015	0.54
Ethanol	3.507	0.023	0.64
1-Propanol	5.972	0.025	0.42
Iso amyl alcohol	14.690	0.036	0.24
Benzaldehyde	37.136	0.012	0.03

### 4.10 Literature Cited

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### 5. **RESULTS**

### 5.1 Ethanol Modeling

The first objective was the modeling of the largest concentration component, ethanol. Ethanol is the most important component present in the distillation of fruit spirits, because the ethanol concentration in the fruit spirits related directly to the total yield of the available product.

Preliminary modeling of the ethanol concentration in the fruit spirits with CHEMCAD<sup>™</sup> was inconsistent with the experimentally obtained concentration profile from distillations. Both the 150 L Christian-Carl and 10 L Holstein stills used vary the flow rate of the cooling water introduced into the condensing column. As more cooling water flows through the condenser the reflux ratio increases and the distillate flow rate decreases. Because the flow rate of the cooling water increases and decreases throughout the distillation, the reflux ratio is also constantly changing. The reflux ratio is also changing due to changes in the distillate composition.

Figure 5.1 shows the difference between the experimentally determined ethanol concentrations obtained fruit spirits distillations against the concentration of ethanol predicted by the CHEMCAD<sup>™</sup> program with constant reflux ratios. These two results do not agree well because of the varying reflux ratio in the experimental distillations.

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### **Ethanol Water Prediction with Constant Reflux Ratio**

Figure 5.1 Concentration of ethanol (% v/v) against cumulative distillate volume (mL) for an experimental distillation and two simulated constant reflux distillations in CHEMCAD<sup>™</sup>. The reflux ratios used for the CHEMCAD<sup>™</sup> simulations were 2 and 5 and are given in parentheses.

Clearly the lack of agreement between experimental and simulated results is largely due to the variation of the reflux during the experimental batch distillations. A method was developed to introduce variable reflux ratio into the distillation modeling by CHEMCAD<sup>TM</sup>. The first step in this procedure involved distillation of an ethanol/water mixture (8% ethanol v/v) through the 150 L and 10 L stills. The flow rate of each fraction (750 mL and 75 mL cuts respectively) was measured and recorded. Each distillation was performed in triplicate and the average flow rate of the distillate were recorded. For the larger still, sixteen fractions of 750 mL were collected, and nine fractions of 75 mL were collected for the smaller still.

The sixteen fractional cuts in the larger still were reduced to nine distillation steps to be entered into the CHEMCAD<sup>™</sup> program. The first and last 750 L cuts were used as steps 1 and 9. The other fourteen fractions were paired to obtain the data for steps 2 through 7. Cut 2 and 3 were averaged for the data for step 2, cut 4 and 5 were averaged for step 3 and so on. These nine steps were then entered into the CHEMCAD<sup>™</sup> program in terms of L/h for the distillate flow rate. The time of each step in terms of hours were calculated so that CHEMCAD<sup>™</sup> would identify the data points at 750 mL increments for the distillations.

The smaller still, with nine fractional cuts, did not require the averaging of flow rates together to obtain the nine steps entered into the CHEMCAD<sup>TM</sup> program. The same methodology is followed for the small still as above, with the exception of the averaging of the cuts, and the step size of each data point in the program were entered to result in 75 mL fractions.

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With a fixed distillate flow rate data and the step size for analysis by the CHEMCAD program set to yield the appropriate distillate volumes, the reflux ratio was approximated for each step by trial and error such that the resulting ethanol concentration at the end of each step met the concentration of ethanol determined by the experimental distillation. Table 5.1 illustrates the data collected from the experimental distillations and the resulting data input into CHEMCAD<sup>TM</sup>. Table 5.2 shows the reflux ratio entered into the CHEMCAD<sup>TM</sup> program at each step and the resulting ethanol concentration predicted by CHEMCAD<sup>TM</sup> using these values. Figure 5.2 shows the experimental distillation concentrations of the ethanol water mixture, and the predicted values from the CHEMCAD<sup>TM</sup> computer program. Figure 5.3 illustrates the procedure used to acquire the reflux ratio for each step of the distillation model.

### Table 5.1The ethanol concentration, time, and calculated distillate flow rate for<br/>the distillation of an 8% ethanol/water mixture in the 150 L still.

	Cumulative				Ethanol
Cut	Volume	Time	Difference	Flow Rate	Concentration
Number	(mL)	(min)	(s)	(L/h)	(% v/v)
1	750	1.38	83	32.53	83.7
2	1500	2.53	69	39.13	85.4
3	2250	3.67	68	39.71	85.9
4	3000	4.78	67	40.30	87.8
5	3750	5.88	66	40.91	84.5
6	4500	6.97	65	41.54	83.7
7	5250	8.10	68	39.71	83.1
8	6000	9.28	71	38.03	81.5
9	6750	10.52	74	36.49	80.3
10	7500	11.92	84	32.14	78.0
11	8250	13.33	85	31.76	75.1
12	9000	14.92	95	28.42	72.6
13	9750	16.50	95	28.42	67.4
14	10500	18.15	99	27.27	62.7
15	11250	19.87	103	26.21	59.7
16	12000	21.67	108	25.00	59.0

### Table 5.2The flow rates, analysis times, and reflux ratios entered into

### CHEMCAD<sup>™</sup>. Also shown are the concentration of the ethanol

### concentration predicted by CHEMCAD<sup>™</sup> when an 8% ethanol/water

		Step					Ethanol
CHEMCAD	Step Flow	Analysis	Number of				Concentration
Step	Rate	Time	Analysis	<b>Total Time</b>	Total Time	Reflux	Predicted
Number	(L/h)	(h)	Points	(h)	(min)	Ratio	(% v/v)
1	32.53	0.0231	1	0.0231	1.38	2.05	83.70
2	39.42	0.0190	2	0.0421	2.52	3.55	86.16
				0.0611	3.67		85.85
3	40.60	0.0185	2	0.0796	4.77	3.42	86.56
				0.0981	5.88		84.52
4	40.62	0.0185	2	0.1165	6.99	3.82	84.88
				0.1350	8.10		83.12
5	37.26	0.0201	2	0.1551	9.31	3.67	81.94
				0.1752	10.51		80.31
6	31.95	0.0235	2	0.1987	11.92	3.88	77.84
				0.2222	13.33		75.13
7	28.42	0.0264	2	0.2486	14.91	4.22	72.80
				0.2750	16.50		67.44
8	26.74	0.0280	2	0.3030	18.18	4.11	63.14
				0.3310	19.86		59.74
9	25.00	0.0300	1	0.3610	21.66	4.29	59.02

distillation is simulated.

The reflux ratios and distillate flow rates from the steps determined experimentally from a binary ethanol/water distillation are used for the modeling of the fruit fermentations. The ethanol concentration behavior in the distillation of a fruit mash is assumed to behave like that of an ethanol/water binary mixture of the same ethanol concentration present in the mash. It is assumed that the bulk of the fermentation mash behaves as a binary ethanol/water mixture when distilled.

Table 5.3 gives the reflux ratio and flow rate for both sizes of stills used in these experiments. Figure 5.4 shows the plot of the reflux ratio against distillate volume for the 150L still. The initial data point is low at the beginning of the distillation as the cooling

water is not flowing through the condenser. As the cooling water flow rate increases, the liquid reflux will increase while the distillate flow rate remains constant as shown in the second data point. As the cooling water reaches a maximum flow rate, the liquid reflux into the column will decrease, resulting in a lower reflux ratio. Finally as the distillate flow rate begins to decrease, the liquid reflux also decreases which results in the more constant reflux ratio seen on the final three data points. The operating line (L/V) is constantly changing during the distillation to maximize the ethanol concentration of the distillate. The reflux ratio (L/D) begins at a lower value, reaches a maximum, and then decreases through the rest of the distillation

### Table 5.3The distillate flow rate and reflux ratios entered into the

	· ·	10 L still	
Step	Reflux	Flow Rate	Cumulative Distillate
Number	Ratio	(L/h)	Volume (mL)
1	3.94	4.50	75
2	16.8	2.70	150
3	7.72	2.65	225
4	6.17	2.60	300
5	4.85	2.21	375
6	4.17	2.35	450
7	3.73	2.05	525
8	3.62	2.13	600
9	4.18	2.13	675
		150 L Still	
Step	Reflux	150 L Still Flow Rate	Cumulative Distillate
Step Number	Reflux Ratio	150 L Still Flow Rate (L/h)	Cumulative Distillate Volume (mL)
Step Number 1	Reflux Ratio 2.2	150 L Still Flow Rate (L/h) 32.53	Cumulative Distillate Volume (mL) 750
Step Number 1 2	Reflux Ratio 2.2 3.16	150 L Still Flow Rate (L/h) 32.53 39.42	Cumulative Distillate Volume (mL) 750 2250
Step Number 1 2 3	Reflux Ratio 2.2 3.16 2.87	150 L Still Flow Rate (L/h) 32.53 39.42 40.62	Cumulative Distillate Volume (mL) 750 2250 3750
Step Number 1 2 3 4	Reflux Ratio 2.2 3.16 2.87 2.59	150 L Still Flow Rate (L/h) 32.53 39.42 40.62 40.62	Cumulative Distillate Volume (mL) 750 2250 3750 5250
Step Number 1 2 3 4 5	Reflux Ratio 2.2 3.16 2.87 2.59 2.23	150 L Still Flow Rate (L/h) 32.53 39.42 40.62 40.62 37.26	Cumulative Distillate Volume (mL) 750 2250 3750 5250 6750
Step Number 1 2 3 4 5 6	Reflux Ratio 2.2 3.16 2.87 2.59 2.23 2.03	150 L Still Flow Rate (L/h) 32.53 39.42 40.62 40.62 37.26 31.95	Cumulative Distillate Volume (mL) 750 2250 3750 5250 6750 8250
Step Number 1 2 3 4 5 6 7	Reflux Ratio 2.2 3.16 2.87 2.59 2.23 2.03 1.84	150 L Still Flow Rate (L/h) 32.53 39.42 40.62 40.62 37.26 31.95 28.42	Cumulative Distillate Volume (mL) 750 2250 3750 5250 6750 8250 9750
Step Number 1 2 3 4 5 6 7 8	Reflux Ratio 2.2 3.16 2.87 2.59 2.23 2.03 1.84 1.77	150 L Still Flow Rate (L/h) 32.53 39.42 40.62 40.62 37.26 31.95 28.42 26.74	Cumulative Distillate Volume (mL) 750 2250 3750 5250 6750 8250 9750 11250

### CHEMCAD<sup>™</sup> program for each size of still.



Figure 5.2 Experimental and predicted values of the ethanol concentration at volume intervals. The experimental distillation values are from a 8% ethanol and water binary mixture.



Figure 5.3 The procedure used to determine the reflux ratio of each step of the distillation.



Figure 5.4 Change in the reflux ratio over distillate volume. The line of best fit for the reflux ratio is shown.

### 5.2 Simple Rayleigh Distillations

The procedure for identifying the concentration of the compounds present in the fermentation mash, prior to batch distillation, was a simple Rayleigh distillation of the mash and analysis of the distillate. The simple Rayleigh distillation apparatus is shown in figure 4.2. The composition of the distillate from the Rayleigh distillation was normalized from the chromatographic analysis to the equivalent concentrations in an 8% ethanol mixture.

### 5.2.1 Standard Batches

The concentration profile of the standard batches are shown in table 5.4. Two different batches were used to test the ability of CHEMCAD<sup>TM</sup> to simulate the concentration profiles of each of the compounds present in the distilled spirits. The variation in the concentration of the congener compounds in these standard batches allows for classifying the ability to simulate the behavior of each compound by the CHEMCAD<sup>TM</sup> program.

The first step in the process of using the CHEMCAD<sup>™</sup> program for this type of determination, was to perform a Rayleigh distillation of the standard batch. Triplicate simple distillations were performed in an attempt to eliminate errors in terms of the congener concentrations present in the mash. Each simple distillation utilized 250 mL of standard mash and the distillation was allowed to continue until the temperature on the thermometer read 98° C for five minutes. By distilling to this point, the total recovery of the congener compounds is assumed. The distillate was analyzed by gas chromatography as outlined in chapter 4.

### Table 5.4The composition of the standard batches for these studies. The<br/>same concentrations were used for the large batches (750 L) and<br/>small batches (30 L).

	Concentration (Volume			
	Fraction)			
Compound	Batch 1	Batch 2		
Ethanol	8.000	8.000		
Methanol	0.133	0.080		
Acetaldehyde	0.040	0.050		
Benzaldehyde	0.020	0.010		
T-Butanol	0.067	0.010		
1-Propanol	0.120	0.080		
Isoamyl Alcohol	0.100	0.080		
Acetone	0.060	0.050		
Ethyl Acetate	0.027	0.020		
Ethyl Formate	0.020	0.020		
Water	91.413	91.600		

Table 5.5 shows the composition of the congeners present in the distillate of the simple Rayleigh distillations of the first standard batch, after normalization to a concentration of 8% ethanol. The compositions in most cases were reasonably close to the actual composition present in the distilled spirits. In the third set of simple distillations larger errors could be accounted for due to the time that the sample sat before being distilled in the simple distillation apparatus. In all of the other cases, the simple distillation was carried out on the same day as the large scale distillation, and the day following the solution preparation.

The second standard batch was not completely distilled the day after the solution was made. Two large scale distillations were carried out the day after the solution was made, and the first two sets of simple distillation data were taken and run on those days. The rest of the batch was distilled two days later, accounting for evaporative changes to the solution composition before distillation, and altering the composition present after the simple distillation.

# Table 5.5The composition of the first standard batch and the average<br/>composition normalized from the simple distillation procedure. The<br/>concentration of the components after the simple distillation were<br/>normalized to a concentration of an 8% ethanol solution.

	Actual	Simple	Simple	Simple
	Composition	Distillation	Distillation	Distillation
Compound	% v/v	(1) % v/v	(2) % v/v	(3) % v/v
Ethanol	8.000	8.000	8.000	8.000
Methanol	0.133	0.154	0.122	0.272
Acetaldehyde	0.040	0.038	0.066	0.135
Benzaldehyde	0.020	0.031	0.045	0.054
2-Methyl-2-Propanol	0.067	0.009	0.031	0.014
1-Propanol	0.120	0.113	0.118	0.209
Isoamyl Alcohol	0.100	0.120	0.083	0.132
Acetone	0.060	0.052	0.045	0.079
Ethyl Acetate	0.020	0.011	0.001	0.013
Ethyl Formate	0.027	0.015	0.001	0.019
Water	91.413	91.455	91.491	91.073

The simple distillation has been able to generate concentration ranges similar to those of the actual standard batch. Error can be expected from evaporative losses, as well as incomplete distillation during the simple distillation procedure.

For the small scale distillations (10 L) of standard mashes, the same procedure was followed as above. The concentration of the standard batches and resulting concentrations from the Rayleigh distillate analysis can be seen in table 5.6. The composition of Rayleigh distillate is shown as a mean and standard deviation of the triplicate runs of the simple distillate on the standard batch. Table 5.6The average composition of the congener components of the second<br/>standard batch used for the small (10 L) scale distillations. Three<br/>Rayleigh distillations were averaged for these results.

	Standard	Rayleigh Distillate	
	Mixture	Concentration	
			Standard
Compound	Composition	Average	Deviation
Ethanol	8.000	8.000	0.0920
Methanol	0.080	0.076	0.0017
Acetaldehyde	0.050	0.052	0.0023
Benzaldehyde	0.010	0.009	0.0065
2-Methyl-2-Propanol	0.010	0.001	0.0007
1-Propanol	0.080	0.079	0.0017
Isoamyl Alcohol	0.080	0.086	0.0040
Acetone	0.050	0.038	0.0008
Ethyl Acetate	0.020	0.008	0.0000
Ethyl Formate	0.020	0.009	0.0000

The concentrations from the simple Rayleigh distillation and the actual composition of the mixture were entered into the CHEMCAD<sup>TM</sup> computer program. The CHEMCAD<sup>TM</sup> data was then normalized to concentrations of % v/v in 40% ethanol. This concentration range will be used for comparison of the distillate from the large distillation, with that of the CHEMCAD<sup>TM</sup> predictive values. The 40% ethanol solution is the common drinking/bottling strength of brandies, vodkas, whiskeys, gins and most other distilled beverages<sup>1</sup>.

### 5.2.2 Fruit Mash Batches

A mixture of apple varieties was used for the fermentation mash for both scales. This general apple mash was prepared in the standard manner, of crushing the fruit through a rolling mill, and fermented inside a temperature controlled fermenter with stirring. An approximate volume of 600 L of mash was fermented using *saccharomyces cerevisiae* as the yeast. The fermentation lasted two weeks and three distillations were carried out on both the large (150 L) and small (10 L) scale. Before each distillation two 250 ml samples were distilled using the Rayleigh distillation apparatus discussed above. Analysis of the distillate from the Rayleigh distillation conveyed congener concentrations, which were then normalized to a concentration of 8% ethanol. The results of these Rayleigh distillations of the fruit mash are presented in table 5.7.

## Table 5.7Mean congener concentration and standard deviation from analysis of<br/>the Rayleigh distillate from apple fermentation. The concentrations<br/>have been normalized to an ethanol concentration of 8% v/v.

	Mean	Standard
Compound	Concentration	Deviation
Ethanol	8.0000	0.0980
Methanol	0.0981	0.0059
Acetaldehyde	0.0111	0.0004
Benzaldehyde	0.0019	0.0026
T-Butanol	0.0036	0.0004
1-Propanol	0.1401	0.0183
Isoamyl Alcohol	0.0525	0.0155
Acetone	0.0036	0.0008
Ethyl Acetate	0.0013	0.0018
Ethyl Formate	0.0000	0.0000

### 5.3 Batch Distillation with Reflux

Batch distillation of the standard and fruit mashes were carried out in the same manner. The procedure for using the multistage batch still with reflux was outlined in chapter 5. The sample volume for the larger Christian-Carl still is 150 L and the volume for the smaller Holstein still is 10 L. The antifoam agent was only added to the fruit distillations as the standard distillations did not exhibit excessive foaming. Also, the lack of a stirrer in the smaller still caused some of the apple mash to bake onto the copper pot of the still, making cleaning more difficult.

### 5.3.1 Standard Solution Multistage Batch Distillation with Reflux

The batch composition of the standard "mash" solution can be seen in the tables above. The 10 L still distillations each produced nine fractions of 75 mL each for a total collected volume of 675 mL. Sixteen fractions of 750 mL were collected from each of the 150 L still distillations for a total distillate volume of 12000 mL. The concentration of the congener compounds in these distillate fractions were then determined by gas chromatography. The results of these distillations were then compared to the predicted values produced by the CHEMCAD<sup>TM</sup> program. The comparison of CHEMCAD<sup>TM</sup> simulations with the experimental distillations for each compound can be seen below for each compound.

### 5.3.2 Fruit Mash Multistage Batch Distillation with Reflux

Apples used in these batch distillations were allowed to ferment for two weeks, before distillation. The fermentation mash was then pumped/poured into the pot of the still and the sample for the Rayleigh distillation was taken from the pot of the still before the batch distillation commenced. The volume fractions of the distillations were taken at the same intervals above, and the same procedure was used for analyzing the concentrations of the compounds present in each fraction.

### **5.4 CHEMCAD™ Predictive Modeling**

The CHEMCAD<sup>™</sup> program has many different thermodynamic models that can be used for the analysis of chemical processes. Many of these thermodynamic models are not applicable to alcohol distillations. The Thermodynamic Wizard function within CHEMCAD<sup>™</sup> identified the NTRL model as the best thermodynamic model for the compounds used in these experiments. Also used in these experiments were the ESD, UNIFAC, Modified UNIFAC, UNIFAC LLE, and UNIQUAC thermodynamic models.

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The predictive models of CHEMCAD<sup>™</sup> generate the volume fraction of each compound at given time intervals. The concentration of these compounds was then normalized to their concentration in a 40% v/v ethanol solution and the time function was converted to cumulative distillate volume using the flow rate information entered into the CHEMCAD<sup>™</sup> program. These data are then compared against the concentration of each compound present in the distillate of the fruit and standard batch distillations.

### 5.5 Compound Comparison

Comparing the CHEMCAD<sup>™</sup> predicted values with the actual values from the batch distillations are done as concentration of congener in 40% ethanol against cumulative distillate volume. The three thermodynamic models within CHEMCAD<sup>™</sup> that fit the results of the actual distillation are shown to improve clarity. Each compound has sets of thermodynamic models that best fit the profile expressed during the batch distillation process.

### 5.5.1 Ethanol

The ethanol data shown use values of concentration (% v/v) against cumulative distillate volume. Figures 5.5, 5.6, 5.7 and 5.8 show the composition predicted by the CHEMCAD program with the concentrations achieved with experimental batch distillations. The thermodynamic models that best matched the concentration of the distillate were the Modified UNIFAC, NTRL and ESD models. The larger scale batch distillations show better agreement between the predicted values and the experimental

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concentrations than is present in the smaller scale distillations. This is due to the increased holdup present on the trays of the 10 L still.

Because the concentration of the fruit mash is approximated to 8% v/v which is comparable with that which is found in a fruit mash, the average ethanol concentration of the fruit mash is complimentary between the thermodynamic models and the experimental distillation. For example the average concentration of the 10 L fruit distillation is  $71.11 \pm 0.47$  % v/v. The average concentration for the NTRL and ESD models is 68.63% v/v and the average concentration for the Modified UNIFAC model is 70.60 % v/v. These represent the concentration of a blend of the nine fractions collected. Table 5.8 illustrates the average ethanol concentration of distillate collected against that predicted via CHEMCAD<sup>TM</sup>.

## Table 5.8Average ethanol concentration of a blend of all cuts taken during<br/>distillation. The total yield of ethanol produced is similar to those<br/>values predicted by the CHEMCAD™ thermodynamic models shown.

	Batch Distillation	Error	NTRL	ESD	Modified UNIFAC	Total Volume (mL)
10 L Fruit Distillation 10 L	71.11	0.47	68.63	68.63	70.60	675
Standard Batch 150 L Fruit	69.11	1.50	68.10	66.80	69.70	675
Distillation 150 L Standard	75.94	1.36	74.71	73.56	76.02	12000
Batch	74.13	1.44	74.01	72.86	75.11	12000



Figure 5.5 The ethanol concentration of a 10 L fruit distillation compared to the values predicted by the CHEMCAD<sup>™</sup> computer model using three thermodynamic models.



Figure 5.6 The ethanol concentration of a 10 L standard batch distillation compared to the values predicted by the CHEMCAD<sup>™</sup> computer model using three thermodynamic models.



Figure 5.7 The ethanol concentration of a 150 L fruit distillation compared to the values predicted by the CHEMCAD<sup>™</sup> computer model using three thermodynamic models.



Figure 5.8 The ethanol concentration of a 150 L standard batch distillation compared to the values predicted by the CHEMCAD<sup>™</sup> computer model using three thermodynamic models.

### 5.5.2 Methanol

The health hazards associated with methanol require regulation of the concentration of methanol in these type of spirits. The concentration of methanol is higher in the heads portion of the distillate, decreases in the hearts, and then increases again in the tails requiring the distiller to make cuts of the distillate that will be low enough in methanol concentration so that it will be able to be consumed.

Table 5.9 illustrates the average concentration of methanol in the distilled spirits when the cuts are blended together. This type of analysis will give the distiller an idea of where to make the cuts so that their distillate is consumable. The NTRL and Modified UNIFAC models do the best at predicting the concentration of the methanol that is present in the actual distillate.

Figures 5.9 through 5.12 show the experimental concentration of methanol present in the distillate compared with the concentrations predicted by the CHEMCAD<sup>™</sup> thermodynamic models NTRL, ESD, and Modified UNIFAC. The Modified UNIFAC thermodynamic model, similar to the case with ethanol, is the best at modeling the concentration found in the distillate.

### Table 5.9Methanol concentration of blended cuts for each distillation type and

	Methanol Concentration (% v/v in 40% Ethanol)				
					Modified
10 L Fruit Batch	Distillation	Error	NTRL	ESD	UNIFAC
All Cuts	0.416	0.010	0.350	0.209	0.354
Cuts 2-9	0.386	0.005	0.355	0.214	0.358
Cuts 3-9	0.371	0.004	0.360	0.222	0.361
10 L Standard					
Batch					
All Cuts	0.426	0.011	0.355	0.379	0.362
Cuts 2-9	0.402	0.005	0.361	0.384	0.366
Cuts 3-9	0.397	0.006	0.367	0.388	0.368
150 L Fruit Batch					
All Cuts	0.377	0.024	0.372	0.392	0.385
Cuts 2-16	0.370	0.023	0.375	0.395	0.387
Cuts 3-16	0.364	0.022	0.375	0.393	0.381
Cuts 3-15	0.360	0.024	0.369	0.388	0.377
150 L Standard					
Batch					
All Cuts	0.372	0.014	0.314	0.334	0.328
Cuts 2-16	0.365	0.015	0.317	0.336	0.329
Cuts 3-16	0.363	0.014	0.317	0.334	0.324
Cuts 3-15	0.360	0.015	0.311	0.330	0.321

### the predicted values from CHEMCAD<sup>™</sup>.



Figure 5.9 Methanol concentration of a 10 L fruit distillation normalized to a 40% ethanol solution. The three thermodynamic models shown are the closest in approximating the actual data.



Figure 5.10 Methanol concentration of a 10 L standard batch distillation normalized to a 40% ethanol solution.


Figure 5.11 Methanol concentration of a 150 L fruit distillation normalized to a 40% ethanol solution.



Figure 5.12 Methanol concentration of a 150 L standard batch distillation normalized to a 40% ethanol solution.

#### 5.5.3 Fusel Alcohols

Three fusel alcohols were studied in this experiment; *t*-butanol, 1-propanol, and isoamyl alcohol (3-methyl-1-butanol). 1-propanol and isoamyl alcohol represent the bulk of the total fusel alcohol concentration present in these distilled spirits<sup>2, 3, 4</sup>. T-butanol is higher in concentration in pomace fruit than stone fruits. In all cases, the three thermodynamic models in CHEMCAD<sup>TM</sup> that best model the concentration of the fusel alcohols were the UNIFAC, Modified UNIFAC, and UNIFAC LLE models.

Figure 5.13 shows the profile of *t*-butanol present in these distilled spirits in small scale control distillations. The profile of t-butanol is consistent with that of the fruit distillation at the same scale. The concentration of *t*-butanol is higher than predicted in the early cuts of the distillate, and lower than predicted in later cuts. The same trend is seen in larger scale distillations. Figure 5.14 shows the distillate concentration of *t*-butanol in terms of % v/v in 40% ethanol. The larger scale distillation does a better job of approximating the concentration of the *t*-butanol than the smaller scale. The UNIFAC LLE thermodynamic model is the best for mimicking the concentration profile of *t*-butanol.

The next fusel alcohol studied is 1-propanol. Figures 5.15 and 5.16 show the concentration of 1-propanol compared with the predicted values. The larger scale distillation is better described although the concentration range is not correct when compared to the actual values. A similar response can be seen for isoamyl alcohol in figures 5.17 and 5.18.

The fusel alcohol concentration in distilled spirits is important because the quality of the distilled spirits decreases after the maximum of the fusel alcohol concentration is

reached. The undesired aroma associated with fusel alcohols increases in concentration in the later portion of the distillation after the maximum concentration of 1-propanol and isoamyl alcohol is reached. Figure 5.19 shows the predicted CHEMCAD<sup>TM</sup> values of the additive concentration of 1-propanol and isoamyl alcohol, as well as the actual distillate concentration.



Figure 5.13 Standard 10 L batch distillation compared with predicted values from CHEMCAD<sup>™</sup> for *t*-butanol.



Figure 5.14 Comparison of predicted values from CHEMCAD<sup>™</sup> compared with the *t*-butanol concentration in fruit spirit distillate in 150 L distillation.



Figure 5.15 The concentration of 1-propanol present in 10 L fruit distillation compared to predicted values.



Figure 5.16 The predicted values of 1-propanol concentration and the experimental distillate concentration of 1-propanol in 150 L batch distillations.



Figure 5.17 The 10 L distillate concentration of isoamyl alcohol and the values predicted by CHEMCAD<sup>™</sup> using the UNIFAC thermodynamic models.



Figure 5.18 The 150 L batch concentration of isoamyl alcohol present in distilled spirits compared with the predicted CHEMCAD<sup>™</sup> values.



Figure 5.19 The additive values of 1-propanol and isoamyl alcohol which represent the bulk of the fusel alcohol concentration present in distilled spirits.

#### 5.5.4 Aldehydes

The aldehydes studied in this experiment are acetaldehyde and benzaldehyde. Acetaldehyde, with a low boiling point, is the first compound eluted during the distillation. Acetaldehyde does not have positive aromatic characteristics associated with it requiring the culling of the heads from the rest of the distillate. At the tails end of the distillate, benzaldehyde has a positive aroma characteristic associated with it. Benzaldehyde is the last of the compounds studied in this experiment to elute from the distillation column. A high concentration of benzaldehyde can overpower the distillate, often requiring increasing the volume of the tails fraction (i.e. taking the cut earlier) to reduce influence of benzaldehyde on the hearts fraction of the distillate.

Acetaldehyde has a higher concentration in the earlier cuts than the hearts cuts. This can be seen in figures 5.20, 5.21, and 5.22. The concentration predicted by the CHEMCAD<sup>™</sup> thermodynamic models UNIFAC, Modified UNIFAC, and UNIFAC LLE, are not as accurate in the first few cuts of the distillation than in the hearts and tails cuts. The predictive power of these thermodynamic models is to determine where the rate of acetaldehyde concentration change begins to level out. A smaller distillation does not show the dramatic inflection point predicted by CHEMCAD<sup>™</sup> in the larger scale distillation.

Benzaldehyde is not modeled well with the CHEMCAD<sup>TM</sup> thermodynamic models. The small scale distillations, an example of which can be seen in figure 5.23, do not have similar inflection points in the concentration of the predicted values and the actual values, although the concentration is approximately the same. An example of the 150 L scale distillation can be seen in figure 5.24. The UNIFAC LLE thermodynamic model predicts the volume of the concentration maximum for benzaldehyde, however, the concentration of benzaldehyde is not accurately predicted.

Overall the benzaldehyde and acetaldehyde concentrations assist in determining where the heads/hearts cut and hearts/tails cut should be made. The prediction models within CHEMCAD<sup>TM</sup> are more accurate in the larger scale distillation than the smaller one for identifying the volumes where these cuts should be made.



Figure 5.20 Acetaldehyde concentration of 10L fruit batch distillation.



Figure 5.21 Acetaldehyde concentration of 10L standard batch distillation.



Figure 5.22 Acetaldehyde concentration of 150 L fruit batch distillation.



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Figure 5.23 Benzaldehyde in 10 L standard batch distillation.



Figure 5.24 Benzaldehyde in 150 L fruit batch distillation. The benzaldehyde concentration maxima is predicted by the CHEMCAD™ thermodynamic models at earlier distillate volumes than the experimental distillation data shows. The concentration range of the predicted model is lower than the data from the experimental distillation.

### 5.5.5 Other Carbonyl Compounds

The three other carbonyl compounds studied include a ketone, acetone, and two esters, ethyl formate, and ethyl acetate. The esters presented a problem with this study as they were consistently at or below the limit of detection of the gas chromatograph. The ester concentration was, as expected, greater in the first three cuts of the distillate (heads); however, the concentration of these esters varied greatly within the multiple runs of the same sample, due to the limit of detection for the chromatography equipment. The data for the esters therefore is not reliable and is not included.

Acetone is the final compound included in this study. The concentration of acetone decreases through the distillation. This trend is predicted by the CHEMCAD<sup>TM</sup> program, although the concentration predicted by the CHEMCAD<sup>TM</sup> program will need to be improved. A calibration curve may need to be developed to accurately predict the concentration of acetone in the distilled spirits. Figures 5.25 and 5.26 illustrate the concentration of acetone predicted by CHEMCAD<sup>TM</sup> and the concentration of the actual distillation.



Figure 5.25 Predicted and experimental concentration of acetone in a 10 L standard batch distillation.



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Figure 5.26 Predicted and experimental concentration of acetone in a 150 L standard batch distillation.

# 5.6 Summary

The thermodynamic models within CHEMCAD<sup>™</sup> have varying ability to predict the concentration of the compounds studied over time within the distillate. Table 5.10 shows the best fit model for each compound and the two thermodynamic models next closest to fitting the experimental data as well. Overall the three UNIFAC distillation models were best for identifying the distillation profile of the compounds studied by inspection of the data. The ESD and NRTL models were accurate as predictive models for the simple alcohols ethanol and methanol, but were poor comparison models for the fusel alcohols. The Modified UNIFAC model was the best overall model for identifying the concentration profile for the variety of compounds within this study.

The predicted concentration of the distillate does not always agree with the experimental concentrations. This can clearly be seen in the case of benzaldehyde. This is due to inaccurate feed values obtained from the Rayleigh distillations. The mass balance for benzaldehyde holds for the predicted values when carried out to longer distillation time, and it can be concluded that the concentration of the benzaldehyde in the experimental mash was greater than the concentration entered as the feed concentration of benzaldehyde in the CHEMCAD<sup>™</sup> model. Therefore the Rayleigh distillation method does not work well for the prediction of the benzaldehyde concentration.

# Table 5.10 The best fit thermodynamic models within CHEMCAD™ for each of

	Thermodynamic Models		
Compound	Best Fit	Next Best Fit	
Ethanol	Modified UNIFAC	ESD	NRTL
Methaol	Modified UNIFAC	ESD	NRTL
T-Butanol	UNIFAC LLE	Modified UNIFAC	NTRL
1-Propanol	UNIFAC	UNIFAC LLE	Modified UNIFAC
Isoamyl Alcohol	UNIFAC	Modified UNIFAC	UNIFAC LLE
Acetaldehye	UNIFAC LLE	Modified UNIFAC	UNIFAC
Benzaldehyde	UNIFAC LLE	Modified UNIFAC	UNIFAC
Acetone	UNIFAC LLE	NRTL	Modified UNIFAC

the compounds studied in these experiments.

# 5.7 Literature Cited

- 1. United States Code of Federal Regulations, Title 27—Alcohol, Tobacco Products and Firearms, Chapter I, Part 5, Subpart C—Standards of Identity for Distilled Spirits. <www.access.gpo.gov/nara.cfr/cfr-table-search.html>.
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- 3. Piggott, J. R., and Patterson, A. ed., *Distilled Beverage Flavour: Recent Developments*. Ellis Horwood Ltd., 1989.
- 4. Guymon, J.F., Higher Alcohols in Beverage Brandy: Feasibility of Control of Levels. *Wines and Vines*, 53, (1) 1972.

# 6. SUMMARY AND CONCLUSIONS

## 6.1 Process

The process of performing a Rayleigh distillation on a fermentation mash, and then analyzing the distillate for congener compound concentration to determine the approximate concentration of the congener compounds present in the mash worked well for both the standard solution and fermentation mash. Because this method was not accurate at determining the exact concentration of the mash, the concentrations predicted with the CHEMCAD<sup>TM</sup> thermodynamic models were not exact. While the concentration of the compounds were not always precise, the important factor in this process is the ability of CHEMCAD<sup>TM</sup> to mimic the trends of the compounds. By imitating the concentration profile over the distillate volume, a distiller can determine where they need to make fractions, in order to maximize the yield of potable spirits.

The low benzaldehyde concentration from the Rayleigh distillation is likely responsible for the poor prediction of the concentration of the benzaldehyde in the distillate when modeled in the CHEMCAD<sup>™</sup> program. A modification of the procedure for determining the benzaldehyde content in the mash is warranted.

#### 6.2 Fruit Distillation Modeling

Determining the flow rate of the distillate of an ethanol/water mixture is necessary to determine the reflux ratio of the still so that the distillation modeling of the CHEMCAD<sup>™</sup> program can be more accurate. When the initial modeling of the

distillation was done, the concentration of the compounds present was not complimentary to the actual concentration or pattern of concentration over time. By adding the reflux ratio data, and modeling the distillation as a multiple step process, the distillation modeling by CHEMCAD<sup>™</sup> was more accurate.

The goal of this project was to determine if the CHEMCAD<sup>™</sup> program could be used to improve the quality of distilled fruit spirits. With the process outlined in this experiment, a distiller can analyze their fermentation mash using a Rayleigh distillation and gas chromatograph. The resulting data, when input into the CHEMCAD<sup>™</sup> program can predict the concentration of ethanol, methanol, and acetaldehyde in the distillate. The rest of the compounds studied did not yield accurate prediction of concentration by CHEMCAD<sup>™</sup>. The general profiles of these compounds, i.e. concentration maxima, were determined using this method. This process allows the distiller to modify the amount of distillate collected in the heads, hearts, and tails to improve the quality of the distilled fruit spirits. Inaccurate predictions of compound concentrations is due to incomplete recovery of these compounds from the Rayleigh distillation. The feed concentrations for the CHEMCAD<sup>™</sup> models are incorrect resulting in the discrepancy.

# 6.3 Improving Cut Determination for Methanol

As shown in table 5.9, the predicted concentration of methanol in the spirits can be used to determine which cuts should be blended together to meet the regulatory limit of 0.35 % v/v methanol in fruit spirits. This will allow the distiller to make three cuts of heads, hearts and tails, based on the volume of the hearts cut that would produce a

methanol concentration that would meet the federal guidelines. By doing this the distiller would not be required to make many small fractional cuts.

## 6.4 Still Size Comparison

The component concentrations of the 10 L Holstein still were not as accurately predicted as the concentrations of the 150 L industrial scale Christian Carl still distillations. The 10 L still is not necessarily a good indicator of the efficiency of a process and the results from the 10 L still to a 150 L industrial scale distillation do not scale well.

## 6.5 Still Characteristics

Each still has unique characteristics regarding distillate flow rate and reflux ratio. A procedure was developed to determine these characteristics for each still, to improve the modeling of the distillations. The nuances each still possess that alter internal flow parameters, and other parameters, cause differences in the distillation of each still. These characteristics can be considered within this procedure, by determining the reflux ratio and flow rate of a binary ethanol/water mixture of concentration equivalent to that of the feed mash. The variation in distillation from one still to the next can be accounted for in the thermodynamic models by using this method.

# 6.6 Conclusions

1. Measuring the flow rate of the distillate from an 8% ethanol/water mixture can be used to determine the reflux ratio for the operating steps involved in the modeling of distilled spirits. This in turn can be used to account for subtle manufacturing differences between one still and another within the thermodynamic models.

2. Rayleigh distillation can be used to determine the concentrations of the compounds present in fruit mash. These values can then be used as the feed for the distillation simulation software. However, the benzaldehyde concentration was not accurately predicted using this method.

3. The modeling of concentration of the compounds present in distilled spirits is possible using thermodynamic models available on the CHEMCAD<sup>™</sup> computer program. The method for determining the feed values from a Rayleigh distillation of the feed mash works for ethanol, methanol, and acetaldehyde. Improvements need to be made to more accurately predict concentration values for the other compounds.

4. The process does not scale-up well from the 10 L Holstein still to the 150L Christian Carl still. The 150 L scale is more accuratly modeled by the computer simulations than the 10 L scale.

5. By analyzing the concentration of methanol in each distillation cut, the concentration of methanol in the distilled spirits can be approximated using the above method and "blending" the above cuts. This will allow the distiller to use fewer fractions based on the results of the CHEMCAD<sup>™</sup> predictive models.

6. The ethanol concentration predicted by this procedure and the thermodynamic models is a very good approximation of the experimental results. It is important to

remember that the concentration of ethanol in the distilled spirits is the most important factor to the distiller. This process of extracting ethanol, in the form of fruit brandy, from the fermentation mash is the goal of these distillations. This method approximates the concentration of the ethanol better than any of the other compounds. In the end, the distiller is more concerned with the concentration of ethanol than any of the other compounds present.

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# 8. FUTURE WORK

The relationship between the predicted values and the concentration of the fruit brandies for most of the compounds can be studied further and calibration data can be generated to improve the concentration data prediction for all the components present. Improvement in the compound recovery from the Rayleigh distillation should improve the concentration prediction of the CHEMCAD<sup>™</sup> models.

A more in depth examination of the flow rate and reflux ratio of the distillation may also improve this process. In these experiments data was collected in increments of 750 mL on the 150 L still. Smaller volume increments will lead to more information about the behavior of the flow rate of the distillate, and the reflux ratio in the still. Measurement of the reflux ratio and flow rate for industrial stills should improve the ability to model these distillations.

Experimental VLE measurements would increase the ability to model these distillations. Collecting VLE data for multicomponent mixtures using these batch stills will improve the understanding of the process involved in the distillation of fruit brandies.

Finally, as other thermodynamic models become available, they should be studied, in an attempt to better mimic the concentration of the components present in these type of spirits.

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# A. DISTILLATION MODELS

## A.1 Batch Distillation Mathematical Model and Describing Equations

Batch distillation is inherently an unsteady state process in which the transient behavior is caused by an imbalance in the inlet and outlet streams over the entire period of operation<sup>1</sup>. In most applications, the column is brought to steady state at total reflux before product withdrawal begins. It is usually not of interest to follow the behavior while total reflux steady state is being established, since no product is being withdrawn. Therefore, the conditions representing the solution of the total reflux equations based upon a specified initial charge and column parameters are taken as the initial conditions for the first operating step.

The basic unsteady state describing equations employed in the CHEMCAD program are essentially the same as those given by Distefano (1968). The main differences are in terms introduced to handle feeds, side products, heat losses and side heaters, and additional equations for the side product accumulators. According to the CHEMCAD literature, these equations consist of the rigorous unsteady state mass and enthalpy balances and the phase equilibrium relationships. Equilibrium stages with constant volume, mass or molar liquid holdup were assumed. Vapor holdup was neglected and the column hydraulics were not included as part of the simulation. Thermodynamics are completely rigorous, employing the entire selection of K-value, enthalpy, and property methods in CHEMCAD.

The describing equations presented here are based on the constant volume holdup assumption rather than the less realistic constant mole or mass.

**Component Mass Balance** 

$$\frac{d(H_n X_{in})}{dt} = f_{in} + L_{n-1} X_{n-1} - (n + W_{Ln}) X_{in} - (V_n + W_{vn}) Y_{in} + V_{n+1} Y_{n+1}$$

Total Mass Balance

$$\frac{d(H_n)}{dt} = F_n + L_{n-1} - L_n - W_{Ln} - V_n - W_{vn} + V_{n+1}$$

Enthalpy Balance

$$\frac{d(H_nH_{Ln})}{dt} = H_{Fn}F_n + H_{Ln-1}L_{n-1} - H_{Ln}(L_n + W_{Ln}) - H_{vn}(V_n + W_{vn}) + H_{vn+1}V_{n+1} + Q_n$$

Production of the second second

Phase Equilibrium

 $Y_{in} = K_{in} X_{in}$ 

Constitutive

$$\sum_{n} (K_n - 1) X_n = 0$$

Holdup Equations

$$H_n = \frac{G_n \rho_n}{M_{Ln}(X_n)}$$

## A.2 Physical Property Models

Specification of the flow rates, compositions, enthalpies and locations of the feed streams, the locations and molar flow rates of the side product streams, the internal stage heat duties, the column pressure profile and the volume holdups are required for solving the rigorous equations. With this information, at each time interval the composition, temperature, flow rate, and holdup profiles are solved for by these equations. A series of operations steps define the operation of a batch distillation, with specified topping criteria. For this work we change the reflux ratio at each operation step for example. The CHEMCAD software utilizes these operation steps to accommodate these changing parameters for the model equations<sup>1</sup>.

The describing equations that must be solved over each operation step consist of the unsteady state mass and enthalpy balances and the phase equilibrium relationships. In this work, equilibrium stages with constant volume, mass or molar liquid holdup were assumed. Vapor holdup was neglected and the column hydraulics were not included<sup>1</sup>.

The unsteady state mass and enthalpy balances form a large set of coupled, nonlinear ordinary differential equations<sup>1</sup>.

# **B. THERMODYNAMIC MODELS**

#### **B.1** Guidelines to Selecting Thermodynamic Methods

These guidelines are outlined in the help function of the CHEMCAD program. CHEMCAD provides an extensive array of the most up-to-date methods for performing heat and material balances. These techniques cover applications ranging from straight hydrocarbon applications, to chemical models, to a wide variety of special applications involving electrolytes, salt effects, amines, sour, water, to other specialty chemical applications. These methods have been field tested over a period of years and have been demonstrated to give highly accurate results.

To achieve accurate results; however, it is necessary to select the proper method for a given application. This section of the manual provides guidelines for making these selections. It should be noted, however, that the guidelines we will be discussing are for the selection of K-value (phase equilibrium) and enthalpy methods only.

#### **B.2** The K-Value Wizard

The K-value wizard function is designed to recommend a thermodynamic model for the components and application used in the CHEMCAD program. To determine the best fit model, the following criteria are used:

1. First, what general type of model is required (i.e. equation-of-state, activity model, etc) is determined from the component list.

2. Next, the temperature and pressure ranges input by the user is used to determine which equation within a given category is best at the limits of those ranges.

3. If the model is an activity model, the program then looks at the BIP database to see which model has the most data sets for the current problem. It then calculates the fractional completeness of the BIP matrix. If that fraction is greater than the BIP threshold parameter, it uses the chosen activity method; if not it uses UNIFAC.

# **B.3** Conclusions and Recommendations for Thermo Models

CHEMCAD classifies liquids into five categories: ideal, regular, polar (highly non-ideal), electrolytes, and special. For these classifications the following distinctions and qualifications are made:

1. **Ideal Solutions** are systems where the vapor phase behaves essentially as an ideal gas (low pressure) and all the molecules in the liquid phase are virtually the same size. In addition, no intermolecular forces of attraction are assumed to exist. Vapor-liquid equilibria are determined using Raoult's law:

$$K_i = \frac{VP_i}{P}$$

where  $VP_i$  is calculated using the selected vapor pressure equation.

2. **Regular Solutions** are systems where the non-idealities stem from moderate physical interactions, i.e., from differences in the size and shape of the molecules. Intermolecular associations are assumed to be minimal. These systems are best modeled using equations-of-state such as PR, SRK, APIS, BWRS, CS/GS and MSRK.

In all of these cases, both the vapor and the liquid phases are assumed for form regular (i.e., mildly non-ideal) solutions, and K-values are calculated like so:

$$K_i = \frac{\Phi_{li}}{\Phi_{vi}}$$
3. **Polar (Highly Non-Ideal Solutions)** are systems where the liquid phase nonidealities arise predominantly from molecular associations. These systems must be modeled using activity coefficient methods which generally require BIPs for accuracy. The vapor phase is taken to be a regular solution, therefore, ч

$$K_{i} = \frac{\gamma_{i} f_{li}^{\circ}}{P \Phi_{vi}}$$

where

$$f_{li}^{\circ} = VP_{i} \quad and \quad \Phi_{vi} = 1; or$$

$$f_{li}^{\circ} = VP_{i} * \Phi_{vi} * EXP\left(\frac{(P - VP_{i}) * V_{i}}{RT}\right)$$

The equations which fall into this category are: NRTL, UNIFAC, UNIQUAC, Wilson,

T.K.Wilson, Hiranuma, Van Laar, Margules, and GMAC. Wilson, NRTL, and

UNIQUAC are the recommended methods. UNIFAC may be used where data is absent.

This is the type of solution used in this work.

#### 4. **Electrolyte Solutions** are not utilized for these experiments.

#### 5. **Special Systems** are provided for the simulation of common applications which

do not lend themselves to the above approaches. Therefore no information is included.

A summary of the recommendations of the K-values can be seen below:

Hydrocarbons

- Soave-Redlich-Kwong High moderate P & T's.
- API Soave General HC. High moderate P & T's.
- Peng-Robinson High moderate P & T's.
- Benedict-Webb-Ruben-Starling High moderate P & T's.
- Grayson-Streed Moderate pressures and temperatures.
- Maxwell-Bonnell K-charts Low pressure, heavy material.
- ESD Hydrocarbon -water; hydrocarbon-gases
- SAFT Hydrocarbon -water; hydrocarbon-gases

Chemicals

- UNIFAC T = 275K 475K; P = 0-4 atm.; two liquid phases. Non-ideal; group contribution; predictive.
- Wilson Highly non-ideal.

- Vapor Pressure Ideal solutions.
- NRTL Highly non-ideal and 2 liquid phases.
- UNIQUAC Highly non-ideal and 2 liquid phases.
- Margules Highly non-ideal and 2 liquid phases. (4 suffix)
- T. K. Wilson Highly non-ideal and 2 liquid phases.
- Hiranuma (HRNM) Highly non-ideal and 2 liquid phases.
- Regular Solution Moderately non-ideal (Predictive).
- Van Laar Moderately non-ideal.
- Modified SRK (4 parameter) Polar compounds in regular solutions.
- Predictive SRK Polar compounds in non-ideal solutions. Better than UNIFAC at high pressures.
- Wilson Salt Non-ideal solutions with salts dissolved in them.

Special Techniques

- Henry's Gas Law Gases dissolved in water
- Amine (MEA DEA) Gas sweetening
- Sour Water Acid gases and NH3 dissolved in H2O
- K Tables User K's
- Polynomial User K's
- User-Added Subroutine User K's
- TSRK Methanol system; particularly with light gases.
- PPAQ General, but electrolyte systems is most common application
- TEG Dehydration of hydrocarbon streams using tri-ethylene-glycol
- FLOR Flory-Huggins method for polymers
- UPLM UNIFAC for polymers
- ACTXUser specified activity coefficients
- ESD Hydrogen bonding; hydrogen bonding at high pressure
- SAFT Hydrogen bonding; hydrogen bonding at high pressure

## C. MODELS USED

#### C.1 Renon NRTL Model

The NTRL model is recommended for highly ideal solutions and 2 liquid phases. The NTRL method was the model recommended by the K-value wizard by CHEMCAD. The NTRL method can use many different parameters to determine the separation of the components in distillates. The UNIQUAC and NTRL models are widely used for both vapor-liquid and liquid-liquid equilibria.

Because of the non-ideal nature of the solutions used in this work (i.e. polar alcohols, variety of size, hydrogen bonding of alcohols and water, etc.) the NRTL method was chosen as the principle model for performing the calculations<sup>1, 2</sup>.

Liquid phase activity coefficients are calculated by NRTL equation.

The NRTL equations has the following form':

$$\ln \gamma = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_{j}}{\sum_{i=1}^{N} G_{ij} x_{i}} + \sum_{j=1}^{N} \frac{x_{j} G_{ij}}{\sum_{i=1}^{N} G_{ij} x_{i}} \left[ \tau_{ij} - \frac{\sum_{i=1}^{N} x_{i} \tau_{ij} G_{ij}}{\sum_{i=1}^{N} G_{ij} x_{i}} \right]$$

Where

$$\tau_{ji} = A_{ji} + B_{ji} / T + C_{ji} * \ln(T) + D_{ji} * T$$
$$G_{ji} = \exp(-\alpha_{ji} * \tau_{ji})$$
$$\alpha_{ij} = \alpha_{ji}$$
$$T = Temperature in Kelvin$$

The most common usage of the NRTL equation is the three parameter equation. The NRTL equation may be used either as a three-parameter ( $B_{ji}$ ,  $B_{ij}$ , and  $\alpha_{ij}$  only), as a five-parameter  $(A_{ji}, A_{ij}, B_{ji}, B_{ij}, and \alpha_{ij})$ , seven parameter  $(A_{ji}, A_{ij}, B_{ji}, B_{ij}, C_{ji}, C_{ij}, and \alpha_{ij})$ , or a nine parameter equation  $(A_{ji}, A_{ij}, B_{ji}, B_{ij}, C_{ji}, C_{ij}, D_{ji}, D_{ij})$ . -----

Converting Binary Parameters (Bips) from Literature The CHEMCAD help manual states that many data sources use the DECHEMA equation whereas CHEMCAD divides the actual Bips by RT. To use Bips from a source using the alternate format, divide by R (1.97842) for the proper value and divide by T to identify the proper Bip. For example:

Using data from DECHEMA, if A12 = A + B \* T, then CHEMCAD bips are Bij= A / R and Aij = B / R<sup>1</sup>.

**Regressing Bips** 

According to the CHEMCAD program it is possible to use the Tools menu command Bip regression to regress Bips from data. This model is dependent upon the binary interaction parameters of each of the components<sup>1</sup>.

#### C.2 The ESD Equation

The ESD equation (Elliott, Suresh, and Donohue, 1990) is similar to conventional cubic equations of state like the Soave (1972) equation or Peng-Robinson (1976) equation for hydrocarbons and gases, but provides accuracy competitive with UNIQUAC, NRTL, or Wilson's equation for hydrogen bonding mixtures. It also provides high accuracy for hydrogen bonding mixtures at high pressure like the interpolation methods of Dahl et al. (1991), Schwartzentruber and Renon (1989), and Wong et al. (1992). It also provides accuracy for hydrocarbon + water mixtures that is comparable with that of the adaptation of the Soave equation by Kabadi and Danner

(1986). The ESD equation is based on treating the hydrogen bonding interactions as chemical reactions in accordance with the formalism developed by Wertheim (1986) unlike the interpolation methods. The ESD equation uses the critical properties and acentric factor to estimate the pure-component parameters when no parameters are listed in the databank. Parameters estimated in this way are based on neglecting selfassociation. For associating compounds, the ESD equation still matches the experimental critical temperature, but adjusts the size and shape parameters to obtain an optimal representation of vapor pressure data. If the accuracy is insufficient for any particular application, it should be possible by limiting the range of conditions to develop specific pure component parameters that provide sufficient accuracy. The accuracy of VLE correlations by the ESD equation has been studied for a wide range of mixtures by Puhala and Elliott (1993). The treatment of the association thermodynamics applied here is restricted to linear Acceptor-donor association like alcohols and water and binary associations like carboxylic acids. This restriction permits an increase in computational efficiency of about 100-fold relative to the completely general formulation (Elliott, 1996). Evaluations to date for mixtures containing ethers, esters, and ketones, as well as alcohols, aldehydes, amines, and glycols have shown little or no reduction in accuracy as a result of this restriction<sup>1</sup>.

The use of the ESD methods for this work is due to the polar mixture containing alcohol, water, aldehydes, ketones and esters. The hydrocarbon + water base model for the ESD equations is different from that of the polar solution models of UNIFAC, UNIQUAC and NRTL.

#### Summary of Equations<sup>1</sup>

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$$\frac{PV}{RT} = 1 + \frac{4\langle c\eta \rangle}{1 - 1.9\eta} - \frac{9.5\langle q\eta Y \rangle}{1 + 1.7745\langle \eta Y \rangle} + Z^{0.5506}$$

where,

$$Z^{0.5506} = \rho \frac{\partial A^{0.5506} / RT}{\partial \rho}$$

$$\frac{A^{0.5506}}{RT} = \sum x_i N d_i [2 \ln(X_i^A) + 1 - X_i^A] + \sum x_i N d_i \left[ \ln(X_i^C) + \frac{1 - X_i^C}{2} \right]$$

$$\eta = \rho \sum x_i b_i$$

$$\langle c\eta \rangle = \rho \sum \sum (cb)_{ij} x_1 x_1$$

$$\langle q\eta Y \rangle = \rho \sum \sum (qb)_{ij} Y_{ij} x_1 x_1$$

$$q_i = 1 + 1.90476 * (c_i - 1)$$

$$Y_{ij} = \exp(\varepsilon_{ij} / kT) - 1.0617$$

$$(cb)_{11} = (c_1 b_1 + c_1 b_1) / 2$$

$$(qb)_{11} = (q_1 b_1 + q_1 b_1) / 2$$

$$\varepsilon_{ii} = (\varepsilon_{ii} \varepsilon_{ii})^{1/2} (1 - k_{ii})$$

$$\langle \eta Y \rangle = \rho \sum b_1 Y_i x_1$$

 $X_iA$  = the fraction of linear proton acceptor sites not bonded  $X_iC$  = the fraction of binary (carboxylic) bonding sites not bonded The procedure for determining the fractions of bonding is given by Elliot (1996).  $b_i$ ,  $c_i$ , and  $\varepsilon_{ii}/k$  are adjustable pure component parameters.

#### C.3 UNIFAC

In the UNIFAC K model, the liquid phase activity coefficients for each species are calculated from the UNIFAC group contribution method. The limitations of UNIFAC are temperature range from 275K to 425 K and pressure up to a few atmospheres. Also this UNIFAC reads the group contribution parameter stored in the VLE database<sup>1</sup>.

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Because UNIFAC is a Gibbs excess model it is theoretically capable of predicting a second liquid phase. In practice liquid-liquid behavior cannot be adequately predicted from VLE data. The user is recommended to use UNIFAC LLE to model a two phase system with the UNIFAC models<sup>1</sup>.

### **UNIFAC Equation**<sup>1, 2</sup>

 $\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$ (combinatorial) (residual)

where

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + I_i - \frac{\Phi_i}{x_i} \sum_j x_j I_j$$
  
and  
$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum \theta_i \tau_{ij} \right) - \sum \frac{\theta_i \tau_{ij}}{\sum \theta_i} \right]$$

 $\lim \gamma_i = q_i \left[ 1 - \lim_{j \to j} \left( \sum_{j \to j} \sigma_j \tau_{ji} \right) - \sum_{j \to j} \frac{1}{\sum_{j \to j} \theta_j \tau_{2j}} \right]$ 

where

$$I_{i} = \frac{z}{2}(r_{i} - q_{i}) - r_{i} - I) \qquad z = 10$$
  

$$\theta_{i} = \frac{q_{i}x_{i}}{\sum_{j} r_{j}x_{j}}$$
  

$$\phi_{i} = \frac{r_{i}x_{i}}{\sum_{j} r_{j}x_{j}}$$
  

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right)$$
  

$$r_{i} = \sum_{k} v_{k}^{(i)}R_{k}$$
  

$$q_{i} = \sum_{k} v_{k}^{(i)}Q_{k}$$
  

$$R_{i} = \frac{V_{avi}}{15.17}$$
  

$$Q_{i} = \frac{A_{avi}}{2.5X10^{9}}$$
  

$$\ln \gamma_{i}^{R} = \sum_{k} v_{k}^{(i)} \left(\ln \Gamma_{k} - \ln \Gamma_{k}^{(i)}\right)$$
  

$$\ln \Gamma_{i} = Q_{i} \left[1 - \ln\left(\sum_{m} \theta_{m} \Psi_{mi}\right) - \sum_{m} \frac{\theta_{m} \Psi_{im}}{\sum_{n} \Psi_{nm}}\right]$$
  

$$\theta_{m} = \frac{Q_{m} X_{m}}{\sum_{n} Q_{n} X_{n}}$$
  

$$\Psi_{mn} = \exp\left(-\frac{U_{mn} - U_{nn}}{RT}\right) = \exp\left(-\frac{a_{mn}}{T}\right)$$
  

$$T = temperature in Kelvin$$

### C.4 UNIFAC LLE

As the UNIFAC model is a Gibbs excess energy model, it can theoretically predict Liquid-Liquid Equilibria (LLE). In practice, binary interaction parameters regressed from VLE data are insufficient to predict LLE behavior<sup>1</sup>.

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CHEMCAD provides an alternate UNIFAC model which uses binary interaction parameters regressed from LLE data. The UNIFAC VLE model equations are used without change. Group interaction parameter values differ from the UNIFAC VLE model<sup>1</sup>.

It was necessary to develop additional subgroups for 1-propanol (P1), 2-propanol (P2), diethylene glycol (DEOH), trichloroethylene (TCE), methylformamide (MFA), and tetramethylenesulfone (TMS). These additional subgroups are only for the UNIFAC LLE model. The LLE subgroups use regressed values of Q and R which differ from UNIFAC VLE subgroups<sup>1</sup>.

#### C.5 Modified UNIFAC (Dortmund)

The Modified UNIFAC model (Dortmund) introduces temperature dependant interaction parameters, allowing for more reliable description of phase behavior as a function of temperature. This method also uses Van der Waals (Q and R) properties which are slightly different than those used in the original UNIFAC method.

Original UNIFAC: 
$$\Psi_{nm} = \exp\left[\frac{-a_{nm}}{T}\right]$$

Modified UNIFAC (Do.) 
$$\Psi_{nm} = \exp\left[\frac{-a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right]$$

The modified UNIFAC (Do.) model uses different component group and subgroup matrices than the original UNIFAC. Published interaction parameters have been included in CHEMCAD. Unpublished parameters can be added into CHEMCAD if your company has access to them<sup>1</sup>. As with the original, the Modified UNIFAC model has the activity coefficient as the sum of a combinatorial and residual part<sup>1</sup>.

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

The combinatorial term in Modified UNIFAC has changed, to allow it to deal with compounds of very different sizes<sup>1</sup>.

$$\ln \gamma_i^C = 1 - V_i' + \ln V_i' - 5 \cdot q_i \left( 1 - \frac{V_i}{F_i} + \ln \left( \frac{V_i}{F_i} \right) \right)$$

Where  $V'_i$  is calculated from relative Van der Waals volumes Rk of different groups.

$$V_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}}$$

#### C.6 UNIQUAC Model

In the UNIQUAC K model, the liquid phase activity coefficients for each species are calculated by the UNIQUAC equation. CHEMCAD supports up to 8 parameters (Aij, Aji, Uij-Uji, Uji-Uij, Cij, Cji, Dij, Dji) for the UNIQUAC model<sup>1</sup>.

#### **UNIQUAC Equation**<sup>1</sup>

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} \cdot q_i \cdot \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \cdot \sum_j^N x_j \cdot l_j - q_i \ln \left(\sum_j^N \theta_j \cdot \tau_{ji}\right) + q_i - q_i \cdot \sum_j^N \left(\frac{\theta_j \cdot \tau_{ji}}{\sum_k^N (\theta_k \cdot \tau_{ki})}\right)$$

Where

$$\begin{aligned} \phi_{i} &= x_{i} * r_{i} / (\sum x_{j} * r_{j}) \\ \phi_{i} &= x_{i} * q_{i} / (\sum x_{j} * q_{j}) \\ \tau_{ij} &= \exp [A_{ij} - (Uij - U_{jj}) / RT + C_{ij} * \ln(T) + D_{ij} * T] \end{aligned}$$

Τ	=	Temperature in degrees Kelvin
$l_i$	=	$(z/2) * (r_i - q_i) - r_i + 1$
z	=	10 (coordination number)
$q_i$	=	van der Waals area parameter $(A_{wi} / (2.5 * 10^9))$ where $A_{wi}$ is the van der
		Waals area)
r <sub>i</sub>	=	van der Waals volume parameter $(V_{wi}/15.17$ where $V_{wi}$ is the van der
		Waals volume)

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For comparison to DECHEMA format values  $a_{ij}$  and  $b_{ij}$ :

$$\begin{array}{rcl} a_{ij} + b_{ij}/T &=& A_{ij} + (U_{ij} - U_{jj}) / RT \\ b_{ij} &=& - (U_{ij} - U_{jj})/R \\ a_{ij} &=& A_{ij} \end{array}$$

The UNIQUAC binary interaction parameters Aij, (Uij - Ujj) and (Uji - Uii) are in cal/gmol.

The binary interaction parameters (BiPs) Cij and Dij are optional.

Several binary interaction parameters (BiPs) are in the UNIQUAC program. The

Thermophysical menu command Edit Bips can be used to view existing Bips for the

system, if the K Value model is UNIQUAC.

The UNIQUAC equation uses qi, the van der Waals area parameter, and  $r_i$ , the van der Waals volume parameter. Values for  $q_i$  and  $r_i$  are required for each component in the mixture.

Values of  $q_i$  and  $r_i$  stored in the databank were computed for use with the UNIQUAC model.

# **D. DATA TABLES**

### Table D.1 Data for Figure 6.1. The CHEMCAD program predicted ethanol

concentrations for constant reflux ratio distillations.

			Reflux	Ratio 2				
Cumulative								Ethanol/
Distillate			Modified		UNIFAC			Water
Volume (mL)	NTRL	BWRS	UNIFAC	UNIFAC	LLE	UNIQUAC	ESD	Distillation
750	78.22	89.74	79.61	79.61	76.31	78.16	78.16	78.39
1500	77.32	90.84	78.87	78.87	75.60	77.28	77.28	82.24
2250	76.31	90.79	78.03	78.03	74.81	76.29	76.29	82.47
3000	75.18	90.71	77.06	77.06	73.91	75.1 <b>8</b>	<b>75.18</b>	82.49
3750	73.94	90.55	75.96	75.96	72.90	73.97	73.97	80.98
4500	72.57	90.28	74.72	74.72	71.77	72.63	72.63	80.03
5250	71.09	89.85	73.33	73.33	70.51	71.17	71.17	80.43
6000	69.48	89.19	71.80	71.80	69.12	69.59	69.59	78.27
6750	67.75	88.28	70.12	70.12	67.59	67.89	67.89	77.50
7500	65.90	86.66	68.28	68.28	65.92	66.05	66.05	77.00
8250	63.92	85.06	66.29	66.29	64.12	64.09	64.09	74.74
9000	61.81	83.18	64.13	64.13	62.16	62.00	62.00	73.67
9750	59.57	80.54	61.81	61.81	60.07	59.78	<b>59.78</b>	71.13
10500	57.21	76.06	59.33	59.33	57.84	57.43	57.43	66.18
11250	54.74	70.78	56. <b>68</b>	56.6 <b>8</b>	55.47	54.96	<b>54.96</b>	63.64
12000	52.15	64.65	53.89	53.89	52.97	52.37	52.37	60.45
			Reflux	Ratio 5				
Cumulative								Ethanol/
Distillate			Modified		UNIFAC			Water
Volume (mL)	NTRL	BWRS	UNIFAC	UNIFAC	LLE	UNIQUAC	ESD	Distillation
750	84.52	91.30	84.99	85.25	82.38	84.62	82.18	78.39
1500	84.25	91.29	84.76	85.07	82.11	84.35	81.89	82.24
2250	83.96	91.28	84.51	84.87	81.80	84.05	81.57	82.47
3000	83.61	91.27	84.21	84.63	81.45	83.70	81.20	82.49
3750	83.21	91.27	83.87	84.36	81.05	83.30	80.77	80.98
4500	82.74	91.26	83.47	84.04	80.59	82.83	80.28	80.03
5250	82.19	91.25	83.00	83.65	80.05	82.26	79.71	80.43
6000	81.51	91.22	82.42	83.19	79.42	81.57	79.02	78.27
6750	80.65	91.16	81.71	82.61	78.66	80.70	78.18	77.50
7500	79.52	91.02	80.80	81.88	77.74	79.57	77.13	77.00
8250	78.00	90.75	79.58	80.95	76.59	78.05	75.80	74.74
9000	75.93	90.21	77.91	79.70	75.12	76.02	74.05	73.67
9750	73.23	89.22	<b>75.58</b>	77.93	73.20	73.38	71.7 <b>9</b>	71.13
10500	69.87	87.72	72.43	75.27	70.65	70.07	68.93	66.18
11250	65.8 <b>8</b>	83.35	68.44	71.38	67.37	66.11	65. <b>48</b>	63.64
12000	61.30	76.45	63.62	66.26	63.33	61.55	61.45	60.45

## Table D.2 Experimental and predicted results for ethanol in fruit spirits and

			10 L F	ruit Distillation				
	Experimental	Distillation			CHEMCAD Mod	el Distillation		
Cumulative								
Distillate Volume		Standard				Modified		
(mL)	% Ethanol (v/v)	Deviation	NRTL	ESD	UNIFAC	UNIFAC	UNIFAC LLE	UNIQUAC
75	72.96	0.33	75.55	75.55	78.75	77.18	73.92	75.55
150	75.33	0.40	78.00	78.00	80.51	79.27	76.29	78.00
225	75.76	0.30	76.60	76.60	79.41	78.05	74.98	76.64
300	74.91	0.88	74.35	74.35	77.81	76.17	73.08	74.44
375	74.25	0.23	70.30	70.30	74.97	72.56	69.73	70.43
450	72.69	0.51	66.41	66.41	71.65	68.82	66.29	66.58
525	69.83	0.20	62.09	62.09	67.38	64.49	62.27	62.28
600	65.12	0.41	58.67	58.67	63.71	60.97	59.03	58.87
675	59.16	0.97	55.74	55.74	60.39	57.89	56.26	55.96
			150 L F	Fruit Distillation				
	Experimental	Distillation			CHEMCAD Mod	el Distillation		-
Cumulative								
Distillate Volume		Standard				Modified		
(mL)	% Ethanol (v/v)	Deviation	NRTL	ESD	UNIFAC	UNIFAC	UNIFAC LLE	UNIQUAC
75	71.94	2.14	73.99	72.10	75.82	74.22	70.44	73.88
150	74.08	1.63	76.76	75.21	78.11	76.83	73.63	76.65
225	74.09	1.19	75.82	74.54	77.84	76.47	73.34	75.76
300	73.63	1.34	73.83	72.61	76.79	75.23	72.14	73.85
375	71.95	2.27	69.98	68.75	74.43	72.12	<b>69</b> .35	70.08
450	69.00	1.56	66.22	65.00	71.45	<b>68.6</b> 6	66.21	66.37
525	66.16	0.97	61.98	60.80	67.39	64.52	62.37	62.16
600	62.96	1.73	58.60	57.50	63.87	61.13	59.25	58.81
675	58.15	0.68	55.71	54.72	60.65	<b>58</b> .15	56.56	55.94
		-	10 L F	ruit Distillation				
	Experimental	Distillation			CHEMCAD Mod	lel Distillation		
Cumulative								
Distillate Volume		Standard				Modified		
(mL)	% Ethanol (v/v)	Deviation	NRTL	ESD	UNIFAC	UNIFAC	UNIFAC LLE	UNIQUAC
750	77.15	1.25	79.66	78.40	81.33	80.06	77.26	79.54
1500	82.52	1.28	82.36	80.84	83.45	82.49	80.56	82.10
2250	82.22	0.32	82.55	81.34	84.00	83.04	81.15	82.39
3000	82.35	1.26	81.49	80.44	83.17	82.12	79.83	81.46
3750	80.58	0.53	81.34	80.22	82.96	81.90	79.56	81.34
4500	81.29	2.68	80.44	79.27	82.08	80.94	78.39	80.48
5250	80.16	1.20	80.11	78.86	81.68	80.55	77.93	80.16
6000	79.14	1.12	78.35	77.09	80.14	78.96	76.08	78.42
6750	78.04	1.27	77.62	76.32	79.49	78.40	75.43	77.72
7500	77.97	1.11	75.09	73.85	77.65	76.56	73.46	75.28
8250	75.47	2.22	73.64	72.40	76.65	75.50	72.47	73.89
9000	73.70	2.28	69.85	68.68	74.19	72.36	69.72	70.16
9750	71.67	1.67	67.43	66.33	72.32	70.12	67.85	67.76
10500	67.48	1.59	64.01	63.03	69.20	66.77	64.97	64.36
11250	64.21	0.67	60.87	60.03	65.8 <del>9</del>	63.53	62.19	61.21
12000	61.07	1.28	60.49	59.78	65.01	62.94	61.96	60.82
			150 L Stand	ard Batch Distil	ation			
	Experimental	Distillation			CHEMCAD Mod	el Distillation		
	1	Orendered				Madified		
Distillate Volume		Standard				Modified		
(mL)	% Ethanol (V/V)	Deviation	NHIL	ESU		UNIFAC	UNIFAC LLE	UNIQUAC
750	70.25	4.38	/5.9/	73.77	75.77	74.35	70.61	75.84
1500	//.69	0.77	77.16	74.42	76.03	75.63	72.92	76.63
2250	78.55	1.41	79.68	78.18	80.37	79.87	78.00	79.35
3000	78.59	1.17	80.51	19.57	81.96	81.04	79.01	80.47
3750	78.41	0.90	80.86	79.86	82.28	81.26	79.21	80.83
4500	/9.27	rva	80.40	79.31	81.81	80.61	/8.32	80.37
5250	78.79	0.49	80.25	79.07	81.61	80.38	11.97	80.20
6000	78.96	0.68	78.60	77.46	80.24	78.93	76.16	/8.55
6750	77.01	0.13	77.89	76.76	79.67	78.47	75.56	77.86
7500	76.88	1.16	75.29	74.33	77.93	76.77	73.67	75.41
8250	75.20	1.99	73.83	72.89	77.00	75.82	72.77	74.03
9000	72.72	1.96	70.04	69.17	74.65	72.82	70.15	70.34
9750	70.12	2.48	67.63	66.82	72.88	70.66	68.37	67.97
10500	67.50	2.22	64.23	63.50	69.85	67.37	65.56	64.60
11250	64.96	1.02	61.09	60.48	66.60	64.17	62.82	61.48
12000	61.26	2.24	60.73	60.23	65.79	63.62	62.63	61.11

### standard batch distillations.

## Table D.3 Congener concentration experimental and predicted values for 10 L

		10 L	Fruit Distillation				
		Conge	ener Concentratio	on (% v/v ir	n 40% Ethan	ol)	
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.656	0.383	1.26E-01	0.054	0.701	0.075	0.313
150	0.491	0.167	1.41E-01	0.032	0.811	0.084	0.324
225	0.362	0.119	1.42E-01	0.022	0.938	0.077	0.284
300	0.353	0.069	1.48E-01	0.016	0.951	0.075	0.267
375	0.356	0.048	1.49E-01	0.013	1.005	0.072	0.278
450	0.369	0.028	1.47E-01	0.010	1.035	0.052	0.287
525	0.384	0.008	1.39E-01	0.007	1.057	0.045	0.299
600	0.386	0.003	1.31E-01	0.005	1.002	0.000	0.276
675	0.389	0.007	1.29E-01	0.003	0.920	0.000	0.188
		Stand	ard Deviation of	Congener	Concentratio	n	
Cumulative Distillate			<b>_</b>				Isoamyl
	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.048	0.014	7.24E-04	0.056	0.007	0.000	0.010
150	0.012	0.005	1.97E-04	0.016	0.005	0.001	0.006
225	0.003	0.003	4.47E-04	0.002	0.005	0.001	0.010
300	0.006	0.005	1.64E-03	0.006	0.018	0.001	0.023
375	0.002	0.001	1.82E-04	0.018	0.006	0.000	0.005
450	0.004	0.001	6.64E-04	0.005	0.009	0.000	0.008
525	0.003	0.000	5.70E-04	0.001	0.004	0.000	0.003
600	0.003	0.001	4.28E-04	0.001	0.005	0.000	0.004
675	0.009	0.001	6.97E-04	0.003	0.013	0.000	0.004
			<u>N</u>	RTL			
Cumulative Distillate			<b>-</b>	•			Isoamyl
	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
/5	0.310	0.213	4.86E-17	0.049	1.444	0.039	0.154
150	0.318	0.176	1.35E-18	0.043	1.331	0.037	0.088
225	0.322	0.126	2.14E-20	0.032	1.265	0.031	0.148
300	0.331	0.090	2.13E-19	0.024	1.170	0.026	0.220
3/5	0.344	0.065	1.75E-20	0.018	1.062	0.022	0.266
450	0.358	0.048	1.84E-18	0.014	0.962	0.019	0.277
525	0.373	0.035	7.25E-19	0.011	0.868	0.017	0.280
600	0.387	0.026	2.40E-18	0.009	0.780	0.014	0.278
6/5	0.403	0.018	1.95E-19	0.007	0.697	0.012	0.273
Cumulative Distillate				SD			loopmid
	Mathanal	Acatoldobudo	Penzeldebude	Acotono	1 Brananal	T Butanal	Aleehol
		Acetaidenyde		Acetone	0.765		
150	0.104	0.113	2.37E-17	0.020	0.765	0.020	0.002
225	0.100	0.050	1 125.20	0.022	0.000	0.019	0.043
300	0.100	0.000	1.125-20	0.017	0.001	0.010	0.077
375	0.170	0.040	0.025.01	0.013	0.029	0.014	0.119
375	0.190	0.037	J.JOC-21	0.010	0.604	0.013	0.152
	0.210	0.029	1.11E-10	0.009	0.579	0.012	0.107
525	0.240	0.023	4.0/ E-19 1 BAE 10	0.007	0.008	0.011	0.100
675	0.204	0.017	1 1045-10	0.000	0.552	0.010	0.109
0/5	0.203	0.013	1.402.13	0.005	0.500	0.009	0.190

### fruit distillations.

		10 L Fruit	Distillation (conti	inued)			
			UN	IIFAC			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.230	0.238	5.58E-17	0.048	0.765	0.063	0.245
150	0.221	0.189	2.53E-17	0.043	0.700	0.052	0.179
225	0.240	0.120	4.77E-19	0.031	0.757	0.036	0.230
300	0.263	0.077	1.45E-18	0.023	0.807	0.025	0.279
375	0.293	0.051	4.88E-19	0.017	0.844	0.017	0.309
450	0.318	0.035	5.10E-25	0.013	0.849	0.012	0.300
525	0.342	0.024	9.54E-18	0.010	0.844	0.009	0.281
600	0.364	0.017	1.08E-17	0.008	0.835	0.006	0.261
675	0.388	0.012	1.49E-19	0.006	0.823	0.004	0.239
			Modifie	d UNIFAC			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.323	0.222	3.15E-17	0.040	0.884	0.074	0.386
150	0.339	0.183	2.55E-18	0.037	0.827	0.057	0.313
225	0.337	0.122	1.14E-19	0.029	0.861	0.036	0.337
300	0.338	0.083	2.33E-18	0.023	0.878	0.023	0.334
375	0.345	0.058	3.37E-26	0.019	0.876	0.015	0.308
450	0.356	0.042	3.61E-18	0.016	0.861	0.010	0.275
525	0.369	0.030	1.17E-22	0.013	0.843	0.007	0.245
600	0.383	0.022	6.41E-20	0.011	0.823	0.004	0.216
675	0.398	0.015	6.57E-18	0.009	0.803	0.003	0.188
		· · · · · · · · · · · · · · · · · · ·	UNIF	AC LLE			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.320	0.288	2.98E-17	0.068	0.880	0.073	0.385
150	0.324	0.210	3.05E-18	0.053	0.827	0.057	0.316
225	0.331	0.125	3.92E-18	0.034	0.859	0.038	0.339
300	0.341	0.076	6.51E-18	0.022	0.877	0.025	0.338
375	0.354	0.047	5.85E-20	0.014	0.880	0.017	0.317
450	0.367	0.030	4.68E-18	0.010	0.868	0.012	0.286
525	0.381	0.019	1.36E-18	0.007	0.852	0.008	0.255
600	0.395	0.012	1.43E-24	0.005	0.834	0.005	0.226
675	0.409	0.008	7.75E-18	0.003	0.815	0.004	0.199
			UNI	QUAC			
Cumulative Distillate			<b>_</b>	• •			Isoamy
	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
/5	0.311	0.225	1.18E-16	0.045	1.433	0.037	0.209
150	0.320	0.183	1.30E-19	0.041	1.346	0.035	0.139
225	0.324	0.126	3.76E-19	0.031	1.252	0.030	0.200
300	0.333	0.088	7.53E-19	0.024	1.143	0.026	0.253
3/5	0.346	0.062	7.88E-19	0.019	1.034	0.022	0.275
450	0.359	0.044	1.30E-17	0.015	0.939	0.019	0.276
525	0.373	0.032	9.70E-21	0.012	0.851	0.017	0.270
600	0.388	0.023	1.36E-18	0.010	0.770	0.015	0.263
675	0.403	0.016	1.39E-18	0.008	0.692	0.013	0.254

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## Table D.4 Congener concentration experimental and predicted values for 10 L

		10 L Star	dard Batch Disti	llation			
		Conge	ener Concentratio	on (% v/v ir	40% Ethan	ol)	······································
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	<b>T-Butanol</b>	Alcohol
75	0.616	1.710	0.140	2.296	0.905	0.405	1.102
150	0.438	1.002	0.159	1.341	1.053	0.326	1.466
225	0.319	0.668	0.173	0.966	1.094	0.181	1.550
300	0.331	0.398	0.182	0.777	1.072	0.086	1.389
375	0.354	0.257	0.182	0.637	1.050	0.066	1.150
450	0.383	0.131	0.174	0.494	1.002	0.048	0.844
525	0.417	0.051	0.162	0.373	0.951	0.000	0.601
600	0.452	0.009	0.156	0.281	0.910	0.000	0.445
675	0.520	0.000	0.153	0.187	0.865	0.000	0.306
		Stand	lard Deviation of	Congener	Concentratio	n	
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.052	0.140	0.004	0.041	0.022	0.013	0.022
150	0.002	0.050	0.003	0.024	0.027	0.006	0.047
225	0.002	0.018	0.007	0.019	0.037	0.005	0.108
300	0.002	0.025	0.002	0.028	0.011	0.015	0.030
375	0.007	0.007	0.001	0.015	0.006	0.016	0.029
450	0.017	0.001	0.002	0.007	0.007	0.001	0.031
525	0.010	0.006	0.001	0.013	0.011	0.000	0.004
600	0.003	0.008	0.002	0.016	0.016	0.000	0.029
675	0.001	0.000	0.001	0.006	0.011	0.000	0.012
			N	TRL			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	<b>T-Butanol</b>	Alcohol
75	0.313	0.954	3.33E-07	0.827	0.747	0.118	0.310
150	0.321	0.790	2.19E-07	0.732	0.689	0.112	0.179
225	0.326	0.564	2.90E-07	0.538	0.655	0.094	0.301
300	0.336	0.404	4.23E-07	0.403	0.606	0.079	0.451
375	0.351	0.292	7.15E-07	0.308	0.550	0.067	0.552
450	0.365	0.215	1.06E-06	0.242	0.499	0.058	0.576
525	0.380	0.158	1.55E-06	0.191	0.450	0.051	0.581
600	0.396	0.115	1.99E-06	0.150	0.405	0.044	0.577
675	0.412	0.083	2.41E-06	0.117	0.362	0.038	0.568
			E	SD	-		
Cumulative Distillate							Isoamyi
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	<b>T-Butanol</b>	Alcohol
75	0.345	1.522	3.50E-05	0.693	0.427	0.012	0.001
150	0.354	0.990	2.12E-05	0.647	0.415	0.010	0.001
225	0.357	0.530	3.06E-05	0.509	0.422	0.012	0.001
300	0.364	0.289	4.83E-05	0.408	0.424	0.016	0.002
375	0.375	0.160	8.67E-05	0.332	0.423	0.019	0.004
450	0.386	0.091	1.32E-04	0.277	0.419	0.022	0.006
525	0.399	0.051	1.95E-04	0.232	0.416	0.025	0.008
600	0.411	0.028	2.52E-04	0.194	0.412	0.027	0.011
675	0.424	0.016	3.06E-04	0.162	0.407	0.030	0.013

standard batch distillations.

		101 Standard	Batch Distillation	(continued	0		_
			I IN				
Cumulative Distillate						<u> </u>	lenamy
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.233	1.083	0.137	0.820	0.390	0.195	0.485
150	0.224	0.866	0.109	0.735	0.356	0.160	0.354
225	0.244	0.546	0.103	0.531	0.388	0.112	0.463
300	0.267	0.351	0.091	0.389	0.415	0.078	0.573
375	0.298	0.229	0.074	0.287	0.436	0.054	0.647
450	0.324	0.158	0.058	0.221	0.440	0.038	0.632
525	0.348	0.110	0.045	0.173	0.438	0.027	0.594
600	0.370	0.077	0.035	0.135	0.433	0.019	0.551
675	0.394	0.053	0.027	0.105	0.427	0.013	0.506
			Modifie	d UNIFAC			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	<b>T-Butanol</b>	Alcohol
75	0.332	1.012	0.141	0.673	0.454	0.230	0.788
150	0.349	0.838	0.111	0.634	0.423	0.178	0.630
225	0.345	0.556	0.106	0.497	0.443	0.114	0.695
300	0.345	0.377	0.092	0.395	0.454	0.073	0.700
375	0.352	0.262	0.074	0.319	0.454	0.047	0.650
450	0.363	0.189	0.059	0.266	0.446	0.031	0.583
525	0.376	0.137	0.047	0.223	0.437	0.021	0.518
600	0.390	0.099	0.037	0.186	0.427	0.014	0.457
675	0.405	0.070	0.028	0.155	0.416	0.009	0.399
			UNIF	AC LLE			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.327	1.322	0.094	1.173	0.450	0.226	0.780
150	0.332	0.969	0.060	0.921	0.422	0.179	0.635
225	0.338	0.575	0.083	0.586	0.441	0.119	0.697
300	0.348	0.347	0.096	0.378	0.453	0.079	0.710
375	0.361	0.214	0.093	0.249	0.456	0.053	0.672
450	0.374	0.136	0.081	0.169	0.451	0.036	0.608
525	0.388	0.087	0.069	0.116	0.442	0.025	0.543
600	0.402	0.056	0.058	0.079	0.433	0.017	0.482
675	0.416	0.035	0.048	0.053	0.423	0.011	0.424
			UN	IQUAC			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
75	0.319	1.007	1.52E-04	0.760	0.741	0.114	0.422
150	0.327	0.822	6.85E-05	0.691	0.696	0.108	0.281
225	0.331	0.566	1.28E-04	0.524	0.648	0.092	0.407
300	0.340	0.394	2.77E-04	0.404	0.593	0.079	0.521
375	0.353	0.278	6.68E-04	0.319	0.536	0.068	0.572
450	0.366	0.200	1.15E-03	0.257	0.487	0.059	0.574
525	0.381	0.144	1.77E-03	0.208	0.442	0.052	0.564
600	0.395	0.103	2.34E-03	0.168	0.400	0.045	0.548
675	0.411	0.073	2.90E-03	0.135	0.360	0.039	0.529

## Table D.5 Congener concentration experimental and predicted values for 150 L

		150	L Fruit Distillation	xn			
		Cong	ener Concentrat	ion (% v/v ir	n 40% Ethano	ol)	_
Cumulative Distillate					<u>E'31</u>		Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
750	0.493	5.263	0.064	1.983	0.446	0.704	0.159
1500	0.452	0.567	0.062	0.861	0.477	0.197	0.172
2250	0.443	0.261	0.069	0.464	0.532	0.062	0.215
3000	0.430	0.152	0.080	0.289	0.599	0.012	0.281
3750	0.386	0.092	0.097	0.209	0.677	0.009	0.370
4500	0.365	0.060	0.114	0.165	0.737	0.005	0.459
5250	0.356	0.037	0.138	0.137	0.803	0.004	0.573
6000	0.352	0.020	0.164	0.115	0.849	0.003	0.685
6750	0.336	0.009	0.198	0.095	0.894	0.000	0.821
7500	0.324	0.002	0.236	0.081	0.916	0.000	0.948
8250	0.335	0.003	0.275	0.072	0.912	0.000	1.023
9000	0.332	0.000	0.296	0.062	0.875	0.000	0.995
9750	0.339	0.000	0.289	0.055	0.793	0.000	0.754
10500	0.333	0.000	0.232	0.049	0.715	0.000	0.443
11250	0.349	0.000	0.183	0.042	0.658	0.000	0.275
12000	0.413	0.000	0.161	0.035	0.625	0.000	0.203
		Stan	dard Deviation of	f Congener	Concentratio	n	
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	<b>T-Butanol</b>	Alcohol
750	0.031	0.872	0.002	0.080	0.009	0.056	0.011
1500	0.037	0.102	0.001	0.049	0.012	0.024	0.007
2250	0.010	0.072	0.001	0.056	0.001	0.012	0.005
3000	0.049	0.036	0.003	0.041	0.004	0.011	0.014
3750	0.036	0.016	0.001	0.015	0.011	0.002	0.004
4500	0.054	0.013	0.000	0.014	0.017	0.002	0.010
5250	0.033	0.006	0.001	0.008	0.007	0.001	0.004
6000	0.026	0.006	0.001	0.008	0.003	0.000	0.002
6750	0.022	0.004	0.002	0.005	0.015	0.000	0.015
7500	0.019	0.003	0.003	0.005	0.015	0.000	0.024
8250	0.023	0.000	0.002	0.006	0.019	0.000	0.019
9000	0.016	0.000	0.003	0.004	0.019	0.000	0.020
9750	0.011	0.000	0.004	0.005	0.018	0.000	0.030
10500	0.007	0.000	0.010	0.004	0.019	0.000	0.040
11250	0.003	0.000	0.010	0.004	0.016	0.000	0.030
12000	0.006	0.000	0.006	0.003	0.017	0.000	0.018

#### fruit distillations.

		150 L Fru	it Distillation (cor	ntinued)			
			1	NRTL			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
750	0.322	0.262	5.72E-08	0.089	1.114	0.046	0.059
1500	0.378	0.249	3.19E-08	0.134	0.767	0.054	0.015
2250	0.375	0.186	3.31E-08	0.078	0.780	0.046	0.018
3000	0.346	0.126	4.37E-08	0.033	0.941	0.034	0.037
3750	0.346	0.093	4.61E-08	0.023	0.937	0.029	0.045
4500	0.339	0.064	5.60E-08	0.014	0.981	0.023	0.075
5250	0.341	0.046	6.04E-08	0.010	0.953	0.020	0.096
6000	0.339	0.031	8.26E-08	0.007	0.950	0.016	0.199
6750	0.345	0.022	9.33E-08	0.005	0.887	0.013	0.261
7500	0.354	0.015	1.35E-07	0.004	0.817	0.011	0.449
8250	0.366	0.011	1. <b>64E-0</b> 7	0.003	0.738	0.009	0.533
9000	0.383	0.007	2.51E-07	0.002	0.656	0.008	0.633
9750	0.400	0.005	3.12E-07	0.002	0.583	0.007	0.647
10500	0.419	0.004	4.09E-07	0.001	0.513	0.006	0.646
11250	0.439	0.003	5.08E-07	0.001	0.449	0.005	0.632
12000	0.459	0.002	5.06E-07	0.001	0.389	0.004	0.606
				ESD			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
750	0.348	0.453	5.02E-06	0.072	0.639	0.002	0.000
1500	0.415	0.426	2.45E-06	0.115	0.521	0.001	0.000
2250	0.410	0.161	2.57E-06	0.077	0.532	0.002	0.000
3000	0.373	0.049	3.67E-06	0.037	0.604	0.002	0.000
3750	0.373	0.024	3.96E-06	0.029	0.615	0.002	0.000
4500	0.364	0.010	5.09E-06	0.020	0.650	0.003	0.000
5250	0.366	0.005	5.65E-06	0.015	0.660	0.003	0.000
6000	0.363	0.002	8.43E-06	0.011	0.693	0.004	0.001
6750	0.368	0.001	9.87E-06	0.009	0.698	0.004	0.001
7500	0.374	0.001	1. <b>56E-0</b> 5	0.007	0.709	0.006	0.001
8250	0.384	0.000	1. <b>96E-0</b> 5	0.005	0.706	0.007	0.002
9000	0.397	0.000	3.16E-05	0.004	0.703	0.009	0.003
9750	0.410	0.000	4.02E-05	0.004	0.697	0.010	0.004
10500	0.425	0.000	5.41E-05	0.003	0.689	0.011	0.005
11250	0.441	0.000	6.82E-05	0.002	0.680	0.012	0.006
12000	0.456	0.000	6.82E-05	0.002	0.671	0.013	0.006

		150 L Fru	it Distillation (cor	ntinued)			
			U	NIFAC			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
750	0.198	0.332	0.040	0.089	0.502	0.078	0.173
1500	0.169	0.437	0.019	0.132	0.342	0.077	0.068
2250	0.175	0.185	0.020	0.077	0.360	0.055	0.076
3000	0.197	0.057	0.029	0.032	0.456	0.035	0.131
3750	0.205	0.033	0.030	0.022	0.480	0.025	0.149
4500	0.223	0.017	0.034	0.014	0.546	0.017	0.209
5250	0.234	0.010	0.033	0.010	0.575	0.012	0.241
6000	0.260	0.006	0.035	0.006	0.662	0.007	0.361
6750	0.276	0.004	0.031	0.005	0.692	0.005	0.412
7500	0.308	0.002	0.027	0.003	0.759	0.003	0.541
8250	0.332	0.001	0.022	0.002	0.783	0.002	0.582
9000	0.374	0.001	0.017	0.002	0.818	0.002	0.633
9750	0.407	0.001	0.013	0.001	0.821	0.001	0.606
10500	0.445	0.000	0.009	0.001	0.816	0.001	0.560
11250	0.482	0.000	0.007	0.001	0.803	0.000	0.505
12000	0.518	0.000	0.005	0.001	0.786	0.000	0.448
			Modifi	ed UNIFAC			· · · · · · · · · · · · · · · · · · ·
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
750	0.353	0.304	0.038	0.070	0.620	0.096	0.365
1500	0.464	0.427	0.015	0.107	0.432	0.097	0.142
2250	0.455	0.200	0.016	0.074	0.451	0.058	0.157
3000	0.390	0.067	0.027	0.038	0.561	0.028	0.268
3750	0.385	0.041	0.028	0.029	0.582	0.018	0.296
4500	0.365	0.023	0.035	0.020	0.646	0.010	0.391
5250	0.364	0.015	0.035	0.016	0.668	0.006	0.424
6000	0.348	0.009	0.039	0.011	0.740	0.004	0.552
6750	0.350	0.006	0.035	0.009	0.755	0.002	0.563
7500	0.347	0.004	0.030	0.007	0.789	0.001	0.594
8250	0.354	0.003	0.024	0.006	0.788	0.001	0.551
9000	0.364	0.002	0.019	0.004	0.783	0.001	0.495
9750	0.377	0.001	0.014	0.004	0.765	0.000	0.432
10500	0.394	0.001	0.011	0.003	0.745	0.000	0.372
11250	0.413	0.001	0.008	0.002	0.723	0.000	0.316
12000	0.433	0.000	0.006	0.002	0.698	0.000	0.265

## Table D.6 Congener concentration experimental and predicted values for 150 L

	150 L Standard Batch Distillation								
		Conge	ener Concentration	on (% v/v ir	n 40% Ethano	ol)			
Cumulative Distillate							Isoamyl		
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol		
750	0.473	2.291	0.126	2.475	0.799	2.373	0.635		
1500	0.396	0.768	0.146	1.473	1.038	1.230	1.144		
2250	0.377	0.610	0.142	1.230	1.014	0.792	1.077		
3000	0.356	0.381	0.145	0.911	1.007	0.399	1.042		
3750	0.345	0.257	0.149	0.750	1.003	0.245	1.035		
4500	0.348	0.190	0.153	0.643	1.014	0.156	1.042		
5250	0.336	0.159	0.155	0.517	0.986	0.020	0.969		
6000	0.346	0.133	0.152	0.482	0.958	0.006	0.862		
6750	0.339	0.077	0.141	0.335	0.922	0.000	0.780		
7500	0.355	0.057	0.148	0.343	0.883	0.000	0.651		
8250	0.360	0.025	0.142	0.262	0.828	0.000	0.509		
9000	0.368	0.003	0.135	0.205	0.758	0.000	0.368		
9750	0.376	0.000	0.129	0.159	0.701	0.000	0.275		
10500	0.380	0.000	0.126	0.124	0.650	0.000	0.210		
11250	0.388	0.000	0.123	0.088	0.598	0.000	0.155		
12000	0.401	0.000	0.122	0.064	0.535	0.000	0.110		
			E	rror					
Cumulative Distillate							Isoamyl		
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol		
750	0.013	0.394	0.094	0.040	0.198	0.309	0.168		
1500	0.020	0.069	0.077	0.126	0.053	0.088	0.001		
2250	0.018	0.008	0.077	0.067	0.065	0.039	0.006		
3000	0.021	0.029	0.077	0.022	0.081	0.034	0.038		
3750	0.021	0.015	0.077	0.000	0.071	0.005	0.026		
4500	n/a	n/a	n/a	n/a	n/a	n/a	n/a		
5250	0.017	0.005	0.079	0.087	0.047	0.001	0.042		
6000	0.024	0.024	0.077	0.010	0.056	0.001	0.010		
6750	0.015	0.027	0.094	0.186	0.055	0.001	0.029		
7500	0.024	0.015	0.081	0.006	0.064	0.000	0.001		
8250	0.010	0.000	0.083	0.022	0.083	0.000	0.011		
9000	0.012	0.000	0.084	0.001	0.078	0.000	0.006		
9750	0.010	0.000	0.088	0.000	0.091	0.000	0.009		
10500	0.011	0.000	0.091	0.001	0.081	0.000	0.004		
11250	0.014	0.000	0.094	0.004	0.058	0.000	0.017		
12000	0.001	0.000	0.098	0.006	0.075	0.000	0.008		

### standard batch distillations.

		150 L Standard	Batch Distillation	n (continue	d)		
			N	RTL			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
750	0.270	1.185	7.07E-07	1.103	0.697	0.430	0.071
1500	0.320	1.189	4.09E-07	1.718	0.486	0.522	0.019
2250	0.313	0.856	4.17E-07	0.992	0.493	0.438	0.022
3000	0.286	0.560	5.37E-07	0.408	0.591	0.317	0.046
3750	0.286	0.409	5.63E-07	0.284	0.589	0.271	0.056
4500	0.281	0.281	6.75E-07	0.178	0.617	0.217	0.094
5250	0.284	0.201	7.25E-07	0.128	0.600	0.185	0.120
6000	0.285	0.134	9.79E-07	0.084	0.599	0.146	0.248
6750	0.291	0.096	1.10E-06	0.063	0.561	0.124	0.324
7500	0.301	0.065	1.57E-06	0.045	0.518	0.102	0.556
8250	0.312	0.047	1.88E-06	0.034	0.469	0.086	0.661
9000	0.328	0.033	2.86E-06	0.026	0.417	0.072	0.790
9750	0.342	0.023	3.56E-06	0.020	0.371	0.062	0.809
10500	0.359	0.016	4.69E-06	0.015	0.327	0.052	0.810
11250	0.376	0.011	5.83E-06	0.012	0.287	0.044	0.792
12000	0.393	0.008	5.79E-06	0.009	0.249	0.037	0.761
				ESD			
Cumulative Distillate							Isoamyl
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol
750	0.300	2.077	6.04E-05	0.905	0.401	0.022	0.000
1500	0.364	2.041	3.08E-05	1.482	0.328	0.014	0.000
2250	0.353	0.762	3.15E-05	0.980	0.334	0.014	0.000
3000	0.318	0.228	4.42E-05	0.468	0.380	0.019	0.000
3750	0.317	0.110	4.77E-05	0.357	0.387	0.020	0.000
4500	0.309	0.049	6.11E-05	0.245	0.409	0.025	0.000
5250	0.311	0.025	6.77E-05	0.191	0.415	0.027	0.001
6000	0.307	0.011	1.00E-04	0.135	0.436	0.036	0.001
6750	0.312	0.006	1.17E-04	0.108	0.439	0.041	0.001
7500	0.317	0.003	1.84E-04	0.083	0.445	0.054	0.002
8250	0.325	0.002	2.30E-04	0.068	0.444	0.062	0.002
9000	0.337	0.001	3.70E-04	0.054	0.442	0.077	0.004
9750	0.348	0.000	4.71E-04	0.045	0.438	0.088	0.005
10500	0.360	0.000	6.33E-04	0.037	0.433	0.100	0.006
11250	0.374	0.000	7.98E-04	0.030	0.428	0.112	0.008
12000	0.386	0.000	7.97E-04	0.024	0.422	0.119	0.008

150 L Standard Batch Distillation (continued)										
	UNIFAC									
Cumulative Distillate							Isoamyl			
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	<b>T-Butanol</b>	Alcohol			
750	0.167	1.538	0.443	1.120	0.308	0.739	0.203			
1500	0.142	2.108	0.207	1.715	0.211	0.737	0.081			
2250	0.147	0.880	0.227	0.989	0.223	0.538	0.092			
3000	0.166	0.270	0.340	0.414	0.284	0.345	0.160			
3750	0.172	0.155	0.352	0.286	0.299	0.250	0.183			
4500	0.187	0.081	0.409	0.178	0.341	0.169	0.257			
5250	0.196	0.049	0.405	0.127	0.359	0.120	0.296			
6000	0.219	0.027	0.442	0.081	0.413	0.078	0.445			
6750	0.232	0.017	0.402	0.060	0.432	0.055	0.508			
7500	0.258	0.011	0.366	0.042	0.475	0.036	0.671			
8250	0.278	0.007	0.302	0.031	0.490	0.025	0.726			
9000	0.313	0.004	0.238	0.022	0.514	0.016	0.798			
9750	0.340	0.003	0.181	0.017	0.516	0.011	0.767			
10500	0.372	0.002	0.134	0.013	0.513	0.007	0.710			
11250	0.404	0.001	0.098	0.010	0.505	0.005	0.642			
12000	0.433	0.001	0.070	0.007	0.495	0.003	0.569			
			Modifie	d UNIFAC						
Cumulative Distillate							Isoamyl			
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol			
750	0.306	1.411	0.418	0.883	0.382	0.919	0.433			
1500	0.402	2.047	0.162	1.366	0.267	0. <del>9</del> 47	0.171			
2250	0.391	0.941	0.181	0.941	0.281	0.574	0.193			
3000	0.334	0.314	0.305	0.480	0.350	0.289	0.332			
3750	0.330	0.193	0.326	0.370	0.364	0.184	0.367			
4500	0.312	0.106	0.407	0.258	0.404	0.108	0.486			
5250	0.310	0.069	0.416	0.203	0.418	0.068	0.529			
6000	0.297	0.040	0.484	0.144	0.464	0.040	0.691			
6750	0.298	0.027	0.447	0.115	0.474	0.025	0.710			
7500	0.295	0.017	0.410	0.087	0.496	0.015	0.756			
8250	0.300	0.012	0.335	0.071	0.496	0.010	0.704			
9000	0.307	0.008	0.261	0.056	0.494	0.006	0.635			
9750	0.318	0.006	0.200	0.046	0.483	0.004	0.556			
10500	0.332	0.004	0.150	0.038	0.471	0.002	0.479			
11250	0.348	0.003	0.111	0.031	0.456	0.001	0.408			
12000	0.364	0.002	0.080	0.025	0.441	0.001	0.342			

	150 L Standard Batch Distillation (continued)									
	UNIFAC LLE									
Cumulative Distillate							Isoamyl			
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol			
750	0.273	1.831	0.129	1.617	0.383	0.886	0.442			
1500	0.294	2.143	0.029	2.116	0.271	0.932	0.182			
2250	0.293	0.869	0.035	0.936	0.286	0.594	0.207			
3000	0.285	0.273	0.083	0.311	0.354	0.316	0.351			
3750	0.287	0.147	0.100	0.182	0.367	0.210	0.385			
4500	0.289	0.073	0.165	0.097	0.406	0.129	0.499			
5250	0.293	0.042	0.199	0.059	0.418	0.085	0.537			
6000	0.297	0.022	0.350	0.033	0.460	0.052	0.683			
6750	0.303	0.013	0.406	0.021	0.469	0.034	0.698			
7500	0.312	0.007	0.562	0.013	0.491	0.022	0.748			
8250	0.321	0.005	0.577	0.008	0.493	0.014	0.707			
9000	0.335	0.003	0.573	0.005	0.495	0.009	0.654			
9750	0.348	0.002	0.491	0.004	0.486	0.006	0.578			
10500	0.363	0.001	0.406	0.002	0.476	0.004	0.502			
11250	0.379	0.001	0.328	0.002	0.463	0.002	0.431			
12000	0.394	0.000	0.259	0.001	0.449	0.002	0.364			
			UN	IQUAC						
Cumulative Distillate							Isoamyl			
Volume (mL)	Methanol	Acetaldehyde	Benzaldehyde	Acetone	1-Propanol	T-Butanol	Alcohol			
750	0.276	1.299	1.37E-04	1.004	0.741	0.402	0.130			
1500	0.337	1.480	4.67E-05	1.609	0.569	0.455	0.037			
2250	0.329	0.929	5.09E-05	0.992	0.568	0.397	0.043			
3000	0.296	0.486	8.94E-05	0.435	0.635	0.312	0.087			
3750	0.295	0.330	1.02E-04	0.316	0.619	0.274	0.103			
4500	0.288	0.206	1.55E-04	0.206	0.618	0.228	0.165			
5250	0.290	0.140	1.86E-04	0.154	0.589	0.198	0.202			
6000	0.289	0.088	3.55E-04	0.104	0.562	0.162	0.367			
6750	0.294	0.061	4.66E-04	0.080	0.520	0.140	0.447			
7500	0.302	0.040	9.88E-04	0.059	0.472	0.116	0.650			
8250	0.311	0.028	1.46E-03	0.047	0.426	0.100	0.713			
9000	0.325	0.019	3.07E-03	0.036	0.380	0.084	0.773			
9750	0.339	0.013	4.39E-03	0.029	0.340	0.072	0.762			
10500	0.354	0.009	6.51E-03	0.023	0.302	0.062	0.740			
11250	0.371	0.006	8.76E-03	0.018	0.268	0.052	0.708			
12000	0.387	0.004	9 12E-03	0.014	0 235	0 044	0.669			

## **LITERATURE CITED**

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