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AN INVESTIGATION OF RELATIONSHIP BETWEEN TRAY USAGE OF THE STILL AND CONGENER COMPOUND CONCENTRATION IN DISTILLED FRUIT SPIRITS

By

Michael Joseph Claus

A THESIS

Submitted to
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ABSTRACT

AN INVESTIGATION OF RELATIONSHIP BETWEEN TRAY USAGE OF THE STILL AND CONGENER COMPOUND CONCENTRATION IN DISTILLED FRUIT SPIRITS

By

Michael Joseph Claus

The relationship between the operating parameters of batch column stills with reflux and the congener (trace compounds that provide flavors and aromas) concentrations in the resulting distilled beverage product is not fully understood. To explore this relationship congener concentration were determined in three different collection fraction, or "cuts," of the batch distillation. Methanol was studied because the distillate must adhere to governmental regulations that limit its concentration in the product. Ethanol was studied as changes in the operating conditions of the still affect the ethanol concentration and resulting yield of the process. Operating condition parameters that were studied include the number of trays used in the distillation as well as the use of the "catalytic converter," a high surface copper packing material thought to catalyze formation of cyanide containing compounds allowing them to be separated from the distillate. The effect of the number of trays used in a distillation on the concentration of ethanol and the highest concentration congeners, methanol, acetaldehyde, ethyl formate, ethyl acetate, 1-propanol, 2-methyl-2-propanol, isoamyl alcohol, and benzaldehyde in the final distilled spirits product is presented.

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I would like to thank the vintners and distillers who have shared their interest in the production of fruit spirits. The growing number of stills at wineries has kept me focused to completion of this thesis. Finally thank you for reading I hope it is useful and enjoyable reading for you.

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1. INTRODUCTION

1.1 Michigan Fruit Brandy Industry

The Michigan fruit brandy industry has been growing since recent changes in the state laws of Michigan regarding the licensing of fruit distilleries. The number of stills in Michigan for the distillation of fruit spirits has grown from zero in 1996 to seven in the year 2000. The distillation of fruit spirits has been practiced for centuries in Europe; however, only recently has the distillation industry grown in the United States. The two competing styles for fruit brandy distillation are alambic, i.e. French style, and the other is batch distillation, i.e. German style. The French style, resulting in cognac style spirits, involves distillation through a simple pot still, requiring multiple distillations in order to obtain high proof spirits. The German style of fruit distillation, which results in eau-de-vie or schnaps, involves a single pass through a batch still with a reflux column to obtain high proof spirits. These spirits are traditionally stored in glass and are served as water clear brandies[1]. The batch column still is designed to preserve the delicate fruit essences, making it the desired distillation process for most fruit spirits.

The United States industry faces challenges that differ from those in Europe. The process of distilling fruit spirits involves fermentation of the whole fruit. Utilization of the whole fruit leads to a better sensory experience for the consumer of the fruit brandy; however, by using the pectin of the fruit, and the stones in stone fruit spirits, the concentrations of many of the congener components (compounds other than ethanol and water) can be greatly increased from other classes of distilled spirits. Many types of congeners are present in the fruit spirits. Some compounds have higher concentration in the early portion of the distillation process, and others are higher in the later portion of the distillation process. Because the distillation process is a method of concentrating, or separating the volatile compounds from the non-volatile compounds, higher concentrations of these volatiles are found in the distillate. Some of these volatile compounds, such as methanol, can have chronic health effects if relatively high concentrations are consumed, and are therefore regulated[1, 2]. Compounds such as urethane (ethyl carbamate) which is thought to be a carcinogen, and methanol, which can cause many health risks, are regulated in many countries, but the regulations differ. The United States has currently set the regulation of methanol in fruit spirits to be 0.35% v/v, where in Europe the regulations for methanol have been set higher and therefore are not as much of a concern there[1, 2]. The regulations on urethane in Canada are set at 400ppb[3]. Currently the United States has not set a regulatory limit, however, the fruit spirits industry needs to minimize the concentration of the urethane in the fruit spirits to avoid regulation.

It is widely known that the greater the number of trays used in a distillation process the more separation of the components will be achieved[1, 4, 5, 6]. An example of this can be seen in Figure 1.1, which represents a sample McCabe-Thiele diagram, which shows that the use of seven trays yields a higher concentration of ethanol in the distillate than using two trays. However, most studies have included two or three component mixtures, whereas fruit spirits have hundreds of different compounds present in the distillate, many of which are positive flavor components[4]. The composition of the fruit distillate must have a good aroma and flavor in order to sell at market, but it must also meet limits for those compounds that are regulated. The compounds that are present in the distillation, other than the two main components, ethanol and water, are called

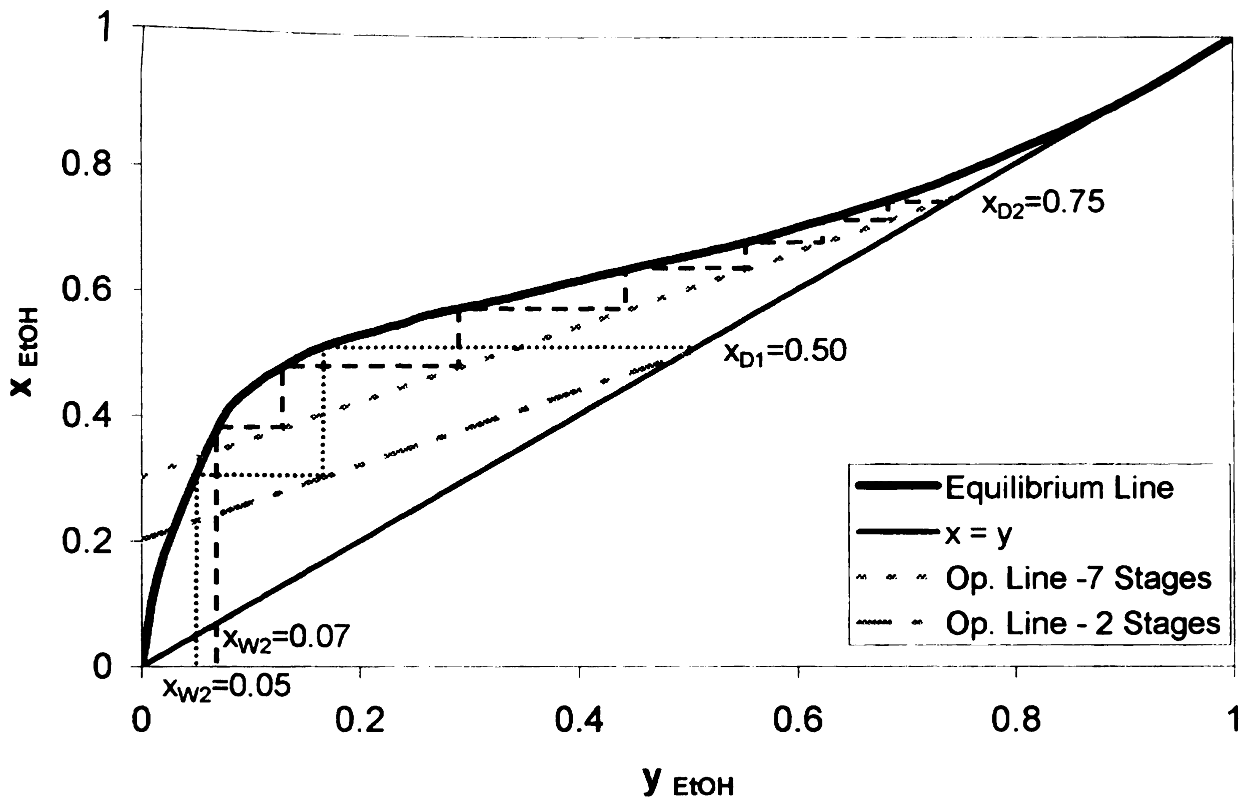

Figure 1.1 McCabe-Thiele Diagram. Using more stages yields a higher concentration of ethanol in the distillate. The values demonstrate the effect and are not experimental data.

congeners. Some congeners are present in greater concentration in the early part of the distillation and others are present in higher concentrations at the end of the distillation, while still others have a more consistent concentration throughout the distillation process.

1.2 Distillation Process

The distillation of fruit brandies can be broken down into four basic steps: fruit processing (mashing), fermentation, distillation, and storage[1]. A representation of the process involved in making fruit spirits can be seen in Figure 1.2. The fruit chosen for distilled spirits can include fruit unsuitable for market such as that fruit which is overripe and those with blemishes, making the fruit from late harvest the ideal choice for use in distillation. Fresh fruit donate better aromatic and flavor properties than that which has been frozen.

The mashing of the fruit can take many forms, from mashing the fruit beneath ones feet, to a modern rolling mill or processing pump. For large volumes of fruit where manual mashing of the fruit is not an economical process, rolling mills and progressive cavity pumps are utilized. Both the rolling mill and pump will crush the pulp of the fruit while keeping most of (~90%) of the pits, in the case of stone fruit, from being cracked. The cracked pits from stone fruit are thought to increase the amount of urethane and benzaldehyde in the distilled spirits[1, 3]. The compound amygdalin is found in the pits of stone fruits and one mole can be hydrolyzed to two moles of glucose, and one mole each of cyanide and benzaldehyde[3]. Benzaldehyde is a positive flavor component and is commonly known as bitter almond oil, but urethane is a suspect carcinogen.

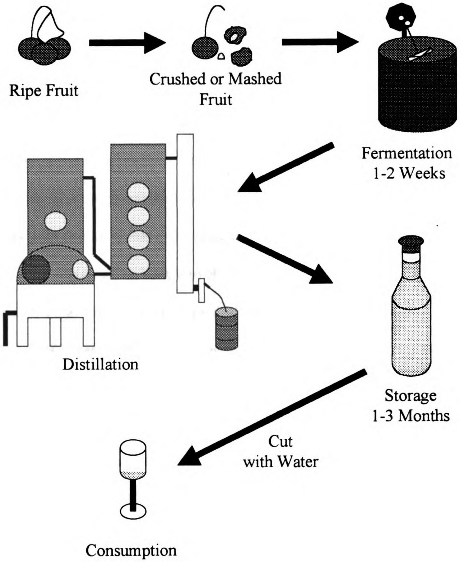

Figure 1.2. The process of making distilled fruit spirits.

The resulting mash from the processed whole fruit is then transported to a fermenter where yeast is added to begin the fermentation. The yeast added must first be inoculated in warm water before being added to the mash. By adding excess yeast, the added strain can effectively compete with the wild strains of yeast present in the mash and prevent their growth. A method of stirring the fermentation is useful for enhanced heat transfer, where a temperature control is essential to the fermenter used. The fermentations of fruit mashes should be kept within the temperature range from between 15° and 20° C. If the temperature becomes too high the yeast will produce more compounds such as ethyl acetate, and fusel alcohols. If the temperature drops too far below 15° C the yeast will be unable to efficiently ferment the fruit mash. Measurement of the brix (% sugar, weight basis) is an ideal way to examine the progress of the fermentation. Brix can be measured using refractive index, and a more detailed observation of the fermentation can be done through HPLC with either refractive index detection, or UV/Vis detection. The pH of the fermentation should also be controlled. The yeast survive in a pH range greater than 2.8 and less than 5.2. A pH range of 3.5 to 4.2 is m commonly used[1]. The pH of the mash can be changed with a number of different acids or bases, however, phosphoric acid or ammonia are considered the favored solutions to change the pH of the solution because each provide either nitrogen or phosphorus nutrients for the yeast. If a fermentation becomes "stuck," or appears to have a high concentration of sugar dissolved in solution, but is not producing the CO_2 side product or not reducing the sugar concentration, the reasoning is often because the yeast does not have enough nutrients. Dibasic ammonium phosphate is the best choice for adding nutrients to a stuck fermentation.

The average fermentation lasts for ten to fifteen days. The fermented mash is distilled in a batch column still with reflux in a single pass. The distillate is collected in volumes referred to as heads (discarded first fraction), hearts (product), and tails (discarded or redistilled last fraction). The clear spirits are then stored at high (>100°) proof. The storage of the spirits lasts for as little as three months prior to proof adjustment with distilled water. The product is then bottled and is ready for consumption.

1.3 Batch Distillation of Fruit Spirits

From an engineering standpoint the mass balances of batch distillation are somewhat different from those for continuous distillation. In batch distillation we are more interested in the total amounts of bottoms and distillate collected than in the rates[6]. This correlates to the German farmer who wishes to maximize distillate per volume of fruit mash than they are about the time it takes to run the still.

The distillation of fruit brandies is more complicated than the simple binary distillation of ethanol and water. There are many compounds present in varying concentrations throughout the process of distillation of fruit spirits. Fruit distillates differ widely in quality and composition, dependent on the raw material used and the processing procedures[3]. These various parameters lead to poor reproducibility of the distilled spirits form one batch to the next. In comparison to other spirit groups (e.g. whiskey, vodka, gin, ...) they contain the highest amounts of alcohols and esters. The sum of volatiles in fruit brandies amount to an average of nearly 2000 mg/ 100 ml ethanol with exceptions of Calvados (apples) and raspberry brandy. This can be compared with a

Scotch whiskey, which has an average sum of the volatiles of about 200 mg/ 100ml ethanol[3].

1.4 Congener Compound Formation

Various acids, esters, and fusel alcohols form the main body of the aroma compounds in the distilled spirits[7]. Some other compounds are also present as congeners, however, the majority of the congeners in the spirits are these aroma compounds. The formation of most of the congeners in the distillation occurs in the fermentation of the mash in the influence of yeast[7]. Fusel alcohols, defined as alcohols with more than two carbons, compose the largest group of aroma compounds in alcoholic beverages. Isoamyl alcohol is the main fusel alcohol synthesized during fermentation by yeast. Other important fusel alcohols include n-propanol, isobutyl alcohol, and optically active amyl alcohol[7]. 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. N-propanol, and branched C_4 and C_6 alcohols are formed from valine, leucine, and isoleucine in the presence of yeast. α-keytobuteric acid is thought to act as in intermediary in formation of n-propyl alcohol and optically active amyl alcohol[7,8]. Fusel alcohols are thought to form in fermentation under both catholic conditions from amino acids and anabolic conditions from sugars[7].

Yeast synthesizes fatty acids irrespective of the nature of the raw materials involved in the fermentation[7]. The acids formed in the fermentation mash are thought to be bacteria products as well as byproducts of the formation of alcohol by the yeast. It has been shown that with semi-aerobic conditions in the fermentation, lower temperatures result in an increased amount of organic acids in the distilled spirits[7].

Carbonyl compounds, specifically aldehydes, are thought to be intermediates in the formation of fusel alcohols, and acids by the yeast. Aldehydes can also be oxidized to form more acids when the fermenter is not sealed properly creating aerobic conditions rather than the anaerobic conditions found in most fermentations[7]. Most esters found in the fermentation are ethyl esters due to the high concentration of ethanol relative to all the other alcohols in the fermentation mash. It has been shown that distillation in the presence of yeast will increase the amount of ethyl esters present in the distillate when compared to the distilled spirits with no yeast present in the distillation pot[7].

Two other compounds of importance in the distillation process can be traced to the pits of stone fruit. Amygdalin contains two moles of glucose for every one mole of benzaldehyde and one mole of cyanide. The hydrolysis of amygdalin in the fermentation produces the benzaldehyde, which is desired, and the prussic acid, which is undesired, as it is thought to be a reagent in the formation of ethyl carbamate[3]. Figure 1.3 shows the hydrolysis of amygdalin.

Methanol is also formed through fermentation of the fruit sugars; however, a prominent source of the methanol is an enzymatic reaction of pectinesterase with the pectin of the fruit. Although methanol is a desired compound for flavor and aroma, and at the same time a regulated compound for the health hazards it possesses, a method for limiting the amount of methanol produced has not been discovered to product.

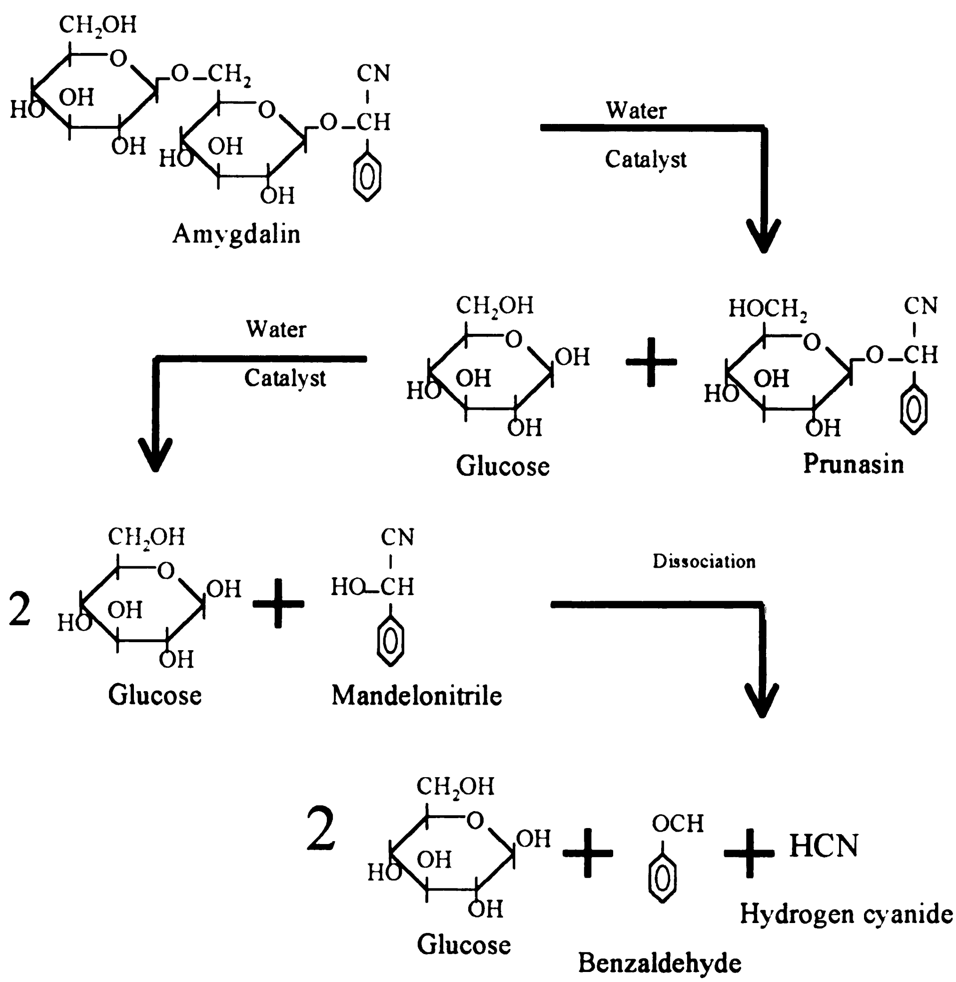

Figure 1.3 **Hydrolysis of amygdalin. The process of the breakdown of amygdalin to benzaldehyde, hydrogen cyanide, and glucose in the fermentation mash[3].**

Overall most of the congeners in the distillation of fruit spirits are products of the fermentation of the fruit by the yeast[7]. The distillation of these compounds also makes more of the congeners especially in the case of ethyl esters. Further synthesis of the flavor and aroma compounds occurs in the storage of the spirits; however, these are mostly oxidative processes between the congeners already present in the spirits[1].

1.5 Catalytic Converter

The catalytic converter of the still contains a high surface area copper packing material in a stainless steel vessel. The distillate vapor is introduced through the bottom of the packing material and from the top of the vessel on its way directly to the condensing column. The catalytic converter has valves located in the distillation stream such that it can be bypassed if desired. The catalytic converter has been thought to remove urethane from the distilled fruit spirits. The theory behind the catalytic converter involves the cyanide containing compounds binding to the copper metal surface in the catalytic converter, and thus being effectively removed from the distillate[9]. These cyanide-containing compounds, which can be traced back to the amygdalin in the pits of the fruit, would form cyanic acid in the distillate, and then during storage of the distillate, the cyanic acid would react with the ethanol to form ethyl carbamate. It is not well know if the catalytic converter will function to effectively remove enough cyanide containing compounds to keep the spirits under the 400 ppb limit the Canadian government has set regulating ethyl carbamate in distilled spirits[3]. The focus of this thesis does not deal with the effectiveness of the catalytic converter as a tool for removal of the cyanide derived compounds from the distillate. Instead, the catalytic converter was studied with respect to its ability to act as an additional tray in the multistage distillation process. The catalytic converter it should be noted is not a true definition of a catalytic converter, however, the German still manufacturers have called it a catalytic converter and the name persists[9].

1.6 Objective

The objectives of this study are to determine a characteristic profile for some of the congeners present in distilled fruit spirits and how changing the operating conditions used in the distillation process affects the concentrations of these components. Another objective is to test the usefulness of the catalytic converter portion of the still as to how it affects the congeners of the distilled spirits. A further aim includes developing a profile for the ethanol concentration in the batch distillation with reflux of fruit spirits and how the number of trays used affect this concentration. The final purpose of these experiments is to develop a method for determining the approximate concentration of the congener components in the bottled fruit spirits from the cuts taken of distillate during the distillation process.

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2. BACKGROUND INFORMATION

2.1 Distillation History

The history of distillation is thought to have stared around 800 BC in China and India with the concentrating of the alcohol from rice and barley beer. Distillation was also used in the Middle East and Mediterranean for the concentrating essences for perfumes. Around 1100 AD in Salerno doctors began using distillation to extract alcohol from wine because it was thought that alcohol had medicinal effects. In 1300 Catalan physicians gave the name aqua vitae, "water of life," to the distillate of wines. This term can be found translated into many different languages[1, 2].

The addition of herbs, spices, or fruit was used to mask the harsh taste of the distillate and was thought to add to the medicinal effect of the spirits. The distillation process used in antiquity involve only a pot and simple one tray column with a condenser. One pass of the wine would yield a harsh tasting distillate, and thus need to be masked. This style of distillation is still common today in the Cognac region of France and the whisky distillers in Scotland. These distillers use multiple passes through their alambic type stills, but storage of these spirits must be done in wooden barrels. The alcohol will extract flavors from the barrels giving the classic flavors to the whisky and cognac. The alambic style still, developed in the middle ages, involves a pot, alembic head, which functions as the distillation column, and a condenser. Multiple passes through this type of still must be made in order to concentrate the ethanol out of whatever mash is used to the concentration desired[1, 2].

In the 19th century the continuous still was developed. This type of still allows the passing of vapor through multiple stages on one distillation. This method avoids the need to send the distillate through the still more than once which leads to losses of the total volume that could be collected. The modern multistage still can be made with over a hundred trays to remove most flavor components for the production of vodkas. The production of fruit spirits by European farmers has been going on for hundreds of years, and uses these multistage stills. The market for these types of fruit spirits, which has begun in the United States in the last decade, is attempting to follow the example of the European farmer in the production of their fruit spirits. While distillation has come a long way, the understanding of the interaction of the hundreds of compounds found in the distillate and how their interaction effect the overall quality of the distillate needs to be studied more[1, 2].

2.2 Distilled Beverage Flavor Analysis

Fruit distillates differ widely in quality and composition, dependent upon the raw materials used and the processing procedures. In comparison with other distilled spirits fruit distillates have more volatiles, as well as the highest amount of esters and alcohols. The sum of the volatiles in fruit spirits in comparison to other distilled beverages can be seen in Figure 2.1. The concentration of volatile compounds in fruit distillates can be as much as one hundred times as much as could be found in gin or vodka[3].

Methanol is quantitatively the main congener of stone and pome fruit brandies. Methanol poses a health hazard, as methanol is associated with acute and chronic health effects, however, it is also a desired component for flavor and aroma. Because a certain

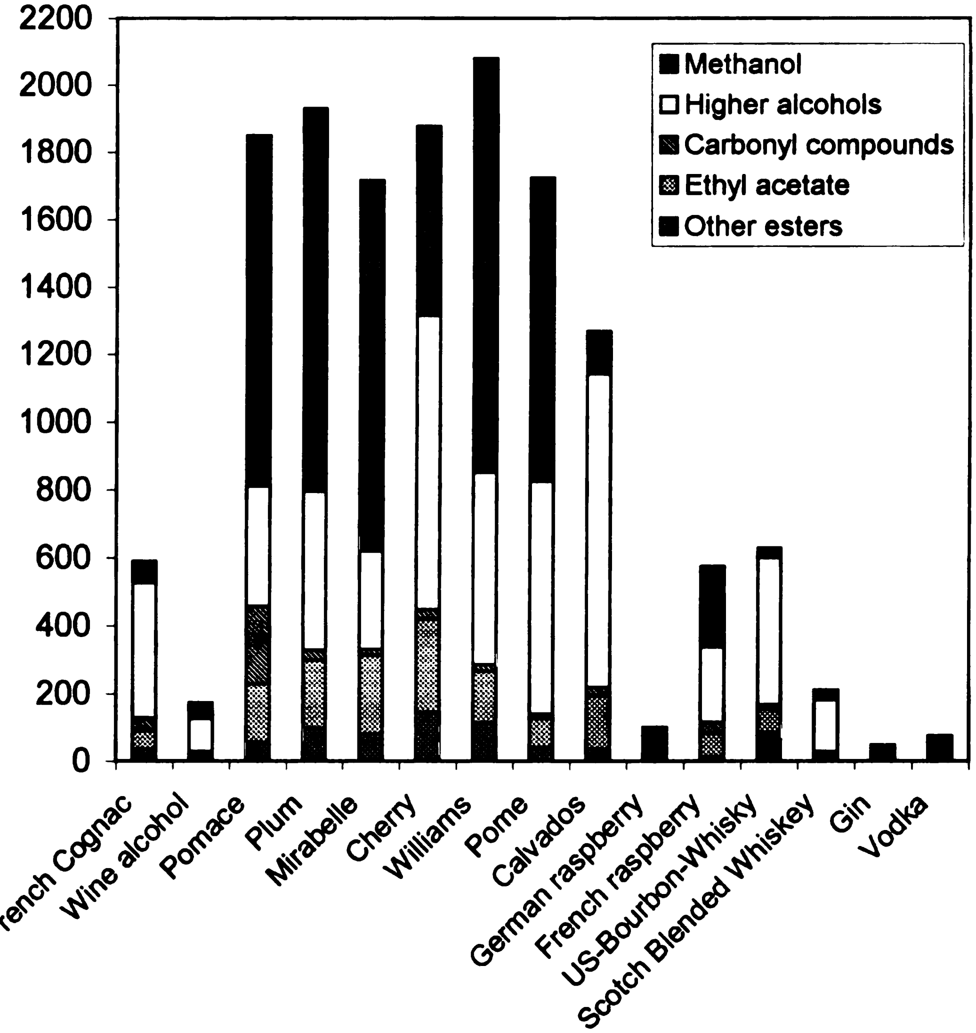

Figure 2.1 **Volatiles in distilled spirits. The amount of volatile congeners in the distilled spirits per 100 mL of alcohol, notice fruit spirits have higher amounts of volatiles than other distilled beverages[4].**

minimum amount of methanol is formed by enzymatic cleavage from the pectin of the fruit, methanol has been used for the evaluation of the authenticity and possible adulterations such as addition of neutral alcohol to the distillate, or addition of sugar to the mash[3].

Fruit spirits contain high amounts of 1-propanol, 1-butanol, 2-butanol, and 1-hexanol when compared with other types of spirits. Isoamyl alcohol and optically active isoamyl alcohol are also main components of fruit spirits, however, they are in a range comparable to other types of spirits. Other alcohols are present in smaller amounts, and of these benzyl alcohol is the most important, as it can be formed from the benzaldehyde which forms from the hydrolysis of amygdalin in the pits of the fruit[3].

Acetaldehyde is the most important of the carbonyl compounds. Even though it has a low boiling point, acetaldehyde can dissolve in the ethanol water matrix and stay in solution. Benzaldehyde, which comes from the pits is also an important carbonyl compound in stone fruit spirits, as it can give an indication as to how much cyanide is in the distillate[3, 5].

The main ester component in fruit spirits is ethyl acetate and ethyl lactate, which composes 80% of the total ester concentration in the fruit spirits. Ethyl acetate is also present in the distillates of fruit brandies, and ethyl benzoate and benzyl acetate are present in higher concentration in stone fruit spirits than in other fruit spirits. The distillation procedure can affect the concentration of esters in the distillate. Heads cutting during the distillation results in lower concentrations of acetaldehyde, ethyl acetate and higher fatty acid esters. On the other hand ethyl lactate and diethyl succinate are extreme tails components and can be reduced by making the tails cut earlier in the distillation procedure[3].

Ethyl carbamate (urethane) is thought to form from cyanic acid reacting in a light catalyzed reaction with ethanol in the storage of distilled spirits. For reasons of health the Canadian government has established a limit on the concentration of ethyl carbamate in fruit spirits of 400 μg / L. The cyanic acid is thought to come from the cyanide that is formed in the hydrolysis of amygdalin in the fermentation of the spirits[3, 5].

2.3 Methanol Health Hazards and Regulation

Methanol has many acute health hazards associated with it. Methanol can cause damage to a number of organs in the human body, including the liver, kidney, and nervous system. In some cases the ingestion of methanol has caused temporary or permanent blindness and even death. Methanol can not be made non-poisonous, although, the treatment for ingestion of methanol involves giving the patent ethanol. Ethanol can act as an inhibitor to the methanol effects on the body[6, 7].

The United States Environmental Protection Agency recommends a minimum acute toxicity concentration of methanol in drinking water to 3.9 parts per million. The EPA has also set the permissible exposure limit in air as 200 parts per million for an eight hour time weighted average[8].

Methanol has been widely regulated in its production in fruit spirits throughout Europe. The German government regulates the maximum methanol content in fruit brandies at different levels based upon the fruit used. In cherry spirits methanol is regulated at 400 mg/100 mL absolute alcohol, while Bartlett pears have a regulatory limit of 790 mg/100 mL absolute alcohol. Italy and Austria have limits set at 800 mg/100 mL absolute alcohol, and 1000 mg/100 mL absolute alcohol, respectively[9]. The United States regulates the amount of methanol in distilled fruit spirits at 0.35% v/v for all fruit spirits sold in the United States. This corresponds to a value of 700 mg/100 mL absolute alcohol[10].

Although methanol is heavily regulated in the United States, the laws were written more to prevent the cutting of distilled spirits with methanol, than they were as a concern for having too high a concentration of methanol in the distillate. As ethanol is the antidote for methanol poisoning and the concentration of ethanol is 40% compared to the methanol concentration of 0.35%, one would have to assume that the ethanol would be lethal before the methanol would. However, a low concentration of methanol is still desired to avoid any toxicological effects[3].

2.4 Making Quality Fruit Spirits

Many factors effect the quality of distilled spirits. The choice of fruit is important, in that the higher quality fruit will yield higher quality distillate. The ripest fruit is desired, because it has more sugar, which in turn would mean more alcohol in the fermentation. Fruit without visible blemishes is preferred, as fruit with imperfections in the skin are also avoided. Sticks and stems should be removed from the fruit to keep them out of the fermentation. Overall, however, the fruit chosen does not need to be as perfect as that shipped to market by the farmer. This will allow the farmer to sell the fruit to the distiller that he would not be able to sell at market[2, 9].

The fermentation conditions also are important. Temperature control is the most important condition in the fermentation. The amount and quality of yeast is another factor that should be considered important in the distillation. Bakers yeast will not give the same quality to the distillate as Champagne type yeast. The amount of yeast used should be large enough that the chosen yeast type will be able to compete with undesired bacteria and yeast during the fermentation[2].

Distillation conditions are also important to the overall distillate quality. Heating the mash too quickly can result in baking the mash to the pot of the still. If the mash is allowed to foam, which can happen with fruit high in pectin, the trays can become dirty and loose their effectiveness[11]. Care must also be taken as to where to take the heads, hearts and tails cuts from the distillate as the hearts cut the desired to be as large as possible but yet contain as little of the compounds which cause negative aroma and flavor characteristics as possible.

The dilution of the spirits does not effect the quality of the distillate very much. However, it is possible to determine if there are imperfections in the distillate. The addition of water, which should be as pure and free of calcium as possible, can cause the distillate to become cloudy. A cloudy distillate is not desired, and can occur for many reasons including terpenes oiling out of solution, or hard water causing the cloudiness[9]. The dilution of the spirits must not drop the concentration of the distillate below 40% v/v, as by law, the fruit spirits must be above this value in order to be called a fruit brandy[10].

In general the rule for making quality fruit spirits would be, "low-quality in, equals low-quality out." In other words if you use quality ingredients and take care of the fermentation and distillation you might be able to produce good spirits. However, if you use poor ingredients or do not take care in cleaning the still in between runs than you will not produce desirable fruit spirits[2].

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3. MATERIALS AND METHODS

3.1 Experimental Process

3.1.1 Fermentation

Fermentation of the fruit was carried out in 200-gallon homemade fermenters. A 200-gallon HDPE tank was used with a valve was inserted into the side housing of the tank. A trellis was fashioned out of PVC piping and sealed to keep the mash out of it. Copper tubing that is used for the cooling water was wound around this trellis in an attempt for even cooling of the mash. The trellis with copper tubing wound around it was made to fit inside the 200-gallon fermenter. A layer of water-heater insulation was placed around the outside of the 200-gallon tank to decrease heating effects from the environment. A diagram of the 200-gallon fermenter is shown in Figure 3.1.

The top of the fermenter had a notch cut out of it for the stirring shaft as well as holes for cooling water flow in and out of the copper coils around the trellis. The notch was covered with a thin piece of plastic with a hole cut for the stirring shaft. This piece was taped to the fermenter to prevent insects from getting into the fermentation. A piece of piping insulation was taped around the stirring shaft also to prevent bugs from getting in. The mass of the top worked to keep the insects from getting in through the seal between the top of the fermenter and the top of the 200-gallon drum. There were no gas-lock channels installed in the fermenter as the CO_2 produced never seemed build up to a noticeable pressure, and always seemed to release by itself.

The stirring motor had a variable speed control. The shaft had two, three blade propellers. These were set to mix the mash as much as possible at as low speed as

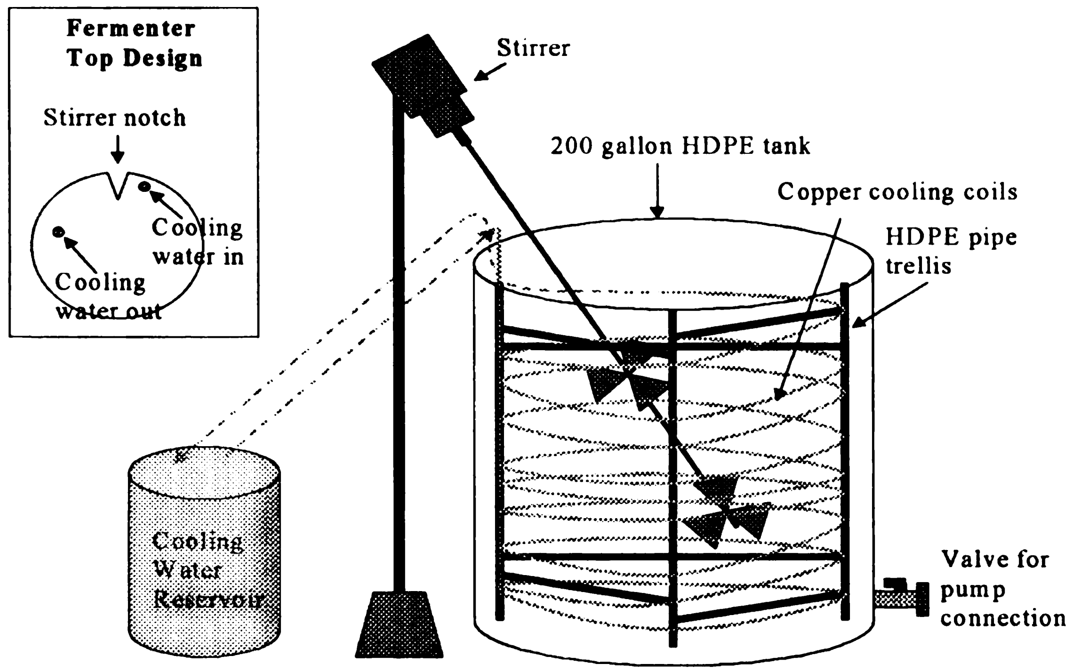

Figure 3.1 **Schematic design of 200 gallon fermentation system. Cooper coil wound around a PVC pipe trellis is used for the cooling of the system.**

possible. The range of speeds used varied from 60 rpm to 210 rpm. The working range desired for the better fermentations was 60 to 110 rpm.

With these fermentations a temperature of 15-20° C was desired[1]. The flow rate of the cooling water through the fermenters was kept constant at about 50 ml per second. The water chiller was set to maintain a temperature in the waterbath of 12° C, which accounted for the initial heat spike associated with fermentations.

For this study, frozen fruit was used. The use of frozen fruit does not give the quality of the distillate that is associated with the use of fresh fruit, however, the ability to perform these experiments in the winter and spring months allowed us to use the still outside of the growing season. The frozen fruit was thawed for 48 hours to room temperature. A cavity displacement pump was used for the mashing of fruit with small or no pits (cherries, pears), and a rolling mill was used for the mashing of the fruit with larger stones (peaches, plums). After mashing the fruit was transported to the 200-gallon fermenters, and allowed to sit for at least an hour such that the initial temperature of the mash was 17°C. This would allow the cooling water to accommodate the initial heat spike from the fermentation without exceeding 21°C. These parameters were never calculated to provide adequate compensation for the heat spike, however, in practice they did work.

For small fermentations (~10 L) a ratio of 5g of dry champagne type yeast for 10 L of fruit mash is recommended. Scaling the amount of mash to 200 gallons (756 L) does not require the same amount of yeast. Only 300g of dry yeast were added to the mash, where a much larger amount could be expected. The yeast is activated in warm water for fifteen minutes before addition to the mash. The yeast used in these experiments was Pries-de-mousse, Champagne type yeast (saccharomyces cerevisiae) purchased from a commercial vendor, Lavlin Inc., in California.

The progress of the fermentation was observed through the measurement of the sugar concentration in the mash. Using a portable refractometer, the percent solid of the mash could be measured. This value, also known as the Brix of the mash, gives an approximate amount of sugar left in the mash. To obtain the results, a sample of mash is first centrifuged, or filtered through a 0.5 μm filter to remove the non dissolved solids. The sample is then dripped onto the faceplate of the refractometer. The readout of the refractometer yields the approximate dissolved solids in the mash. A common value at the start of fermentation for cherries is 13.5 brix and at the end of fermentation the value is below 4 brix.

After fermentation, the fruit mash was pumped in batches into the still such that a volume of mash in the still was about 165 L. An average of five charges for the still was taken per fermentation in the 200-gallon fermenters. For those types of fruit that have stones too large to fit through the cavity of the pump we use, a wet/dry Hoover shop vacuum was used to transfer the mash from the fermenter to the still.

3.1.2 Distillation

The distillation of fruit spirits using the Germanic batch distillation method, involves many steps. First the construction of the still is an important. The design may vary a bit as to the number of trays and the placement of the column of trays, however the underlying importance is that the still be made out of copper. There is an unknown catalytic effect found in copper stills that is not found in stills made of other metals. The basic design to the still we use, constructed by the Christian Carl Ing. GmbH. in Germany, includes steam heating of the pot, one tray over the pot, and three trays, which can be allowed to be open or closed, in a column next to the pot, a "catalytic converter" next to that column, and a condensing column next to that. Two partial condensers are located in the still. The first is at the top of the first tray, and the second is at the top of the second column of trays. Figure 3.2 is a schematic of the Christian Carl still utilized in these experiments.

Two other parts of the still are important in the distillation process. First, a stirring motor is utilized during the distillation to stir the mash and prevent foaming, as well as baking to the surface of the still. For more viscous mashes such as apples or pears, baking can be a problem as there is not uniform heating of the mash occurring. The second piece of equipment in the still is the "puking tube." This tube is for the condensate to return to the pot of the still. It prevents mash from foaming, as well as allowing the condensate to mix with the mash rather than being immediately vaporized in contact with the pot of the still.

The cooling water used is cold tap water. There is a cooling water flow regulator, which is linked to a temperature sensor at the top of the condensing column. The temperature of the distillate is maintained at 72° C, at the top of the column by regulating the flow of cooling water through the flow control device[7]. A manual adjustment can be made as well in an attempt to increase or decrease the rate of distillate from the end of the still. The cooling water at the top of the condensing column, which has been effectively preheated, then feeds the partial condensers at the top of the trays.

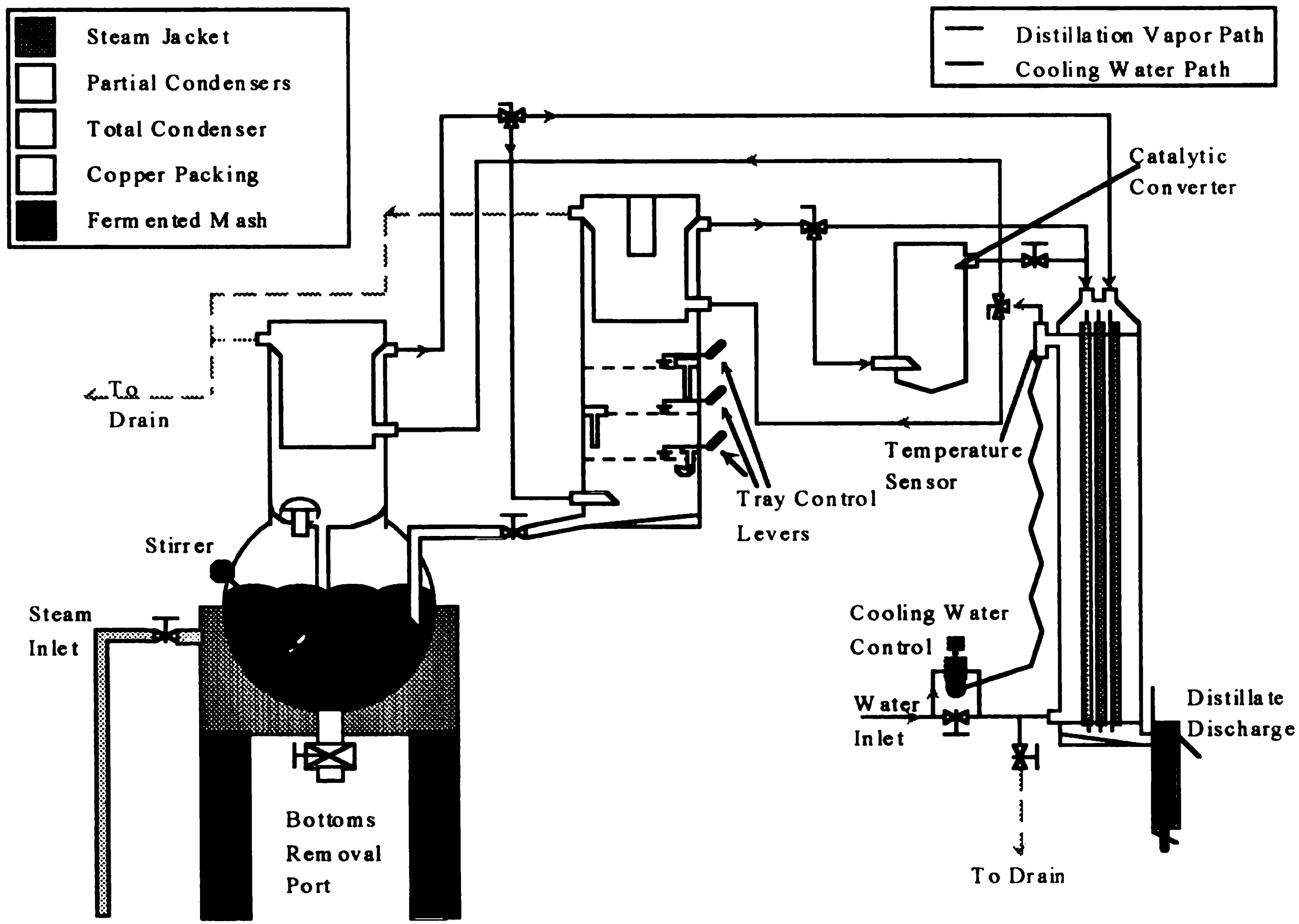

Figure 3.2 Schematic of Christian Carl 165 L Still.

The distillation begins by filling the pot with the fermented mash. During the fill, the cooling water is allowed to fill the condensing column and the two partial condensers. The decision of using the catalytic converter, or opening some of the trays can be made at this time as well. When the pot is full and the still is ready for operation, the stirring motor is turned on. The stirring motor prevents baking of the fruit on the copper surface and can help to prevent foaming of the distillation bottoms up to the trays.

The valve for the cooling water is closed to allow the temperature sensor at the top of the condensing column that regulates the flow of water into the condensing column to take over water flow control. At this point the steam is allowed into the steam jacket surrounding the pot of the still. The steam is slowly brought to a pressure of 0.3 to 0.4 bar. This allows for good heating of the mash, and brings it to a boil in a relatively quick time of about a half hour[7]. The distillation is then allowed to proceed inside the still without interruption until the distillate begins to exit the condenser of the still.

The distillate is mostly ethanol and water. The congeners present in the distillate come out at different times in the distillation process. There are three basic cuts of distillate taken in the distillation process. The first cut is the heads portion of the distillate, which contain congeners with relatively low boiling points. The second cut is the hearts cut, which is the portion that will eventually be consumed. The last cut is the tails, which contains all the heavier congeners and those with relatively higher boiling points. Most notably in the tails portion of the distillate are the fusel alcohols, which are known for their unpleasant aroma[1].

For the experiments in this thesis, the amount of distillate collected per cut was kept consistent. Three 400 ml cuts were taken for the heads portion of the distillate, and increments of 1000 ml were taken for the hearts portion until the concentration was below 60 % A.B.V. The final cut of hearts varied in volume based upon the distiller's analysis of the spirits at the time of distillation. The tails cut was taken at a volume of 1000 ml. Any further alcohol collected went into a communal tails carboy for redistillation, which yields a product with poorer aromatic qualities.

3.1.3 Storage

The spirits are stored in glass jars at high proof. They can be blended before storage, however, the practice was to save each cut separately through the storage process of the fruits and blend them three to six months after distillation. As it is theorized that the formation of ethyl carbamate is a light catalyzed process, the distillate is stored in the dark.

Reactions that occur in the aging process include oxidation, esterification, and actealization. Oxidative processes involve the conversion of aldehydes to acids, and alcohols to aldehydes and water. Esterification reactions involve the addition of alcohols and acids to form esters and water. The most common esterification reaction involves the addition of ethanol and acetic acid to form ethyl acetate. Acetalization reactions involve the addition of an aldehyde and alcohol to form diacetals and water. All of the stoage reactions are dependent on the concentration of the reactants and the temperature and pH of the stored distillate. Most of these reactions are reversible and do not lead to complete yield conversion of any of the reactants to the products[1].

3.2 Analysis of Distilled Spirits

Ethyl alcohol concentrations were measured by a tralles (% alcohol as well as proof) hydrometer with an internal thermometer to perform instantaneous adjustments to the actual alcohol concentration[1]. A sample from each cut was analyzed by gas chromatography. A Shimadzu GC-17A gas chromatograph with flame ionization detection was used for analysis of all samples. A Stabilwax 30m column with an inner diameter of 0.25mm from Restek was used for all measurements. The initial conditions for the chromatographic analysis were column temperature at 40°C, injector port temperature of 240°C and detector temperature at 255°C. The temperature program used for the analysis of the components in the eau-de-vie spirits was initially at 40°C and ramped at 2.5°C/min until a temperature of 190°C was reached. The temperature was held at 190°C for 5 minutes. A Shimadzu autosampler (AOC-20i) with a twelve vial capacity was used to obtain reproducibility of the 0.2 μL injection volume. Each sample took 75 minutes to run due to sampling time, cooling time and run time; therefore, one distillation containing eight different cuts would take 10 hours for complete analysis. Figure 3.3, is a sample chromatograph and Table 3.1 shows the relative retention times of the most common compounds in the fruit spirits, as well as their respective boiling points.

Concentrations of each congener were compared to ethanol, which was used as an internal standard. The concentrations of these congeners were also compared to a calibration curve for the concentration of the congener compared to the concentration of ethanol. Use of the autosampler allowed for retention times for each standard to be reproducible with slight variance due to the concentration difference of the ethanol water mixture from one sample to the next. As the concentration of the ethanol water matrix changes, the retention time of the lower boiling congeners varied by less than half a minute, however the higher boiling compounds could vary by as much as a minute.

3.3 Tray Usage

The number of trays used during the distillation of the fruit spirits as well as the use of the catalytic converter was varied throughout the experiment. The distillations were not run in any set pattern, however, it should be noted that an attempt was made to get in one distillation with each distillation condition per fermentation batch in an attempt to minimize the amount of deviation due to starting material. The operating conditions for the distillations were; all trays closed with the catalytic converter utilized, all trays closed with the catalytic converter bypassed, one tray open with the catalytic converter utilized, one tray open with the catalytic converter bypassed, and two trays open with the catalytic converter bypassed. Because not every fermentation gave five or six distillations, the last operating condition, two trays open with catalytic converter bypassed, was not run very often. Instead an attempt to replicate one of the other operating conditions was often chosen instead of the last condition.

Table 3.1. **Average retention times, from the chromatographic conditions used, for the most common congeners present in distilled fruit spirits. The Boiling points for each congener were also given[3].**

Chemical Name	RetentionTime (min)	Boiling point (deg. C)
Acetaldehyde	2.5	20.8
Ethyl Formate	3.6	54.0
Ethyl Acetate	4.5	77.0
Methanol	4.7	64.7
Ethanol	5.8	78.0
1-Propanol	8.7	97.0
2-Methyl-2-propanol	10.8	82.4
Isopentanol (isoamyl alcohol)	16.3	132.0
Benzaldehyde	33.0	179.0

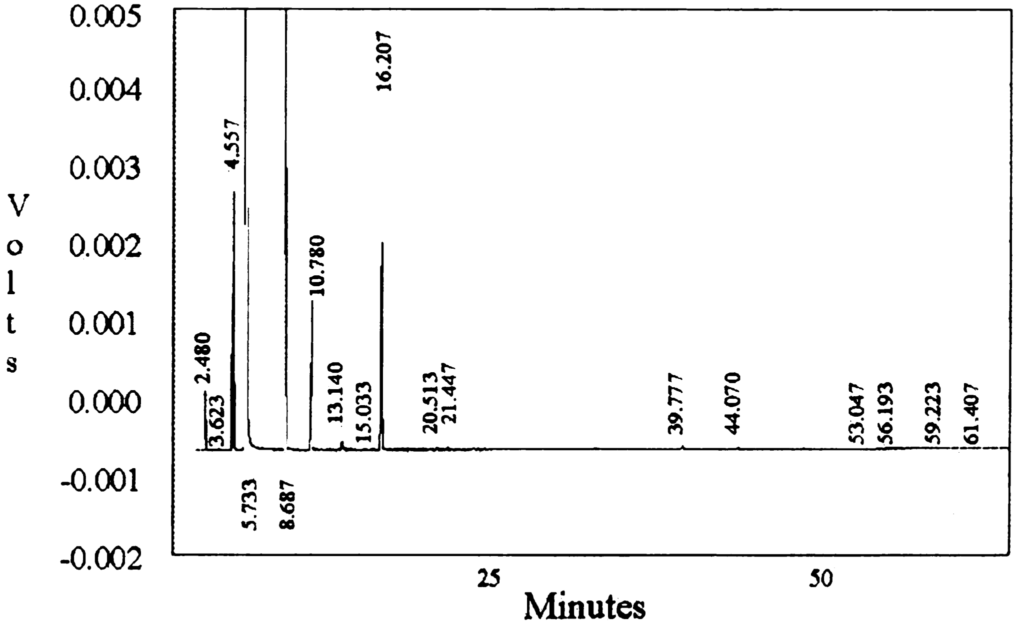

Figure 3.3. Sample Chromatagraph from a cherry eau-de-vie distillation. A Restek 30m Stabilwax column with 0.25mm i.d. was used for analysis. The initial conditions had the column temperature at 40°C, injector port temperature at 240°C, and detector temperature of 255°C. The analysis included a ramp from 40°C to 190°C at 2.5°C/min.

3.4 Literature Cited

1. Tanner, H., and Brunner, H.R., Fruit Distillation Today 3rd ed., (English Translation) Heller Chemical and Administration Society, Germany, 1982.

2. Plank, Alexandr. Personal Correspondence with Author. 1998-2001.

3. The Merck Index, 11th ed. Rahway, New Jersey, 1989.

4. RESULTS AND DISCUSSION

4.1 Composition of Fruit Brandy

The composition of fruit brandy is complex with hundreds of compounds included in the makeup of a good fruit brandy. With the high number of congeners involved in the distillation process, it is difficult to choose which ones to study. For the purposes of this experiment, the compounds chosen were those present in the highest concentration ranges. The compounds studied involve those present in higher concentration in the heads, those in higher concentration in the hearts, and those compounds that have profiles that are not higher in the heads, hearts or tails. The compounds studied in this experiment include; ethanol, acetaldehyde, ethyl formate, ethyl acetate, 1-propanol, 2-methyl-2-propanol, isoamyl alcohol, benzaldehyde, and methanol. A final section will detail how the concentration of these compounds would relate to a bottle of spirits at consumable strength (40% ethanol).

The amount of each congener in the distillate will vary widely from fruit to fruit and can vary based upon fermentation conditions as well. Each congener is profiled to show how the concentration varies at the distillation progresses. The amount of each congener that is found in each distillate is converted from the concentration as found in the high proof distillate to the concentration that would be found in the drinkable strength distillate. The dilution of the ethanol is the only effect taken into account, and the effect of storage reactions on the increase or decrease of the concentration of the congener is ignored.

Finally when looking at the concentration of distillate in each bottle of spirits, the hearts portion is the only portion of the distillate used in calculating the amount of congener present in the distillate.

The compounds that have lower boiling point than ethanol includes; acetaldehyde, ethyl formate, ethyl acetate, and methanol. The compounds that have higher boiling points than ethanol include, 1-propanol, 2-methyl-2-propanol, isoamyl alcohol, and benzaldehyde. These compounds represent the congeners with the highest concentration throughout the fruit used in these experiments.

4.2 Batch Reproducibility

A large variance is introduced in to the concentration of each congener from one distillation to the next. One batch of fermentations will not have exactly the same amount of each compound present in it with variability coming in fruit type, fruit quality, processing methods, yeast used, temperature and pH effects[1]. The distillations would also have an effect not just from the number of trays used but also in which distillation was being performed. The first distillation in the morning would take a little longer to get to temperature than the last distillation of the day.

In an attempt to minimize the differences from the many distillations and fermentations, the data shown will include only those distillations involving plums. The profiles for each of the compounds studied is similar in the distillate of each fruit we have studied; cherry, peach, pear, plum, with differences in concentration, but not overall trends. The plum fermentations involved two separate fermentations with eleven total distillations. Table 4.1 illustrates the distillations involved in the collection of the data

Table 4.1 Fermentation and distillation conditions. The conditions used for each distillation and how they relate to the fermentation batches of the fruit used. The distillation conditions used include: (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.

Fruit	Fermentation #	Run #	Trays Used	CC Used?
Cherry	1	1	All	Yes
Cherry	1	2	All	Yes
Cherry	1	3	All	Yes
Cherry	1	4	All	Yes
Cherry	1	5	All	Yes
Peach	1	1	All	Yes
Peach	1	2	All	No
Peach	1	3	2	No
Peach	1	4	2	Yes
Plum	1	1	All	No
Plum	1	2	2	No
Plum	1	3	2	Yes
Plum	1	4	All	Yes
Plum	2	1	2	Yes
Plum	2	2	All	No
Plum	2	3	2	No
Plum	2	4	All	Yes
Plum	4	1	All	No
Plum	4	2	All	Yes
Plum	4	3	2	Yes
Note: Plum fermetnation (3) was lost due to pump failure in the cooling water system				

for these experiments. As the profile of each congener was desired, and the concentration range for each distillation could be greatly different from distillation to distillation, the runs were averaged where possible to show the trend. Other cases where the concentration ranges deviated, the profile that showed the general trend for a particular congener throughout all the fruit distilled in this study, was used. Error bars were not included in the figures because there was a wide variety in concentration from one distillation to the next.

Attempts were made to run as many distillations as possible from one batch in a day. This was to minimize the amount of extra fermentation time the last batch distilled would have. Rinsing the sides of the fermenter after charging the still in order to remove any of the mash on to the sides diluted the rest of the mash, and was kept to a minimum. Upon completion of fermentation, the fermenter was completely cleaned with a dilute bleach solution to remove any excess yeast or mash stuck to the trellis or sides of the still.

Cleaning the still between distillations was completed with a water wash. The cleaning of the trays involved the use of nozzles inside the still at each tray position. Changing the flow of cooling water through the piping around the still allowed the cooling water to flow to these nozzles where they rinsed the inside of the still. The cooling water flowed to the pot where it mixed with the hot mash and cooled it as well. Where visible fouling or excess mash adhered to the inside of the still was present, a damp piece of cheesecloth was used to remove the dirt. The cleaning of the pot of the still involves use of cold water on the inside of the pot of the still, after the bottoms of the distillate were removed.

Care was taken to be as reproducible as possible with the distillations. One batch of cherry distillations shows how unpredictable the distillation reproducibility can be. Five distillations run under the same conditions produce five different ethanol profiles. Figure 4.1 illustrates this data. The five distillations were all run on the same day, from the same fermentation batch under the same distillation conditions. The amount of ethanol in each distillate varied through uncontrollable parameters and each run was kept as constant as possible. Variety of this sort is even more common in the congeners, although every attempt was made to prevent variability from distillation to distillation.

4.3 Distillate Analysis

Analysis of the distillate was carried out by GC-FID. The retention times of the peaks we compared to the retention times of standards for each congener. Standards were also used to develop a calibration curve for each congener. The amount of ethanol in each distillate was measured by hydrometer, and corrected for temperature effects. As the distillate is diluted after storage and before consumption, the concentration was set to the ratio of ethanol in distillate and a 40% ethanol distillate. All data shown for each congener were calculated to show the concentration as they would appear in a 40% ethanol brandy. The effect of storage on the concentration of the congeners was not taken into account. The concentration of esters would probably increase during storage, however, because the storage reactions are equilibrium reactions, there is no way of knowing if the concentration of each congener would increase or decrease during the storage.

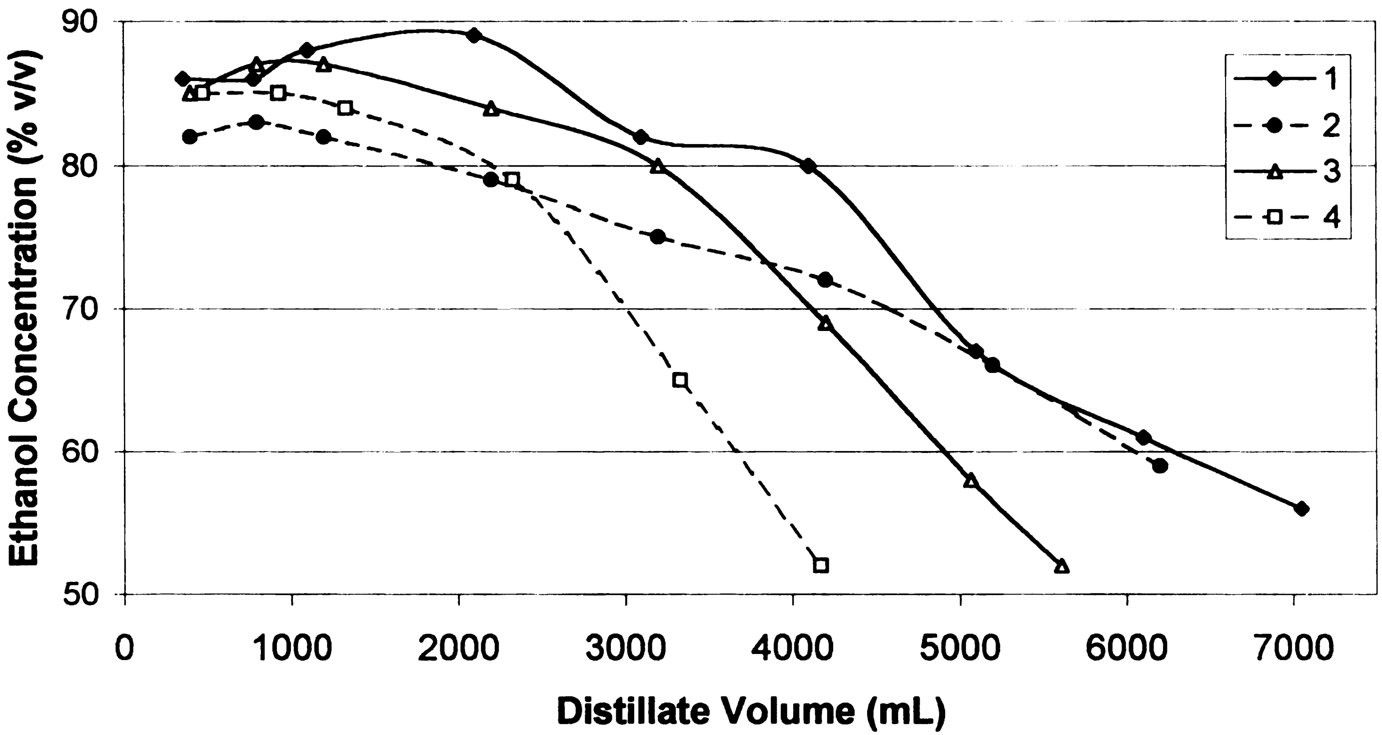

Figure 4.1 Ethanol concentration as a function of cumulative distillate volume for cherry spirits distillations. All distillations were from the same fermentation batch and were run with the same operation conditions used. All distillations were carried out with all the trays used and the catalytic converter used as well.

The number of trays used in the distillation process were varied from run to run, as was the use of the catalytic converter. The four types of distillations that were run include; all trays engaged (in use) with the catalytic converter also used, all trays engaged with the catalytic converter bypassed, one tray open (two engaged) with the catalytic converter used, and two trays engaged (one left open) with the catalytic converter bypassed. The effect of tray number on ethanol and the congeners as well as the effect the catalytic converter would have on the compounds studied in the distillate were studied.

4.4 Effect of Tray Usage

4.4.1 Ethanol

The end goal in the distillation of fruit spirits is to maximize the number of bottles of 40% ethanol that can be made with the highest quality. These spirits are usually bottled in 375 mL bottles. As each distillation contained the same amount of mash, and hopefully the same amount of ethanol (if the yeast did its job correctly). Overhead product was collected with 1200 mL of heads, (in three 400 mL volumes) and volumes of 1000 mL of hearts until a concentration of < 65% alcohol was achieved. This varied the amount of hearts collected in each distillation as some batches gave 3000 mL of hearts and others gave 5000 ml of hearts. A final 1000 mL was collected as tails.

The profile of ethanol concentration throughout the distillation of fruit spirits, begins at a concentration of about 84% ethanol. The concentration increases until a concentration between 87% and 90% is reached. The concentration then slowly decreases for the next 1000 to 4000 mL. This portion constituted the largest portion of the hearts of the distillate. The concentration will then decrease at a faster rate until the distillation is complete. The amount of distillate collected is dependent upon the parameters the distiller wants to follow.

Figure 4.2 shows the average concentration of ethanol per distillation volume, with varying distillation conditions. Figure 4.3 shows how the average runs in Figure 4.2 would translate into bottles of 40% fruit spirits. Figure 4.3 shows that the more trays that are engaged, the higher amount of 40% spirits will be collected.

The distillate collected with all the trays engaged and with the catalytic converter used also, had the largest portion of distillate collected. The amount of distillate collected with three trays but with the catalytic converter bypassed included the second largest volume of distillate. This trend follows as would be expected, and corroborates the theory that the greater number of trays will produce a larger volume of higher concentration ethanol distillate.

4.4.2 Acetaldehyde

Acetaldehyde is the main component emerging before methanol in the distillation of cherry spirits. It has a distinctive aroma characteristic, which can cause an eau-de-vie to have a poor aromatic characteristic when present in too high of a concentration[2]. As acetaldehyde has a low boiling point, its largest concentration is distilled into the heads portion of the distillate. However, when fewer trays are used a larger concentration proceeds into the hearts portion of the distillate. Acetaldehyde is completely soluble in both water and ethanol; therefore it is not easily separated from the spirits. The acetaldehyde does stay in the distillate even though it has such a low boiling point.

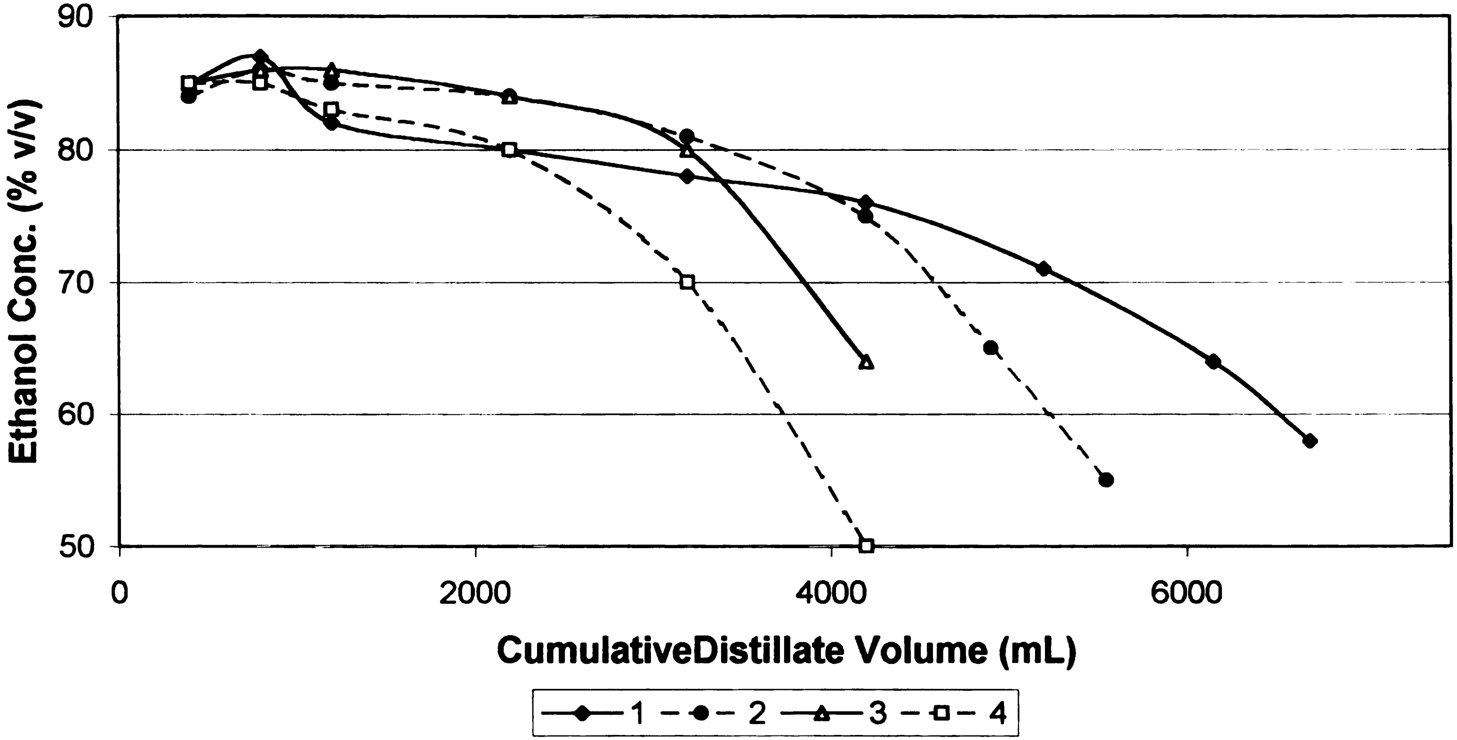

Figure 4.2. The average concentration of ethanol (% v/v) as a function of cumulative distillate volume with varying distillation conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.

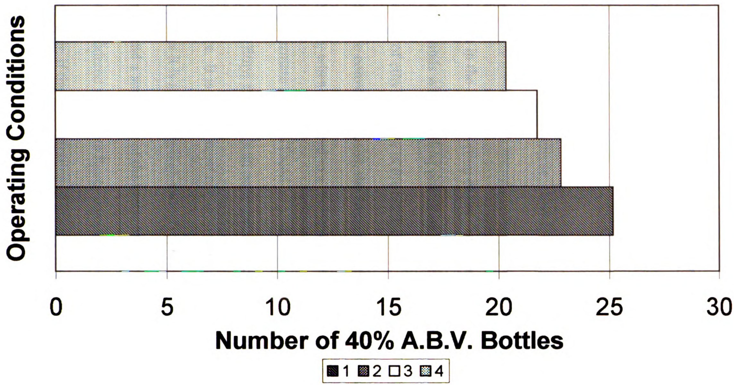

Figure 4.3. Translation of the data in Figure 4.2 into bottles of 40% ethanol, plum brandy at the four different operating conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.

A plot of the acetaldehyde profile can be found in Figure 4.4. It should be noted that unlike other congeners that have a boiling point less than ethanol, there is acetaldehyde present in all parts of the distillation. The amount of acetaldehyde does decrease as the distillation continues, however, the concentration does not reach zero in any portion of the distillation.

4.4.3 Ethyl formate

Unlike acetaldehyde, ethyl formate does decrease to a point where we were unable to measure it in the distillate. Again, the largest portion of ethyl formate was present in the heads portion of the distillate, which would be expected for those compounds whose boiling points are less than that of ethanol. Figure 4.5 shows the profile of ethyl formate in the distillations. When all the trays are engaged and the catalytic converter is used, the amount of ethyl formate in the distillate is the lowest amount, when compared to a distillation using only two trays in which a greater amount ethyl formate could be found.

Ethyl formate is an ester that can be expected to form during the storage of the distillate. It is not the most common ester in the distillate, which would be ethyl acetate, however it is present in high enough concentration that we were able to detect it in the heads and a small part of the hearts of the distillation. Ethyl acetate, like most esters, can be considered a positive flavor component in the distillate at lower concentrations, however, if the concentration of ethyl acetate gets to be too large, the quality of the aroma of the fruit spirits will decrease.

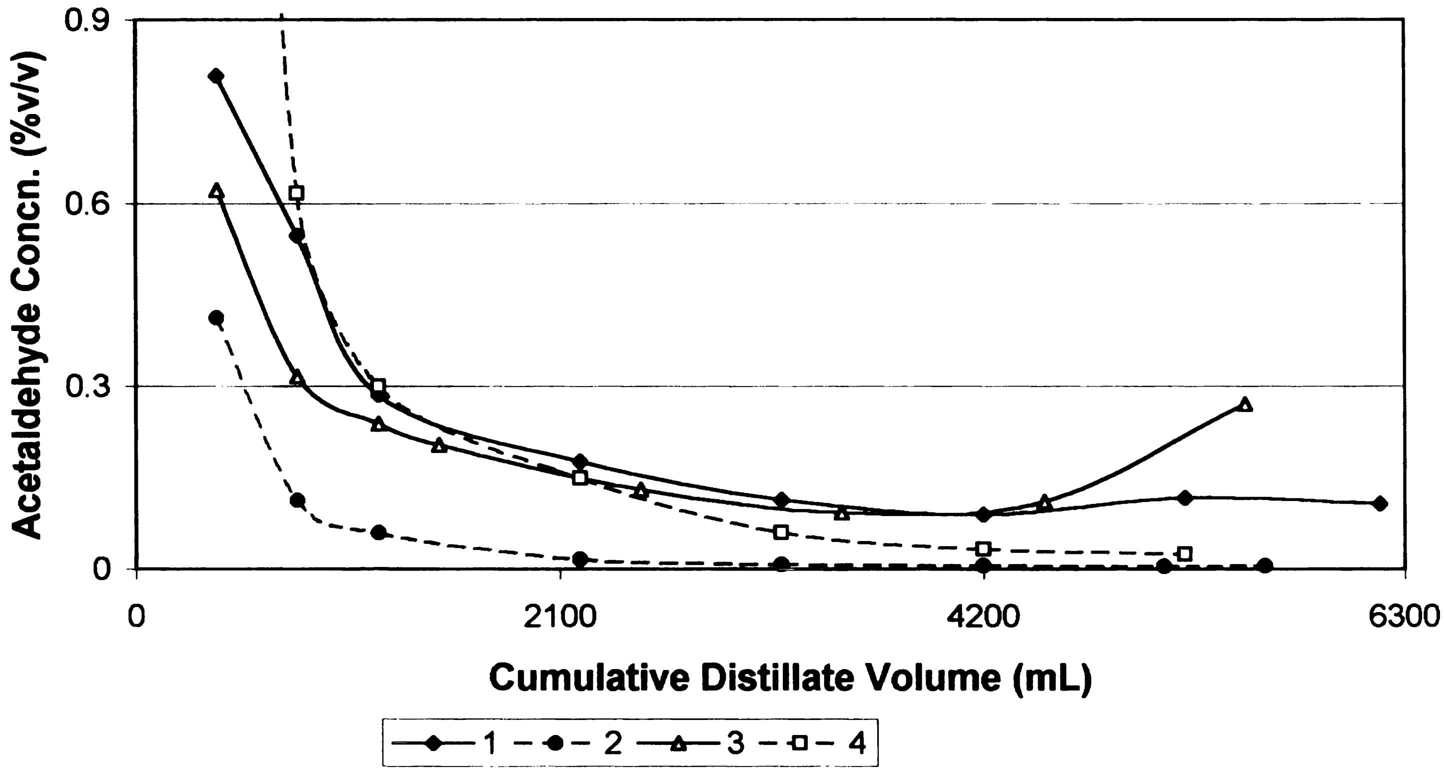

Figure 4.4. **Acetaldehyde profile. Concentration of acetaldehyde in plum distillate as a function of cumulative volume of distillate at four different operating conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.**

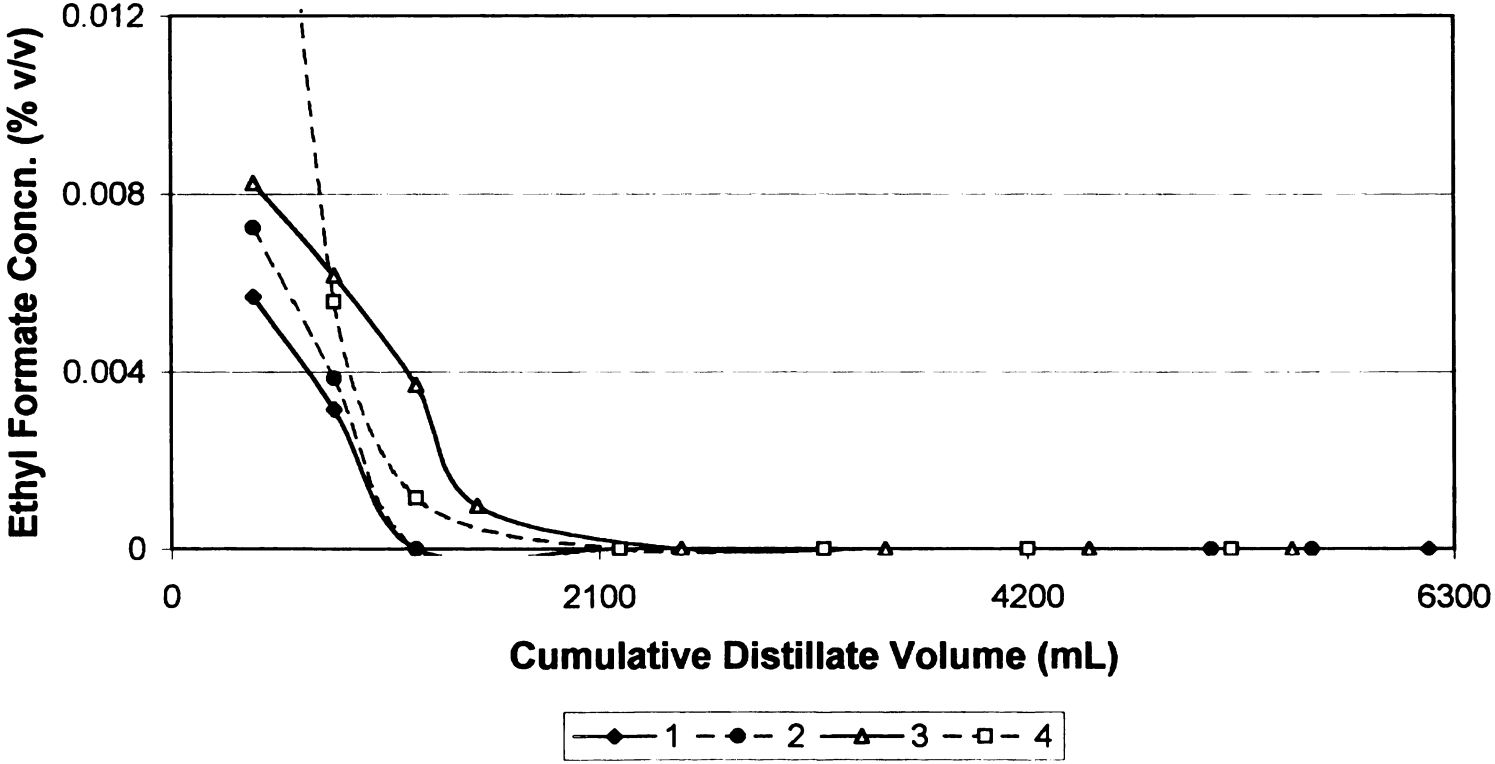

Figure 4.5 Ethyl formate profile. Concentration of ethyl formate in plum distillate as a function of cumulative volume of distillate at four different operating conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.

4.4.4 Ethyl acetate

After acetaldehyde, ethyl acetate is the most abundant of the minor components of cherry distillates boiling before methanol[2]. The ethyl acetate distillation profile acts in a similar manner as the acetaldehyde and ethyl formate. There is a higher concentration of ethyl acetate in the heads and early hearts portion of the distillate, than other portions of the distillate. The amount of ethyl acetate in the late hearts and tails increases only in those distillations using the catalytic converters. The catalytic converter may act as a surface for esterification reactions to occur as the concentration of ethanol decreases. Figure 4.6 illustrates this point, and shows the profile of ethyl acetate in the distillate.

4.4.5 1-Propanol

Fusel alcohols compose the largest group of aroma compounds in alcoholic beverages[3, 4]. 1-Propanol is the simplest of the fusel alcohols, and it has the lowest boiling point of all the fusel alcohols. The amount of 1-propanol and isoamyl alcohol can be considered as an indicator of the total amount of fusel alcohols in the distillate. Because Fusel alcohols donate an unpleasant, damp cloth aroma to the distillate, minimizing the amount of fusel alcohols in the distillate is a goal of every distillation.

The concentration of 1-propanol in the distillate increases gradually, reaches a maximum, a little past half way through the total hearts collected, and then decreases. Figure 4.7 illustrates this profile of 1-propanol. The amount of 1-propanol in the cuts reaches a maximum in the hearts portion of the distillate. The only ways to effectively remove the higher concentrations of 1-propanol from the distillate would be to make the tails cut earlier in the distillation, or redistill the collected distillate. Redistillation, would

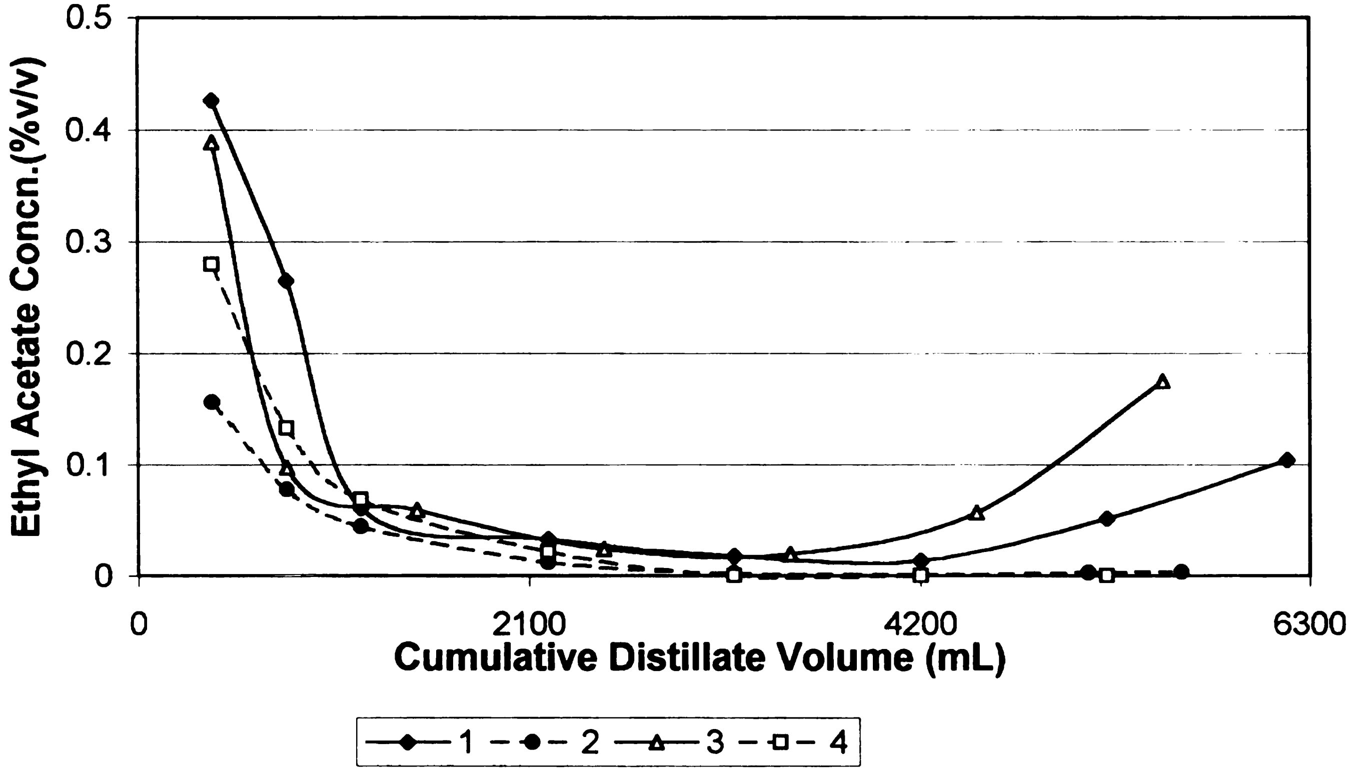

Figure 4.6. **Ethyl acetate profile. The concentration of ethyl acetate in plum distillate as a function of cumulative volume of distillate under four different operating conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.**

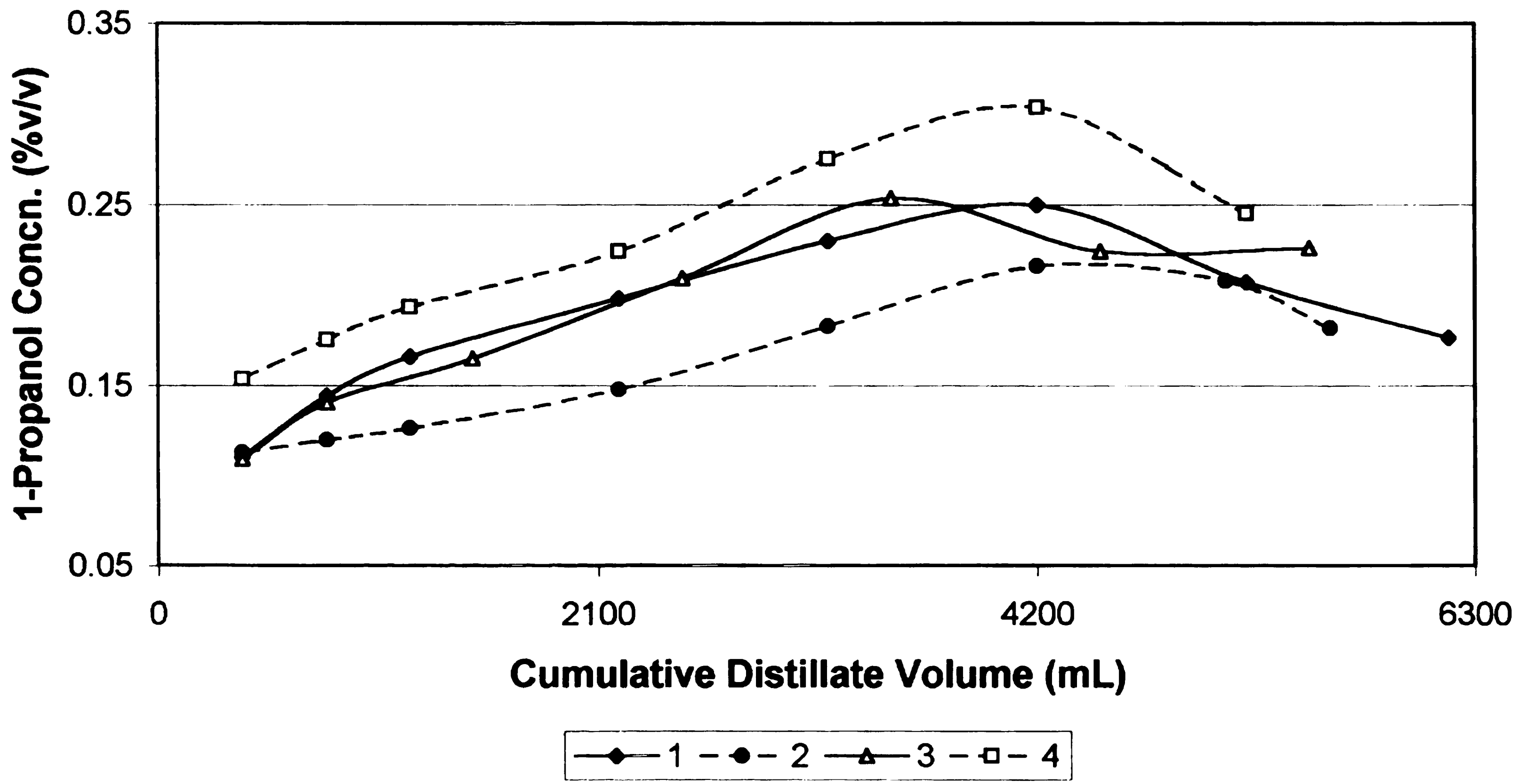

Figure 4.7. **1-Propanol concentration in plum distillates as a function of cumulative volume of distillate with different operating conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.**

reduce the concentration of the other flavor components and cause a loss of yield, making the 1-propanol a difficult compound to reduce in the distillate.

4.4.6 2-Methyl-2-propanol

The profile of 2-methyl-2-propanol, which can be found in Figure 4.8, is similar to the concentration profile of the other fusel alcohols, 1-propanol and isoamyl alcohol. The amount of 2-methyl-2-propanol is less than one third of the concentration of 1-propanol, or isoamyl alcohol in the spirits however. The catalytic converter seems to bring the maximum concentration point of the profile to a fraction earlier than that of the distillations bypassing the catalytic converter. The 2-methyl-2-propanol has a retention time between 1-propanol and isoamyl alcohol. The amount of 2-methyl-2-propanol was greater in the plum distillates than cherry or peach distillates.

4.4.7 Isoamyl alcohol (isopentanol, 3-methyl-1-butanol)

Isoamyl alcohol (3-methyl-1-butanol) is the main fusel alcohol synthesized during fermentation by yeast, with 1-propanol considered another important fusel alcohol. However, these two compounds distill earlier than most of the other fusel alcohols and therefore they are considered to be early indicators of the balance of the remaining fusel alcohols. The fusel alcohols produce a "damp cloth" aroma that is undesirable in the production of spirits[5]. 1-propanol, and isoamyl alcohol are present in the hearts in small quantities, and increase in concentration at the end of the hearts cut and begin to decrease in the tails. Most fusel alcohols will be present in greater concentrations in the tails than in the hearts. As these two compounds are precursors to the other fusel alcohols

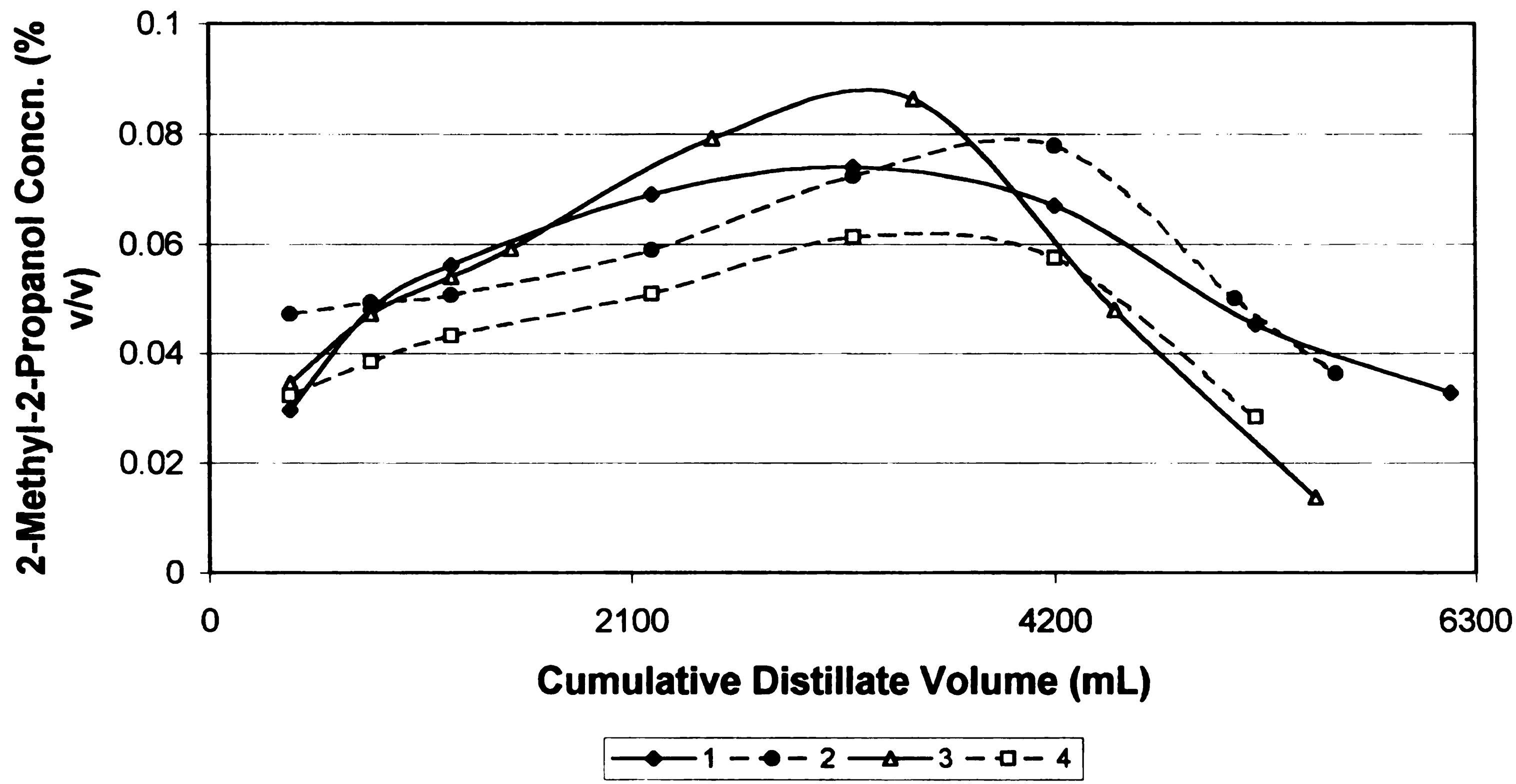

Figure 4.8 2-Methyl-2-propanol profile. Concentration of 2-methyl-2-propanol in plum distillate as a function of cumulative volume of distillate at four different operating conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.

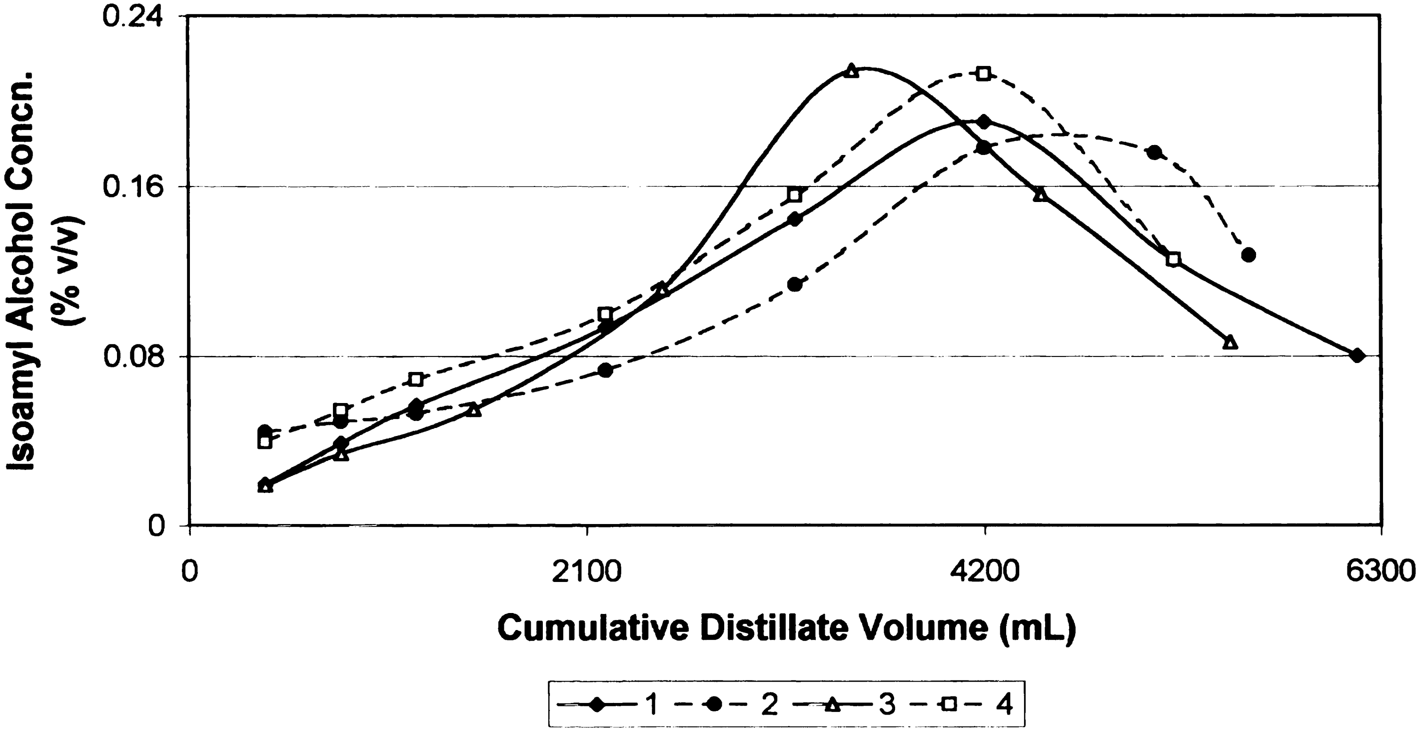

Figure 4.9. **Isoamyl alcohol profile. Isoamyl alcohol concentration in plum distillate as a function of cumulative volume of distillate under four different distillation conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.**

measuring the presence of 1-propanol or isoamyl alcohol on line would allow for an easier determination of where to make the hearts/tails cut.

A plot of the concentration of isoamyl alcohol can be seen in Figure 4.9. Again the catalytic converter shifts the maximum of the concentration to an earlier volume than when the catalytic converter is bypassed. As this trend can also be seen in 2-methyl-2-propanol, and to a lesser extent in 1-propanol, the catalytic converter may be concentrating the fusel alcohols in the hearts, rather than the tails of the spirits. As the catalytic converter acts as an additional tray causing the fusel alcohols with lower boiling points to emerge earlier in the distillation due to the increased separation of all the components present.

4.4.8 Benzaldehyde

Benzaldehyde is a positive flavor component of fruit distillate. Benzaldehyde has many trade names including, "the essence of cherry," and "bitter almond oil." The amount of benzaldehyde may be loosely related to the concentration of ethyl carbamate in the spirits, as the molar amounts of cyanide and benzaldehyde produced in the hydrolysis of amygdalin in the fermentation are equivalent. The profile of the benzaldehyde in fruit spirits can be seen in Figure 4.10. Benzaldehyde does not appear in similar concentrations in pear spirits, as there is no stone with amygdalin to produce the benzaldehyde. The higher number of trays in the distillation pushed the benzaldehyde further towards the tails portion of the distillate. A noticeable shift in concentration maximum occurs between two trays with catalytic converter and the three trays. The catalytic converter seemed to have little effect between the run with all trays with the

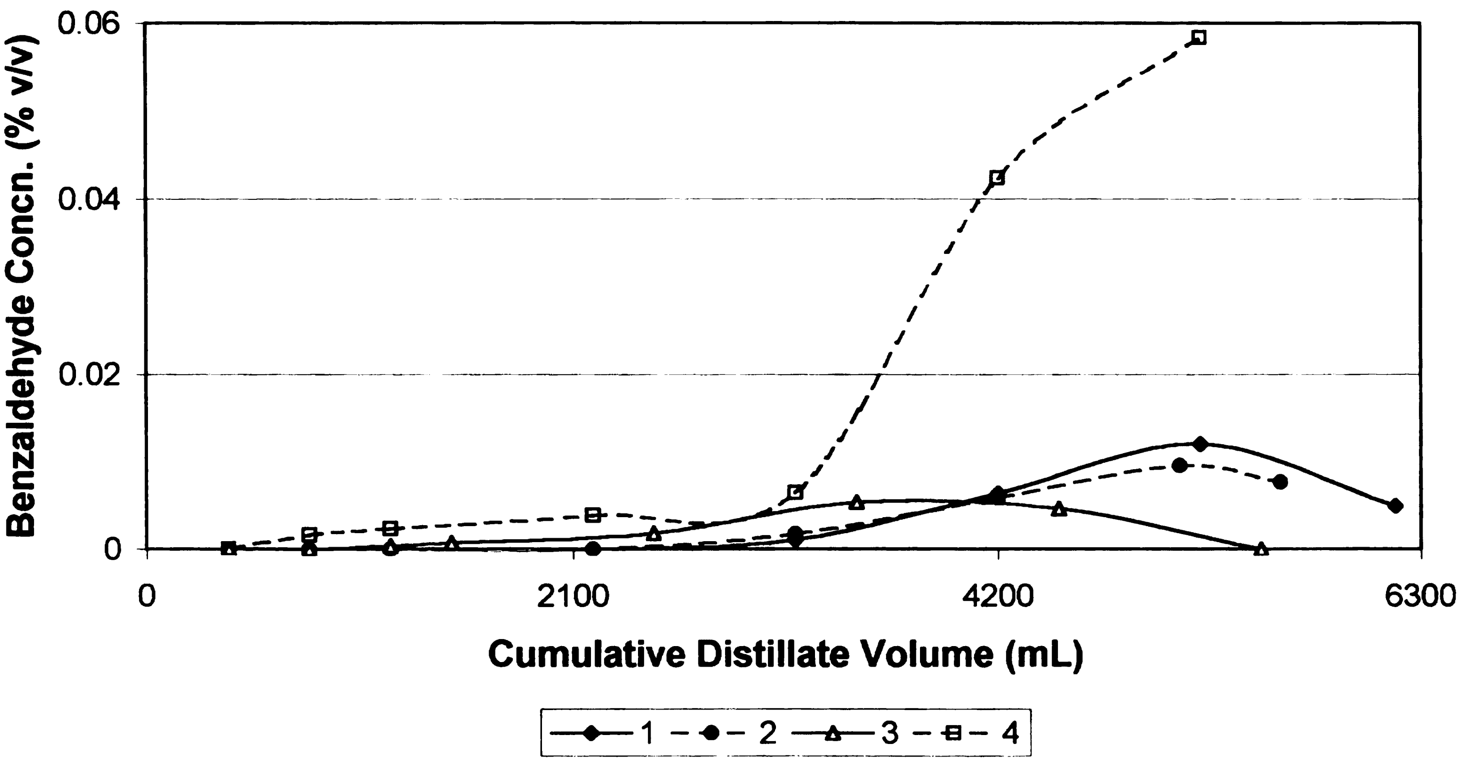

Figure 4.10 Benzaldehyde profile. Benzaldehyde concentration in plum distillate as a function of cumulative volume of distillate under four different distillation conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.

catalytic converter, and the distillation with only three trays used without the catalytic converter. Currently there is not a demand for the regulation of benzaldehyde, however, if a relationship between the concentration of benzaldehyde and the concentration of the ethyl carbamate in the spirits can be found, it may be possible to use that relationship to regulate the ethyl carbamate through analysis of benzaldehyde.

4.4.9 Methanol

Methanol is a health hazard that is regulated by the FDA at 0.35% (v/v) in distilled spirits[6]. The amount of methanol we produce in the hearts of our spirits is just above that level. The methanol profile exists such that the methanol concentration is higher in the heads, drops in the hearts to a lower concentration, and then increases again in the tails. Of the compounds examined, methanol has a unique distillation profile. Figure 4.11 shows the methanol concentration curves per cumulative distillation volume for the operating conditions used. The distillation profile of methanol in this type of multistage batch distillation is different than it would be for an alambic style distillation[7]. It is important to test each cut to minimize the methanol concentration in the hearts cut. Methanol is considered by many to be a positive flavor constituent in distilled spirits. It is difficult to separate the methanol from the ethanol water mixture further without loss of many of the other flavor components from the distillate. Treating the fermentation mash, with some methanol inhibitor is probably the easiest way to minimize the amount of methanol in the distillate. The concentration must be below 0.35% (v/v) but it is desirable to have the concentration close to regulatory limit, as it is a positive flavor component.

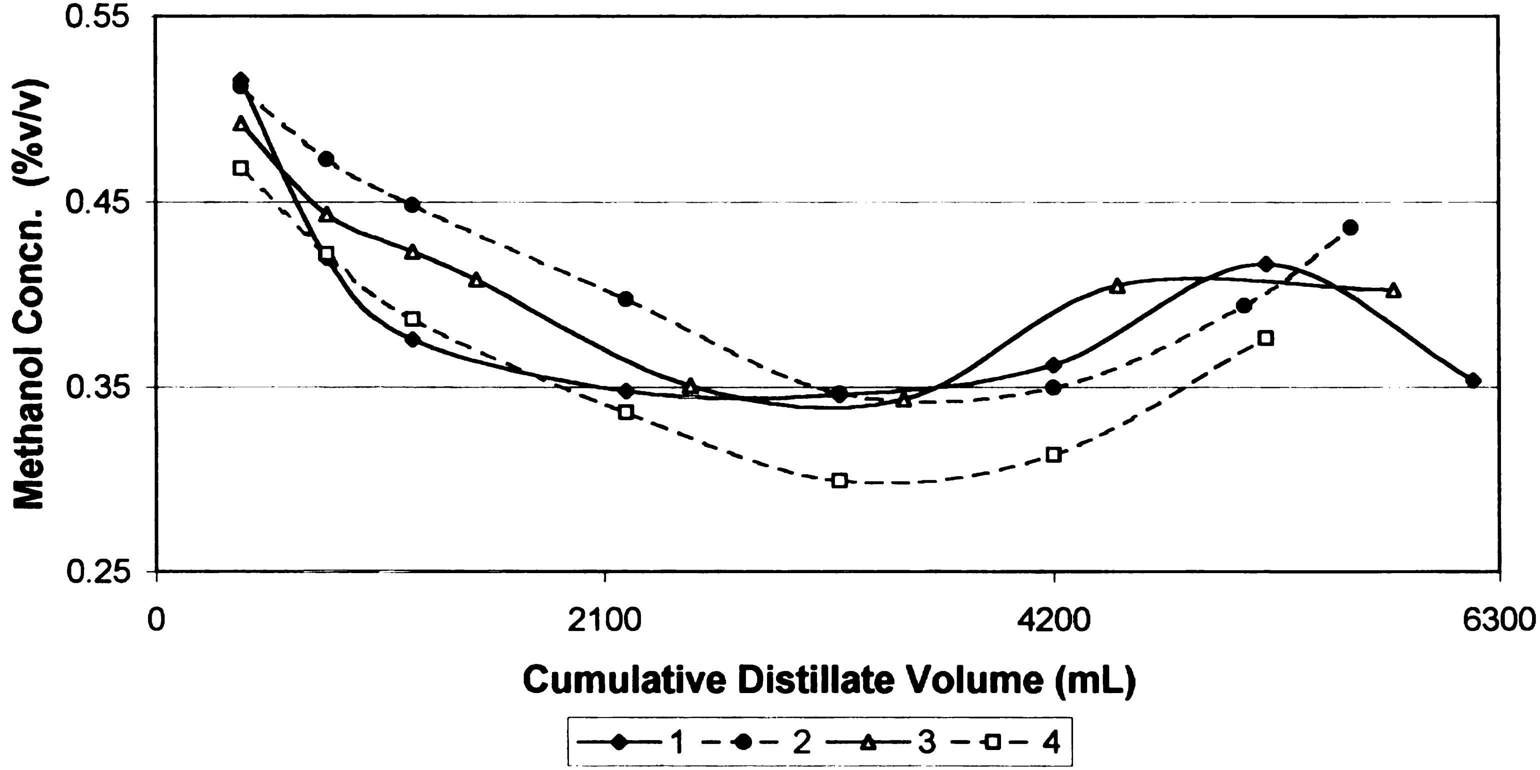

Figure 4.11. **The concentration of methanol in plum distillates as a function of cumulative volume of distillate under different distillation conditions. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter.**

4.4.10 Bottles of fruit spirits

Figure 4.12 shows the concentration of acetaldehyde, ethyl acetate, methanol, 1-propanol, isoamyl alcohol, and benzaldehyde, as they would exist when the distillate was diluted to 40% ethanol. A higher number of trays produce a lower concentration of acetaldehyde in the distillate, although the catalytic converter seems to increase the amount of acetaldehyde in the hearts of the distillate. The isoamyl alcohol shows the effect of the trays on the congeners with boiling points greater than ethanol. The more trays that are used results in a reduced concentration of congener. This is useful for controlling the fusel alcohols as they have an undesired aroma characteristic.

4.5 Catalytic Converter Use

The use of the catalytic converter as studied in this experiment, had a number of different trends. First, in the earlier stages of the distillation, the catalytic converter, acting as an additional stage, decreased the amount of esters that would be found in the hearts by increasing the amount in the heads of the distillate. The effect on aldehydes in the earlier portion of the distillation was not very clear, and there seems to be no effect or trend that was apparent. As methanol is the only alcohol that is present before the ethanol, the catalytic converter had the effect of reducing the concentration present in the distillate.

Later in the distillation the catalytic converter had the effect of shifting the maximum concentration range of the fusel alcohols to an earlier volume than that of the distillation run with similar conditions without the catalytic converter. The catalytic converter also caused increased ester formation in the tails of the distillate.

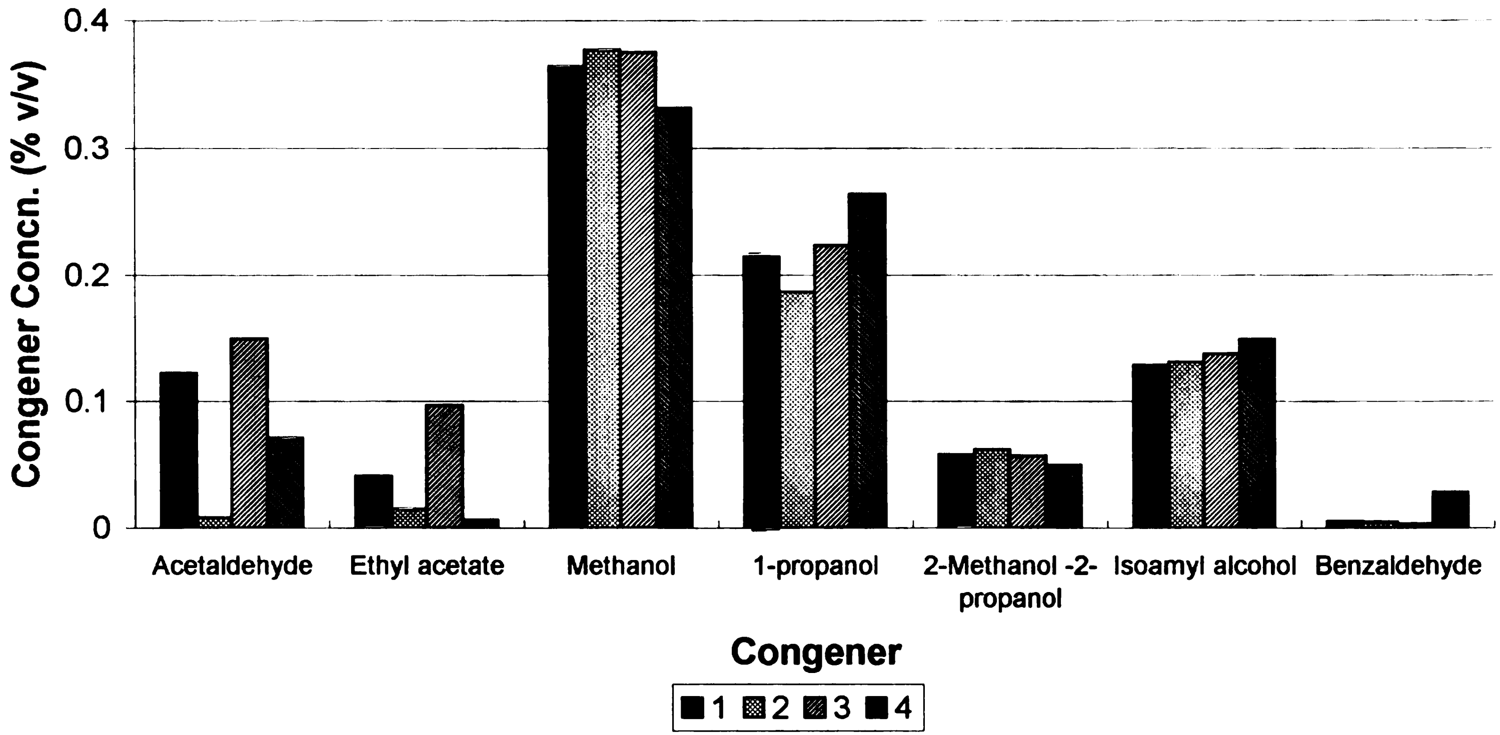

Figure 4.12. **Congener concentration in drinking strength eau-de-vies (40% ethanol v/v) produced by blending and dilution of hearts cuts. (1) All trays used and catalytic converter engaged, (2) all trays used with no catalytic converter, (3) two trays used with catalytic converter engaged, (4) two trays used with no catalytic converter. The concentration range of ethyl acetate was too small to be included with this data set.**

The concentration of ethanol was also effected by the catalytic converter. The ethanol concentration, and volume of useful alcohol were greater with all the trays engaged and the catalytic converter used. The amount of alcohol, both volume and concentration, were lowest in the run without the catalytic converter and only two trays used. The catalytic converter seems to resemble an additional tray in the distillation, however, the amount of increased separation caused by the catalytic converter is not equal to that of an additional tray. The run with all trays used, and no catalytic converter had more separation of the alcohol from the congeners, than the run with only two trays used while still using the catalytic converter.

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5. SUMMARY AND CONCLUSIONS

The distillation of fruit beverages has been occurring since ancient times, and there is still a section of the process that is not fully understood. The number of trays used in distillation has been known to cause better separation of the components in the distillate with more trays used, however, the effect on the congener compounds has not been fully studied. If any attempt is to be made to develop a process for *in situ* analysis of the distillation of fruit spirits, the happenings of the congeners in the distillate must be more fully understood.

The variation of the distillation conditions involved in this study, shows that each congener is affected by the number of trays used in the distillation, as well as the catalytic converter. Changing the number of trays can increase or decrease the amount of congener in the hearts portion of the distillate. This study has shown that using the maximum allowable number of trays in out still, the spirits will be less likely to contain high concentrations of the undesired congeners, while not removing too much of the desired congeners.

Maximizing the number of trays used on the still has yielded a larger volume of higher concentration ethanol. This will translate into more bottles of spirits for sale at market and therefore an increase in profits for the distiller. As mentioned earlier, maximizing ethanol production is just one goal of the distiller, because, if the ethanol is not of a good quality, the consumer will be less likely to purchase the spirits. To see how the quality of the fruit spirits could be improved, the concentration variance of the congener compounds was explored.

Low boiling compounds such as acetaldehyde, ethyl formate, and ethyl acetate, which are present in the distillate as products of fermentation conditions, and esterification reactions in the distillation process, are present in higher concentration in the earlier volumes of the distillate. Acetaldehyde is present throughout the distillate, however, using more trays in the distillation has the effect of having lower concentrations of acetaldehyde in the distillate. While acetaldehyde is thought to contribute to the headache associated with hangover, reducing the concentration of acetaldehyde can make for a more enjoyable drinking experience. The catalytic converter, however, while it at times acts as an additional tray, tended to increase the concentration of the distillate in the fruit spirits when compared with using the trays without the catalytic converter. The same effect is seen with benzaldehyde, so the catalytic converter can be thought to increase the reactions producing aldehydes in the distillation process.

The esters studied, ethyl formate, and ethyl acetate, were also low boiling compounds present in higher concentration in the earlier volume of the distillation process. The amount of these esters in the distillate decreased greatly over the heads and first hearts cut of the distillate. The amount of distillate collected as hearts, and where the heads/hearts cut is made will have a large effect on the overall concentration of the esters in the distillate. The ester concentration will also vary in the storage of the fruit spirits, making this study a preliminary guess at the concentration of the esters in the final product of the spirits. However, the general trend of more trays making for a lower concentration of the ester in the distillate can be seen.

Fusel alcohols present in the mash as a side product of the yeast in the fermentation are known to have an undesired aroma in higher concentrations. The amount of these fusel alcohols in the distillate should be minimized in an attempt to make quality distilled fruit spirits. The fusel alcohols studied included; 1-propanol, 2-methyl-2-propanol, and isoamyl alcohol. The higher number of trays used in the distillation shifted the concentration maxima for the fusel alcohols towards the tails portion of the distillate, thus making it possible to collect more quality distillate, before the unpleasant fusel alcohol aroma would ruin the quality of the distillate.

Benzaldehyde is present in fruit distillate as a fermentation product, as well as a product from the amygdalin in the stones of the fruit, can be considered a positive flavor component. By varying the number of trays used in the distillation the concentration can be shifted to be greater at a later distillate volume when more trays are used. The use of more trays also led to a slight increase in the overall concentration in the benzaldehyde in the distillate, this trend could be due to variation in the fermentation mash, however.

Methanol is the compound most interesting in the distillation of these fruit sprits. The concentration of methanol in the distillate looks like the other low boiling components in the heads and early hearts portion of the distillate, decreasing in concentration as the distillate volume collected increases. However, methanol also has a similar profile as the high boiling components in the later volumes of the hearts distillate into the tails of the distillation. The minimum of the concentration of methanol occurs in the middle of the hearts portion, making the concentration fall near the regulatory limits, making it possible to sell the distillate legally. No distinct change in concentration can be seen through the change in the number of trays used in the distillation, and the catalytic converter, while it changed the distillation profile, did not have an effect that could be easily distinguished. Regulation of methanol through changing distillation conditions seems to be an unlikely prospect.

Overall the profile of the more common congeners found in fruit spirits were studied for how the distillation conditions affect their concentration in the distilled spirits. The analysis of these effects can lead to better tasting, and smelling fruit spirits. The amount of quality distillate produced per fermentation can be increased by deciding on where to make the heads/hears cut on order to minimize acetaldehyde, methanol, and ester concentrations in the hearts, as well as deciding on the hearts/tails cut to minimize the fusel alcohol content of the hearts of the spirits. The production of quality fruit spirits should benefit from this study.

6. FUTURE WORK

Analysis of the congeners in fruit spirits can be difficult over a short time frames as they have similar properties in being low molecular mass organic compounds, while having a broad range of boiling points. The advent of High Speed Gas Chromatography (HSGC) or a GC accelerator may allow the separation and analysis of the congener compounds in the distillate over a quick time frame (2 minutes vs. over an hour). This could allow for the distillate to be a sampled at the top of the condensing column and analyzed before the bulk of the distillate is condensed at the bottom of the condensing column. This could open a broad avenue for better control of the distilled spirits market, and prevent high concentrations of harmful compounds such as ethyl carbamate, from being in spirits sold to consumers.

Other work must be done to study the effectiveness of the catalytic converter for the removal of the cyanide containing compounds from the distillate. As the catalytic converter seems to promote ester formation at relatively lower concentrations of ethanol in the distillation process, the inclusion of the catalytic converter in future still sales may need further review.

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