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thesis entitled

REAL TIME MONITORING OF FRUIT SPIRIT DISTILLATION
WITH HIGH SPEED GAS CHROMATOGRAPHY

presented by

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has been accepted towards fulfillment
of the requirements for the

Master of Science	degree in	Chemistry/Chemical Engineering

Major Professor's Signature

22 AUGUST 2003

Date

REAL TIME MONITORING OF FRUIT SPIRIT DISTILLATION WITH HIGH SPEED GAS CHROMATOGRAPHY

By

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A THESIS

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

MASTER OF SCIENCE

Chemistry and Chemical Engineering

2003

Abstract

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By

Deirdre Jane Lindemann

Fruit brandy distillation is typically performed using a batch still with a rectifying column. The process of producing high quality spirits relies heavily on the distiller's sensory abilities to determine the appropriate moment to make cuts and apply adjustments to the still. However, it would be preferred to have an instrumental method of online analysis that could accomplish the same goal, while avoiding human error. Recent advances in high-speed gas chromatography (HSGC) have made online analysis of distillation a possibility. Two methods of high-speed gas chromatography were examined for this purpose. The first method used the Chromatofast GC Accelerator™, which reduces injection bandwidth and allows for good separation using short normal bore columns and fast flow rates. The second method consisted of a headspace sampling system, which relied on the selectivity of the column and proper temperature programming for sufficient and fast separation. Distillations of "synthetic brandy-type" solutions were performed in order to examine both methods for their ruggedness and ability to analyze samples in a reasonable amount of time. The repeatability and quantification were examined for each method. Finally, results on monitoring compound behavior throughout a distillation are presented.

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1. Introduction

1.1 Michigan Fruit Brandy Industry

In the past decade, there has been a growing interest in the fruit brandy industry in the state of Michigan. Wineries in the state are interested in distillation for the fortification of wines as well as to produce spirits. In addition, farmers are interested in new ways to utilize surplus fruit. Major changes in state legislation made in 1996 have made production and distribution of distilled spirits more economically feasible. This has had a dramatic effect on the fruit brandy industry as the number of distilleries in Michigan has increased from zero in 1996 to seven in 2000.

The United States faces many challenges in producing high quality fruit spirits. First of all, fruit brandies contain hundreds to thousands of compounds, which greatly affect the taste and aroma characteristics of the distilled product[1]. Second of all, some of the compounds present in fruit brandy are regulated due to their toxic effects at high levels of exposure[1,2,3]. Therefore, much research needs to be done on several aspects of fruit brandy production in order to ensure the quality of spirits in Michigan and the rest of the country.

Brandy is the product obtained from the distillation of wine or fermented fruit mash. This type of beverage consists mainly of ethanol and water, but it also contains an array of various compounds that create a characteristic flavor and aroma for individual products[1]. There are many different methods of production, often depending on the location where it is made. For instance, there is the French style or alambic style of brandy making, which involves the use of a batch pot still without rectification. This means that there is little or no reflux for the enrichment of the vapor in the still. This type

requires multiple distillations to obtain high proof spirits and results in the "Armagnac" or "Cognac" style brandies. It is often referred to as wine brandy and is stored in oak barrels to obtain a characteristic color and essence from the wood[1]. The German style of distillation involves the use of a batch still with rectification (the use of trays and partial condensers). The still with rectification is designed to capture the essences of the fruit. This type of distillation requires only a single pass through the still to obtain high proof spirits and results in the "Eau-de-vie" or "Schnapps" type brandies. This type of brandy is stored in glass and is served water clear[1].

The German process of distillation is the only method examined in this thesis. This process of fruit spirits distillation uses the entire fruit. As a result, there is a relatively high production of congeners components (components other than ethanol and water) as compared to other classes of distilled spirits such as whiskeys or vodkas[4]. These compounds are further concentrated during the distillation process. These congeners are key in creating the characteristic flavors and aromas of fruit spirits. Some of these compounds can have adverse health effects if present in extremely high concentrations[2]. Others, if present in too high a concentration can produce an undesirable taste or aroma[1]. Therefore, controlling the amounts of these congeners is of the utmost importance in producing a quality product.

The concentrations of congeners can be controlled during distillation through fractionation of the distillate through the use of trays and partial condensers[1]. It is important to know when it is appropriate to perform these various actions during a distillation in order to control the quality. This requires the sensory analysis of the distiller, in other words his or her sense of taste and smell[1]. This can be difficult as the

senses can become overloaded after prolonged periods of exposure. Therefore an instrumental technique may be useful in monitoring the process of distillation. Gas chromatography has typically been used for analysis of fruit spirits after distillation, however recent advances in high-speed gas chromatography have made it feasible for this method to be used as an online technique[1,5]. Using this method for quality control could make it easier for distillers to produce higher quality spirits.

1.2 Brandy Production Process

The process of distilling fruit spirits (Figure 1.1[6]) consists of four basic steps; processing, fermentation, distillation, and storage. The basic starting material is some kind of fruit including seed fruit (apples, pears), stone fruit (cherries, peaches), and berry fruit among others. The value of these fruits is determined by high sugar content and strong aroma. Although fruit that is less desirable may be used, it should not be moldy or rotten as that will affect the quality of the distillate at the end[1].

The first step in the production of fruit brandy is the processing or the mashing of the fruit. To begin, the fruit should be relatively clean and free from soil[1]. Stems and leaves should be removed whenever possible. Crushing of the fruit can be performed many different ways. The fruit can be crushed under feet, through the use of a rolling mill, or by hand with a mortar and pestle depending on the type of fruit and equipment available. The goal is to process the fruit as completely as possible. The more broken down the fruit is, the more efficiently and completely the fermentation will proceed[1].

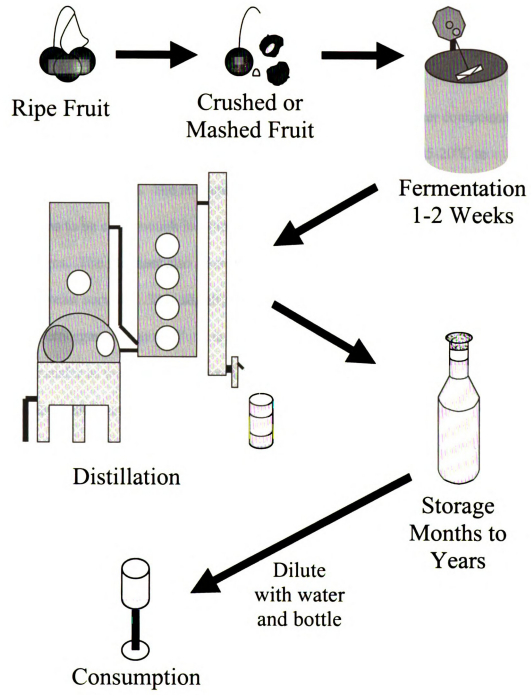


Figure 1.1. The fruit spirits production process.[6]

After processing, the fruit is transferred to a fermenter where yeast will be added in order to initiate fermentation. The primary and desired reaction in a fermentation is the conversion of sugar to form ethanol. This is shown below.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + CO_2$$

In addition there are several side reactions that occur to form the congener compounds in the mash. Fermentations must be kept at a temperature range between 15-20°C to achieve an optimal reaction. The fermentation must be warm enough for the yeast to react, but it has to be cool enough in order to avoid the growth of undesired microorganisms. The pH must also be maintained in a range of 2.8 to 5.2, as this is the range where yeast survives. This slightly acidic pH helps to avoid the growth of unwanted microorganisms as well[1]. It is also useful to stir the fermentation in order to aid in heat transfer as well as to help vent CO_2 from the fermenter. Measurement of the brix of the fermentation mash turns out to be an effective way of monitoring the progress of the fermentation. (Brix is the percent of dissolved solids in the mash, which is assumed to be mostly sugars.) The loss in sugar content corresponds to the production of ethanol. Sugar content can be monitored by the use of a simple hand refractometer or HPLC with a refractive index detector. Depending on the amount of stirring and the conditions of the fermenter, fermentation generally lasts between ten days and two weeks[1].

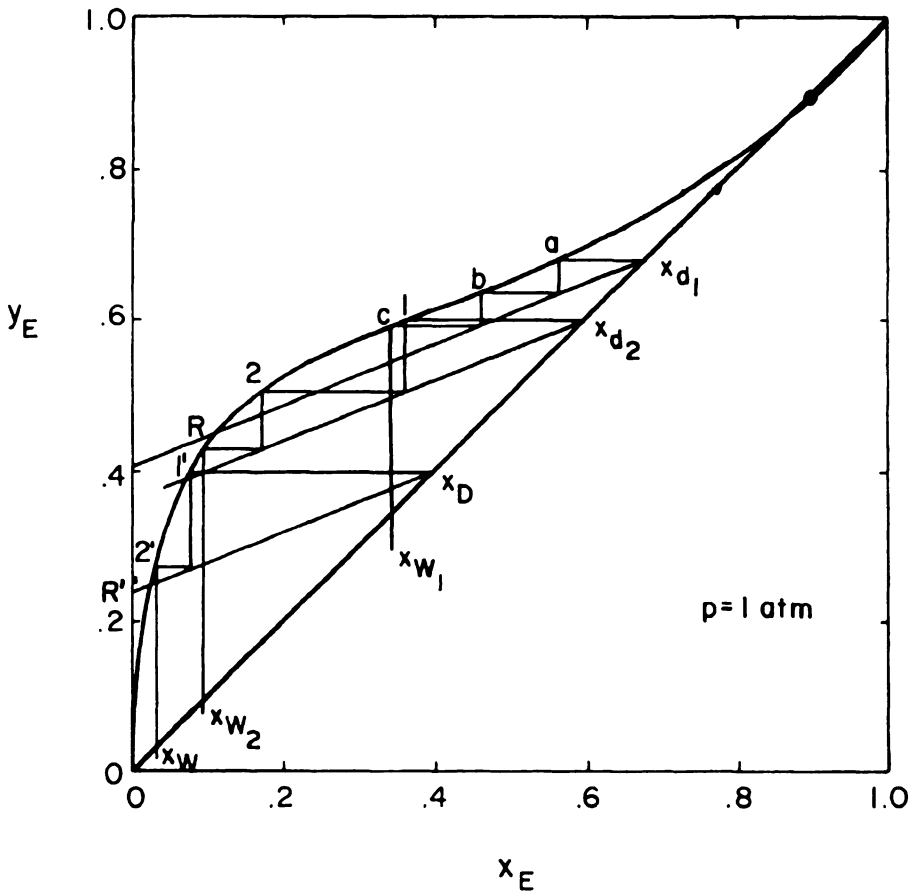
When an acceptable time has passed for fermentation as determined by the conversion of sugars, distillation can then be performed. The still is filled to about 65-75% of volume with mash. Sometimes anti-foaming agents are added. This mash is heated and the alcohol and other volatile compounds vaporize. The idea behind a

distillation is to obtain the greatest amount of ethanol with optimal concentration of congeners to produce a product that is desirable in both taste and aroma. To accomplish this, the distillation is typically broken up into three fractional cuts; heads, hearts, and tails[1]. The heads portion contains relatively higher concentrations of lower boiling point compounds and is generally discarded. The hearts fraction contains the optimal amount of ethanol and congeners and is therefore saved as the potable product. The tails contains relatively higher concentrations of higher boiling point compounds and is also discarded due to an undesirable aroma and taste[1].

After collection of the distillate, the hearts fraction is stored at high proof for several months to several years. The product is then diluted down to 40% and then is bottled and made ready for consumption.

1.3 Distillation

Distillation may be carried out using one of two processes. First, there is distillation without rectification where vapors produced by boiling are condensed and do not return to the still. Second, there is distillation with reflux where part of the condensate returns to the still and comes into contact with the rising vapors. These points of contact are known as plates or stages and they help to make the vapor richer in the higher boiling component[7]. They are also referred to as trays. It is known that the greater number of trays or stages used, the more separation can be achieved[7,8]. This is evident using a McCabe-Thiele diagram shown in figure 1.2[8]. This figure shows the mole fractions of ethanol in the vapor and liquid phase for a water ethanol distillation. Operations were performed for a two stage and a seven stage separation. The seven stage



y_E = Mole Fraction of Ethanol in Vapor
x_E = Mole Fraction of Ethanol in Water

Figure 1.2 McCabe Thiele diagram for batch distillation with reflux showing the effect of increased stages on improved separation[8].

separation yields a higher mole fraction in the distillate. This is typical of a distillation of two components. Fruit brandy distillations are more complicated than this as there are often hundreds of components in a fruit mash to be separated.

1.4 Congener Compounds in Fruit Spirits

Distillation of fruit spirits is more complicated than just a simple ethanol/water distillation. Although the main components are ethanol and water, there are also hundreds of congeners present in varying amounts. In fruit spirits production, the entire fruit is used, including the skins, the pits, the pectin and seeds. This results in various reactions in the fermentation and even distillation and storage that lead to the creation of many congeners. In fact, fruit spirits contain a greater number of congeners compared to other types of beverages such as whiskey, vodka, or gin. This can be seen in Figure 1.3, which illustrates the typical components in various distilled beverages[4,6]. Depending on the amount of these congeners, they can either have a positive or negative effect on the taste and aroma of the resulting distillate. The distillation behavior of these congeners depends on factors such as boiling point and equilibrium relationship to ethanol and water. Conditions of the still and the environment are different each time a distillation is run and each batch of mash, even if it is from the same fermentation, tends to have slight differences. This leads to poor reproducibility of spirits from one distillation batch to the next.

There are various carbonyls, acids, and fusel alcohols present in distilled spirits. Most of these compounds are formed during the fermentation process. The main carbonyl compounds present include esters such as ethyl formate and ethyl acetate and ketones,

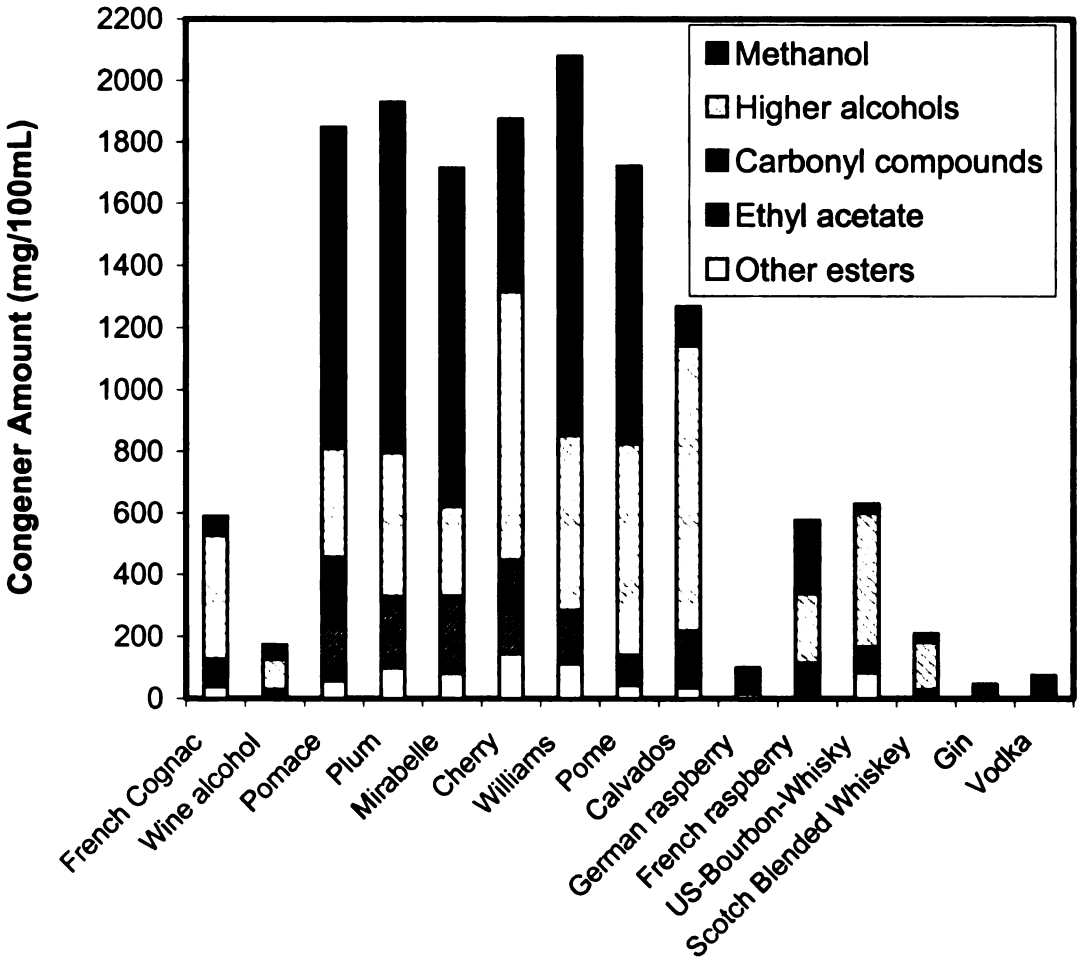


Figure 1.3. **Milligrams of volatile congeners in distilled spirits per 100 milliliters of alcohol. Fruit spirits have higher congener concentrations than other distilled beverages[4,6].**

such as acetone, aldehydes such as acetaldehyde and benzaldehyde[9]. Fusel alcohols, which are alcohols with more than two carbons comprise the largest group of aroma compounds in fruit spirits[9]. The most important fusel alcohol present is isoamyl alcohol. Other fusel alcohols include n-propanol, isobutyl alcohol, and amyl alcohol. The fatty acids present are thought to be products of bacteria as well as a byproduct of the formation of alcohol[9]. However they will not be discussed in this thesis.

Methanol is a major issue in the production of distilled spirits. Although methanol is a desired compound for flavor and aroma, it is regulated for the health risks it poses. Methanol can cause damage to many human organs, such as liver, kidneys, and the nervous system. Methanol can also cause temporary or permanent blindness, or even death[3]. Therefore, the United States Environmental Protection Agency has set limits on the amount of methanol that can be present in drinking water at 3.9 parts per million. The acceptable exposure limit in air is set at 200 parts per million for an eight hour time weighted average. Methanol in fruit spirits has been regulated in Europe from a range of 400mg/100mL to 1000mg/100mL absolute alcohol depending on the variety of fruit spirit being produced. According to the Bureau of Alcohol, Tobacco, and Firearms, the limit is 0.35%v/v for all fruit spirits, which translates to 700mg/100mL absolute alcohol[2].

1.5 Structure of a Batch Still

The construction of the still is very important in controlling the various steps of a distillation. A 150 L Christian Carl still is shown in Figure 1.3[6]. There are varying designs of these stills regarding the number and placement of trays, however, this figure is a good indication of what is typical for brandy stills. Although design opinions vary, it

is agreed that the material used to make up the still must be copper. Copper is a very good heat conductor, shows good resistance to fruit acids, and has catalytic properties that contribute positively to the quality of the fruit spirits produced[1].

The basic design includes a pot, a column with trays, and condensers. The pot contains the mash when the still is filled. In this figure, the pot is heated using a steam jacket connected to a steam inlet. Some fruit mashes are rather viscous and pose difficulties with uneven heating, foaming, and baking. Therefore, many stills may contain a stirrer to ensure not only that the mash is evenly heated, but also to reduce the occurrence of foaming and baking of mash to the surface of the pot. Trays can be opened or closed. The particular still in the present work contains four trays, one over the pot, and three in the column next to the still. A still may also contain a catalytic converter, which is a vessel containing a high surface area copper packing used as both an extra tray in distillation and means for removing cyanide containing compounds from the distillate[6]. There is a function that allows for the distillate to enter through the bottom of the catalytic converter, or allows for the catalytic converter to be bypassed.

Stills contain a condensing column that condenses the distillate vapor into liquid when cooling water is passed through. There can also be partial condensers. The still contains a partial condenser above the tray over the pot and one above the three trays in the column adjacent to the pot. It is possible to choose to allow water to pass through these condensers, or to leave them off. There is a flow regulator to control the flow rate of cooling water through the condenser and partial condensers. By controlling the rate of cooling water that passes through the condensers, one can control the rate of the distillation.

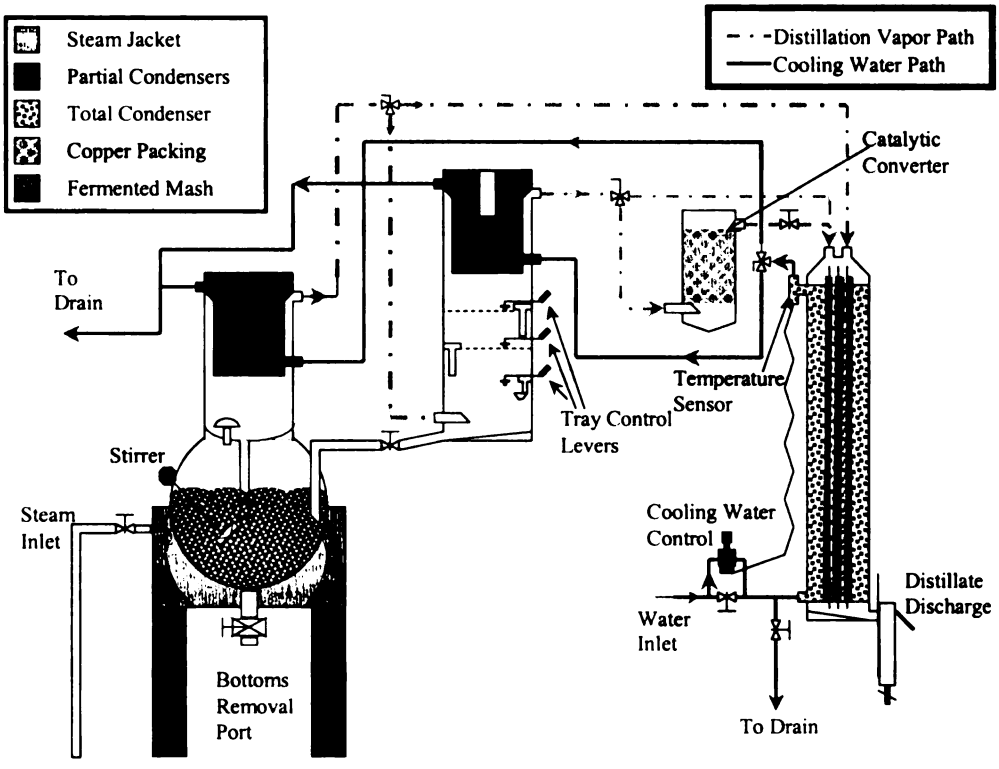


Figure 1.4. A 150 L Christian Carl Batch Still[6].

1.6 Quality Control

The control of quality can come from many aspects of the brandy production process. It was mentioned before that the processing and fermentation steps of the production process can affect quality. In the processing step, fruit of an adequate quality must be used and proper maceration must be performed to ensure good quality. In the fermentation, temperature, and pH must be considered to ensure that the fermentation proceeds appropriately[1].

Finally, adjustments may be made to control the quality of the distillate. First, appropriate fractionation is important. Separating the distillate into the heads, hearts, and tails is essential. Knowing when to apply other devices, such as the catalytic converter or partial condenser are important as well. This thesis will focus on the quality control through manipulation of the distillation.

1.7 Analysis of Fruit Spirits

It is important to know when to make appropriate adjustments during the distillation. The sensory analysis of the distiller has been used since the inception of the practice of distillation. In other words, the distiller makes fractions and other adjustments based on the taste and aroma of the distillate. This practice has been customary, but it has its disadvantages. After prolonged periods of exposure, the distiller's sense of taste and smell begin to overload and become less reliable with each distillation. So it would be advantageous to have some instrumental method to analyze the quality of distilled spirits and be able to make adjustments during the distillation[1].

Gas chromatography (GC) has been used for years to analyze the concentration of congeners present in the distillate[1]. It is a robust and reliable instrument with low limits of detection capable of detecting trace concentrations[10]. The drawback to conventional gas chromatography, however, is analysis time, which often ranges from 40 minutes to an hour for distilled spirits. GC has only been useful for analysis after the distillation.

Advances in high speed gas chromatography (HSGC) have now made it possible to examine distillations using chromatographic methods as an online tool. HSGC can utilize faster flow rates, shorter columns, and sometimes special injection techniques to perform analyses that range from a few seconds to a few minutes[5]. With this technique, it is possible to collect a sample directly from a still and analyze in a fast enough manner that adjustments could be made to control quality during a distillation.

1.8 Objective

The goal of this study will be to examine methods of high speed gas chromatography and how they can be applied to online monitoring of a distillation. An efficient and effective sampling method for extracting sample from a brandy still and injecting it into a gas chromatograph will be demonstrated. It will also be important to examine the speed and efficiency of the actual chromatographic separation. Finally, the method will be applied the method to an actual distillation in order to monitor compounds as they are volatilized.

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2. High Speed Gas Chromatography Background

2.1 Development of High Speed Gas Chromatography

The development of high speed gas chromatography began with the advent of open tubular capillary columns by Golay in 1957[1,2]. Open tubular columns have greater permeability and require lower inlet pressures than packed columns. In addition, there is a less rapid loss in column efficiency with increasing velocity[3]. Since it was more practical to operate at higher flow rates, it was recognized that high speed gas chromatography was possible. The establishment of the principles of high-speed chromatography came in the 1960's. Using open columns, in the 1960's Desty and his co-workers separated nine heptane isomers in 5 seconds using a gas tight syringe which was struck sharply by a mallet to inject a narrow 10 ms vapor plug into a gas chromatograph[1,2].

Despite such breakthroughs, open tubular columns gained slow acceptance due to competition with packed columns, which had been used for years. Packed columns are rugged and had high resolving power and high sample capacity. The first open tubular columns were made of rigid glass, which made them difficult to install and maintain. In addition, open tubular columns lacked good selectivity compared to packed columns since there were not as many available stationary phases. The advent of fused-silica columns along with other technological improvements made open tubular columns more flexible and viable for everyday use[2].

Unfortunately, once open tubular columns gained acceptance, the main goal in their application was not speed as chromatographers were primarily concerned with achieving high resolution. In fact, people often achieved much higher resolution than

needed by using extremely long capillary columns. The reason for this was that there was a limited range of stationary phases, which resulted in low selectivity. So increasing the column length was the simplest way to bypass this problem. If a column is long enough, one can achieve adequate separation without having to be concerned with stationary phases and temperature or pressure programming[2]. Obviously, this leads to an increase in analysis time.

In addition there were technological deficiencies in the instrumentation early in the development of high-speed gas chromatography for which it took years to overcome. First of all, commercial instruments were unable to handle the high speeds. Detectors and other data collection systems were not fast enough to measure rapidly eluting compounds. Also, oven and pressure capabilities were not advanced enough to produce fast and precise programming rates. Additionally, the use of short columns needed for fast separations led to a loss in peak capacity. This shortcoming restricted the complexity of the sample that could be analyzed[1,3].

Fortunately, the needs of field portable GC devices and the need for chromatographs with higher throughput led to greater developments in fast GC technology. Advances in injection systems have reduced the bandwidth of the initial injection to reduce band broadening. Faster detectors, such as flame ionization detectors and time of flight mass spectrometers, can keep up with the faster elution of compounds. In addition, gas chromatographs can be equipped with efficient ovens that are capable of achieving faster temperature program rates. They are also available with more sensitive pressure regulators. The growing need for faster separations combined with several

technological advancements have led to the recent growth in the use of high-speed gas chromatography.

2.2 The Compromise between Speed and Separation

Unfortunately, everything comes at a cost and high-speed GC is no exception. The measures taken for decreasing analysis time often decrease sample capacity and selectivity, and also lead to broadening of peaks. Therefore, a compromise between speed and separation must be found to meet the needs of the analysis at hand.

There are three major approaches that can be applied to achieve this compromise. Minimizing the resolution to a value that is just sufficient is one option[4]. It was discussed before that peaks are often over separated by using extremely long columns. Instead, one could focus on the peaks or critical pairs that are important for the analysis and optimize just enough to separate those compounds. This is probably the simplest method for separation. Another option is to maximize the selectivity of the chromatographic system[4]. Finding appropriate stationary phases, which are selective toward the compounds of interest has been done. It has been shown that more selectivity can mean less concern for column length and method development. Finally, another approach involves speeding up analysis while maintaining the same resolution[4]. If the analysis time is too long even with the minimum accepted resolution, methods that speed up analysis without decreasing resolution can be applied. This is a more complicated route, as it often requires major equipment changes such as the use of narrow bore columns or new injectors.

There is really no universal method for high speed gas chromatography, so finding a method that works is a challenge. The application determines the approach needed to decrease analysis time. In choosing an approach, one needs to consider the amount of speed truly needed to accomplish the goal, the required ruggedness of the instrumentation needed, the complexity of the sample, sample phase, and method needed for sample extraction. Sometimes several methods may need to be used in combination in order to achieve the desired goal. Whatever the goal and method used, it is important to look at every aspect of the GC instrumentation, from injection, to columns, to detectors, to temperature and pressure programming, and carrier gas flow.

2.3 Columns

Two simple methods for reducing the separation time are to shorten the length of the column and to decrease the stationary phase thickness[3,4,5]. Shortening the column obviously speeds up analysis by decreasing the distance the sample has to travel. Decreasing stationary phase thickness reduces the amount of time that the sample interacting with the stationary phase. These methods may speed up the analysis, however they also decrease the efficiency. One must be careful not to lose desired resolution in changing length or thickness.

Another common method for fast separation while maintaining column efficiency is the use of narrow bore columns. This method would fall under the category of maintaining constant resolution. A narrow bore column is one which has an inner diameter of 0.1 mm, and below, compared to a normal bore which has an inner diameter of 0.25mm and greater. Narrow bore columns make it possible to use shorter columns

and faster flow rates while maintaining resolution. The reason for the resolving power of narrow bore columns can be seen in equations 2.1 and 2.2 below[5].

$$HETP = \frac{f(k) \cdot r^2 \cdot u}{D} \qquad \text{Equation 2.1}$$

HETP is the height equivalent to a theoretical plate; f(k) is a function depending on the retention factor, r is the column radius, u is the average linear flow velocity of the mobile phase, and D is the solute diffusion coefficient[3,5]. This equation can be rewritten to include plate number (N).

$$N = \frac{D \cdot L}{f(k) \cdot r^2 \cdot u} \qquad \text{Equation 2.2}$$

This equation shows that when column length is shortened, reducing the column radius and/or increasing linear velocity[5] can maintain column efficiency. In fact, when the length/ID ratio is unvaried, a short narrow bore column has the same efficiency as a conventional column. Gas compression effects are lower and Van Deemter curves are flatter with narrow inner diameter columns. Therefore, higher average velocities can be used without sacrificing efficiency and the analysis time is shortened.[5,6]

The use of narrow bore columns is widespread, however it is not the universal method for performing HSGC. Narrow bore columns require the use of very small sample volumes often on the order of nanoliters[1,3,5]. Such small sample sizes are very difficult to create and injection repeatability is also difficult to. In addition, narrow bore columns require much higher pressures than some GC instruments can provide. Method development is also difficult, especially in quality control[6]. However, it is becoming more convenient to use this method given recent technological advances.

It has also been shown by other research groups that fast gas chromatography can be performed without the use of narrow inner diameter columns. Good separation can be performed using ordinary inner diameter columns with regular injection techniques. In a great number of applications, the efficiency of a capillary column is much higher than necessary. It is believed that normal bore columns can then be shortened to meet the minimum separation requirements of medium complexity mixtures. Loss of efficiency due to shortening columns can be compensated by carefully choosing selectivity in the stationary phase[5]. One can attempt to find one specific column that meets the separation needs for the target compounds. However, selectivity can also be achieved using mixed stationary phases or series coupled ensembles of two capillary columns[7]. These columns can be designed for specific use with the compounds of interest. Increasing the selectivity this way can allow for the use of a shorter column with a normal inner diameter. Using normal inner diameter columns helps to maintain sample capacity which is lost when using narrow inner diameter columns. Therefore, split ratios do not have to be extremely high or the GC instrument can be run in splitless mode. It can also help to avoid the need for more complicated instrumentation.

2.4 Injector Considerations

Most common injection systems are acceptable for high speed GC if applied properly. One must remember, however, that it is often useful to minimize the injection bandwidth whenever possible[4]. This will limit the amount of band broadening during elution through the column and therefore, aid in separation. With a common splitless injection, sometimes decreasing the amount of sample injected is enough to achieve

adequate separation. Sometimes more sample is needed to decrease bandwidth, so split injection may be used. Many operating systems today are capable of achieving very high split ratios that produce injection bandwidths on the range of milliseconds[4].

Although a normal injector may be acceptable for some applications, it might be advantageous to use a special injection technique. In addition to loss in resolution and peak capacity from reducing the column length, the use of high velocities also increases the occurrence of band broadening due to injection. Therefore, the sample's bandwidth not only needs to be reduced, but the peak capacity needs to be used more efficiently. The use of a rapid and controlled injection system can help to alleviate this problem[3].

This special injection technique involves cryofocusing or freezing a sample into a very narrow plug. These plugs can have a bandwidth of smaller than 1ms. For comparison, typical GC instruments produce injection bandwidths of 50-500ms[1]. This very small plug can be injected into a shorter, regular inner diameter column, while using faster flow rates and adequate separation can be achieved. Sacks and coworkers developed such an instrument. This instrument contained a nitrogen cooled, electrically heated cold trap inlet which could be used to decrease sample injection bandwidth. The advantage to this method is that normal columns can be used so sample size restriction is not an issue. In addition this added injection technique can have the technological capability to supply the high pressures needed. Also this instrument can be added on to existing chromatography equipment.

2.5 Temperature Programming

Temperature is a factor in controlling the speed and efficiency of a separation.

For samples of medium to high complexity with a wide range of boiling points, a programmed analysis might be useful. In order to achieve high speed, it is helpful to increase the rate of temperature programming compared to a regular GC. Modern GC ovens can often produce programming rates of 50-100°C/min compared to the normally used 2-10 °C /min. The one drawback to temperature programming is the cooling and recovery time it takes to return the system back to initial conditions. This could be a disadvantage when fast repeated measurements are required. However, there are recently developed systems that not only have faster heating rates, but faster recovery times as well. The EZ Flash system can have a heating rate up to 1200 °C/min and can cool from 300 °C to 50 °C in less than 30 seconds[4].

It has also been shown that isothermal analysis can be done when analyzing relatively simple mixtures[2]. Isothermal methods eliminate the need for recovery and cooling time of the instrumentation. It also eliminates the need for more complicated oven equipment such as the EZ Flash system.

2.6 Pressure Considerations

Pressure is also an important factor in high-speed gas chromatography. For example, the use of narrow bore columns requires high inlet pressures in order to operate[3,4,5]. Pressure programming has even been studied as an alternative to temperature programming in cases where the stationary phase or sample is thermally labile. With pressure programming steeper gradients could be achieved and there is a more rapid return to initial conditions[9]. The newest gas chromatographs can be equipped with

electronic pressure control, which can achieve both extremely high pressures for narrow bore capillary use and tunable pressure for programming purposes[4,9].

2.7 Carrier Gas Flow Rate

Increasing the flow rate of the carrier gas is another way to speed up analysis time in high-speed GC. This can be done until a loss of sufficient resolution is detected. Another option is to change the type of carrier gas used[2,4]. One of the most widely used carrier gases is helium, has one of the highest rates of diffusion. However, hydrogen has an even faster diffusion rate. The drawback to hydrogen is its explosive nature. Despite this problem, many modern chromatographs can be equipped with safety shut-off features that protect against hydrogen leaks and decrease the chance for dangerous explosions[4]. This can make hydrogen gas a viable option.

2.8 Detectors

With faster elution of compounds from a high-speed GC, other instrumentation needs to be fast enough to handle the speed of separation. Detectors, for example, must have a fast enough response time to detect peaks with extremely narrow widths[3,4,6]. They also need to have low limits of detection, especially in cases where a very small sample size is used. Some examples of detectors with fast response times are flame ionization, thermal conductivity, and time-of-flight mass spectrometry.

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3. Experiment : Discussion of Fast GC Setups

3.1 The Chromatofast® GC Accelerator™

The first attempt at obtaining online distillation data involved the use of a special cryofocusing injection apparatus called the Chromatofast® GC Accelerator™ developed by Richard Sacks and his co-workers at the University of Michigan. It is an inlet system that attaches to a conventional gas chromatograph to give it high-speed GC capabilities. It does this by reducing the effects of band broadening during injection in order to deliver narrower peak widths. As mentioned in Chapter Two, decreasing band broadening during injection can make it possible to achieve good separation even when using shorter, normal inner diameter columns and faster flow rates. This is advantageous as it alleviates the need for the use of narrow bore columns with strict sample size requirements. The accelerator we used was purchased from Chromatofast®, Inc. for $21,100.

The Chromatofast® gas chromatograph setup is shown in Figure 3.1. This figure shows the external components of the instrument. There is a sampling interface, which is equipped with a vacuum pump for taking headspace samples. This particular model consists of a Valco connector and a Silco-Steel capillary column for sample extraction. The front panel of the Accelerator™ contains a keypad and LCD display to monitor the status of the instrument as well as to navigate the menu and enter data. There is also a pressure regulator that can be adjusted between 0-60 psig. Finally, there is the heated interface tube, which transfers the cryofocused sample from the Accelerator™ to the GC column. This tube is designed to extend through the wall of the GC oven through a hole in the GC[1].

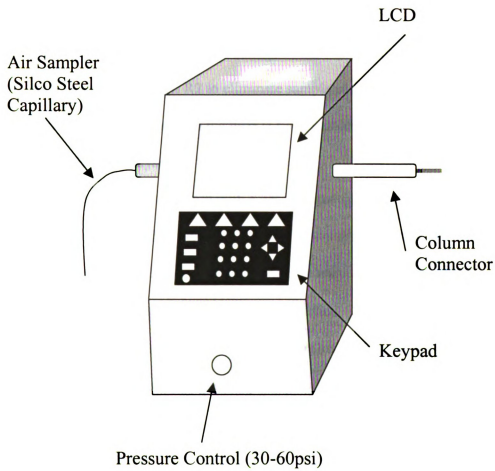


Figure 3.1. Schematic of thr GC Accelerator™ external components. This air sampler makes it convenient for interfacing with a still. There is a keypad and LCD for controlling parameters[1].

A schematic of the Accelerator™ connected to a conventional gas chromatograph is shown in Figure 3.2[2]. The accelerator itself consists of three restrictor columns R1, R2 and R3, two solenoid valves V1 and V2, a vacuum pump, cold trap, and an inlet for carrier gas. The process of sampling and injection involves a sequence of steps, sampling, flush, and fire. In the sampling stage, sample is pulled through R2 and R3 and into the cold trap containing liquid nitrogen where cryfocusing of the sample occurs. In the flush stage, carrier gas travels through V2 and sweeps residual sample from R3 onto the trap as well as sweeps through R2 to eliminate sample carryover. In the analysis step, the flow reverses in the cold trap, and the tube is flash heated. From there, the sample is injected into the GC for analysis[3].

The basic on line analysis setup with a gas chromatograph and still is shown in Figure 3.3. A hole was drilled in the vapor transfer pipe just above the condenser and covered by a septum. The Silco steel air sampling line was connected through the septum where it could collect distillate vapor prior to condensation. The Accelerator™ then cryofocused the sample and injected it into the gas chromatograph for separation. Data was then collected and analyzed using a computer connected to the GC.

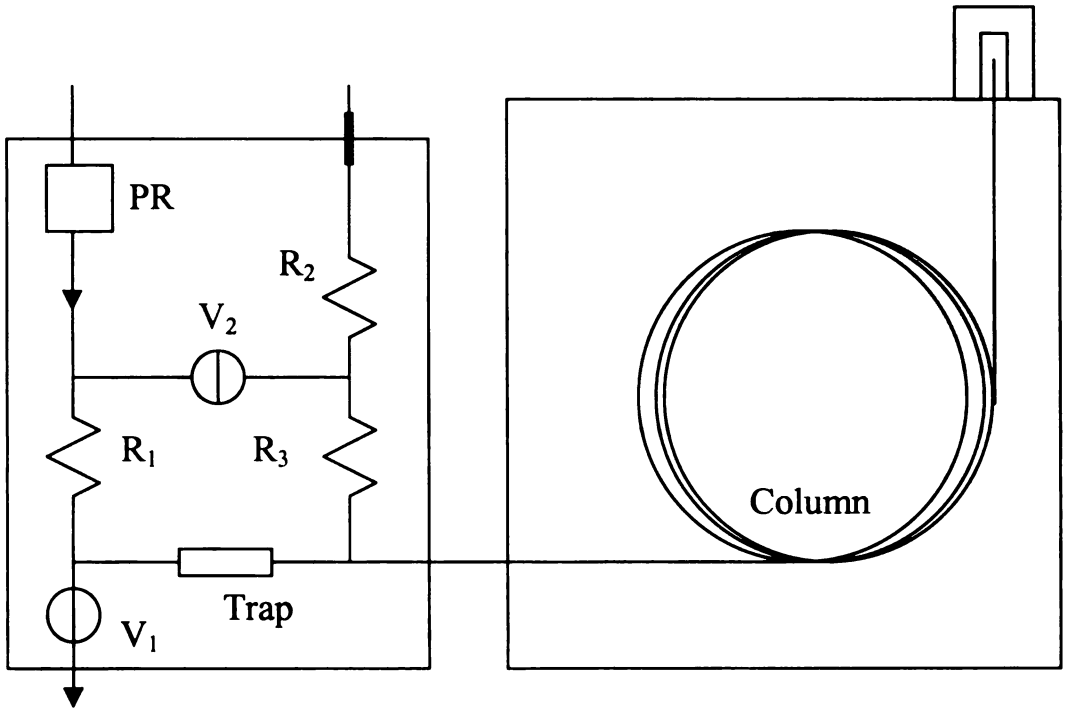


Figure 3.2. Schematic of the GC Accelerator connected to a typical gas chromatograph[2,3]. The accelerator itself consists of three restrictor columns R1, R2 and R3, two solenoid valves V1 and V2, a vacuum pump, cold trap, and an inlet for carrier gas. Sample is pulled through R2 and R3 and into the cold trap containing liquid nitrogen where cryfocusing of the sample occurs. Carrier gas travels through V2 and sweeps residual sample from R3 onto the trap as well as sweeps through R2 to eliminate sample carryover. Finally, the flow reverses in the cold trap, and the tube is flash heated. From there, the sample is injected into the GC for analysis.

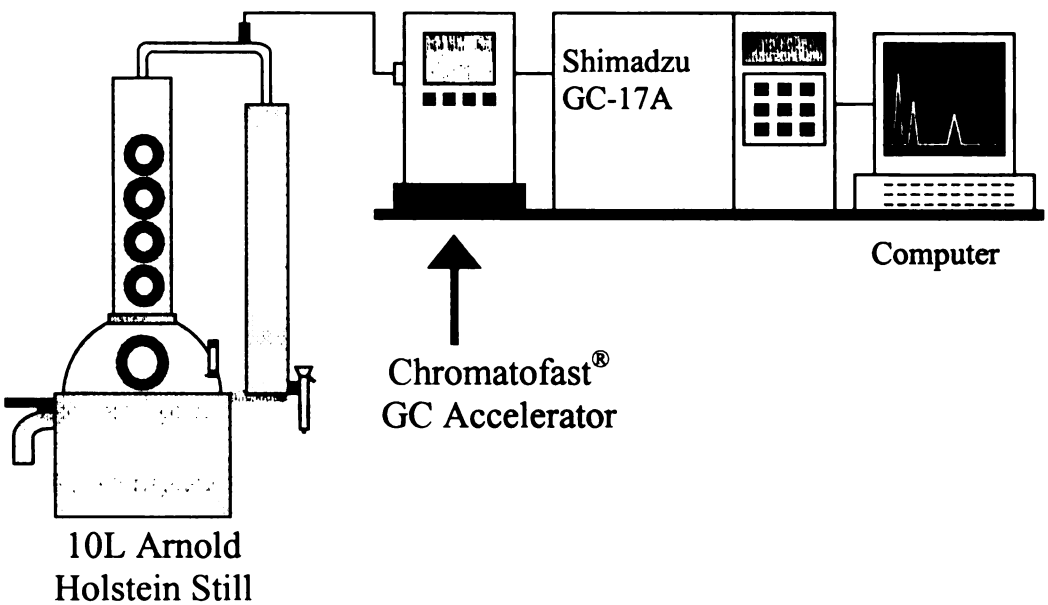


Figure 3.3. Schematic of the online setup with the Arnold Holstein still connected to the GC Accelerator™ and gas chromatograph. Sample from the still is extracted through the Silco-Steel capillary into the Accelerator where it is cryogenically frozen , then flash heated and injected into the GC.

3.2 The Headspace Sampling Setup

The second setup was constructed on the basis that column selectivity would be sufficient enough that adequate separation is possible without the use of a special injection technique or narrow bore column. This headspace sampler setup is an efficient method for extracting vapor samples while a distillation is occurring. The separation of compounds relies on the selectivity of the chromatographic column and appropriate temperature and pressure programming. Adequate separation was achieved even with the use of shorter columns and faster flow rates.

A flow schematic of the headspace sampling instrument connected to a GC is shown in Figure 3.4. This instrument consists of an injection valve assembly, heated transfer line, and purge and trap adapter. Carrier gas supplies a constant flow to both the GC and the headspace sampler assembly throughout the process. Carrier first flows through a line in the GC, where it is passes through the purge and trap adapter. This particular adapter came from Shimadzu, Inc., which made it compatible with our GC. The adapter splits the flow and directs some to the injection valve and some to the GC injector. From the injector, carrier gas flows to the column and eventually to the detector to ensure constant circulation through GC instrument. From the injection valve, carrier flows to the heated transfer line and again to the injector, which flows through the column and the detector. This configuration ensures constant flow through the injection valve and helps to transfer sample from the sample loop to the heated transfer line.

The injection valve serves as the heart of the apparatus as it allows sample to be loaded into the sample loop and then injected onto the column. The injection valve used was a six port, two position electrically actuated valve from VALCO Instruments

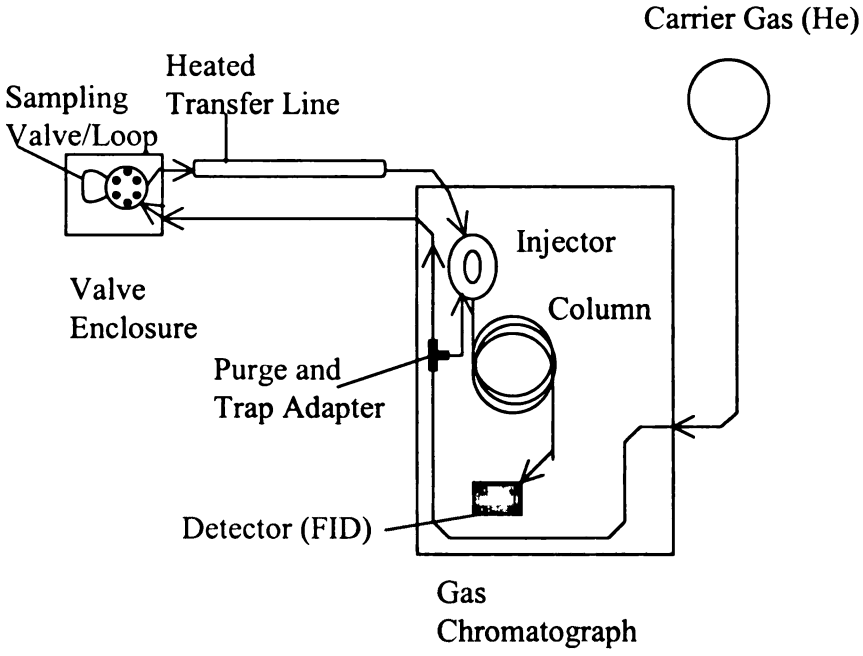


Figure 3.4. A schematic of carrier gas flow through the entire system. Helium from an air cylinder enters through the GC and flows to the purge and trap adapter. The adapter splits the flow and directs carrier gas to both the GC injector and the injection valve. Helium flowing through the injector travels through the column and the detector to ensure flow through the GC. Carrier flowing through the injection valve travels through the heated transfer line, where it enters through the injector and eventually into the column and detector. This ensures that sample is transferred to the GC.

Incorporated. This particular valve has a two-inch standoff so that it can be encased in a valve enclosure, which allows for heating and insulation. The injection valve is connected to a resistively heated block. The temperature of the valve is maintained at least 120°C in order to ensure that the sample remains as a vapor inside the apparatus. Temperature control is achieved using a Valco temperature controller and a thermocouple that is connected just underneath the heating block.

The valve flow diagram shown in Figure 3.5 reveals how carrier gas and sample flows through the system. This valve has six ports, 1 for the sample to be loaded, 2- for venting waste, 3 and 6- for the sample loop, and 4 and 5 for the entrance of carrier gas. In the load position, sample is loaded into the sample loop and directs to the vent. Meanwhile carrier gas is flowing from the GC, through the valve directly to the heated transfer line and onto the column. In the inject position, the ports are switched so that carrier gas flows through the sample loop and pushes sample through to the transfer line. From the transfer line, sample is transferred to the injector and onto the column to be analyzed.

The heated transfer line comes from Tekmar Industries. It consists of copper tubing with an outer diameter of 1/16" and an inner diameter of 0.02". Its insulated line is 60" long. It contains a K-type thermocouple, which is connected to an Omega CN9000 temperature controller. Again the temperature is maintained at least 120°C in order to ensure that the sample remains a vapor. From the transfer line, sample enters into the GC.

The computer is used for both instrument control and data acquisition. As a trigger, the computer signals the electronic actuator on the valve to move into the load

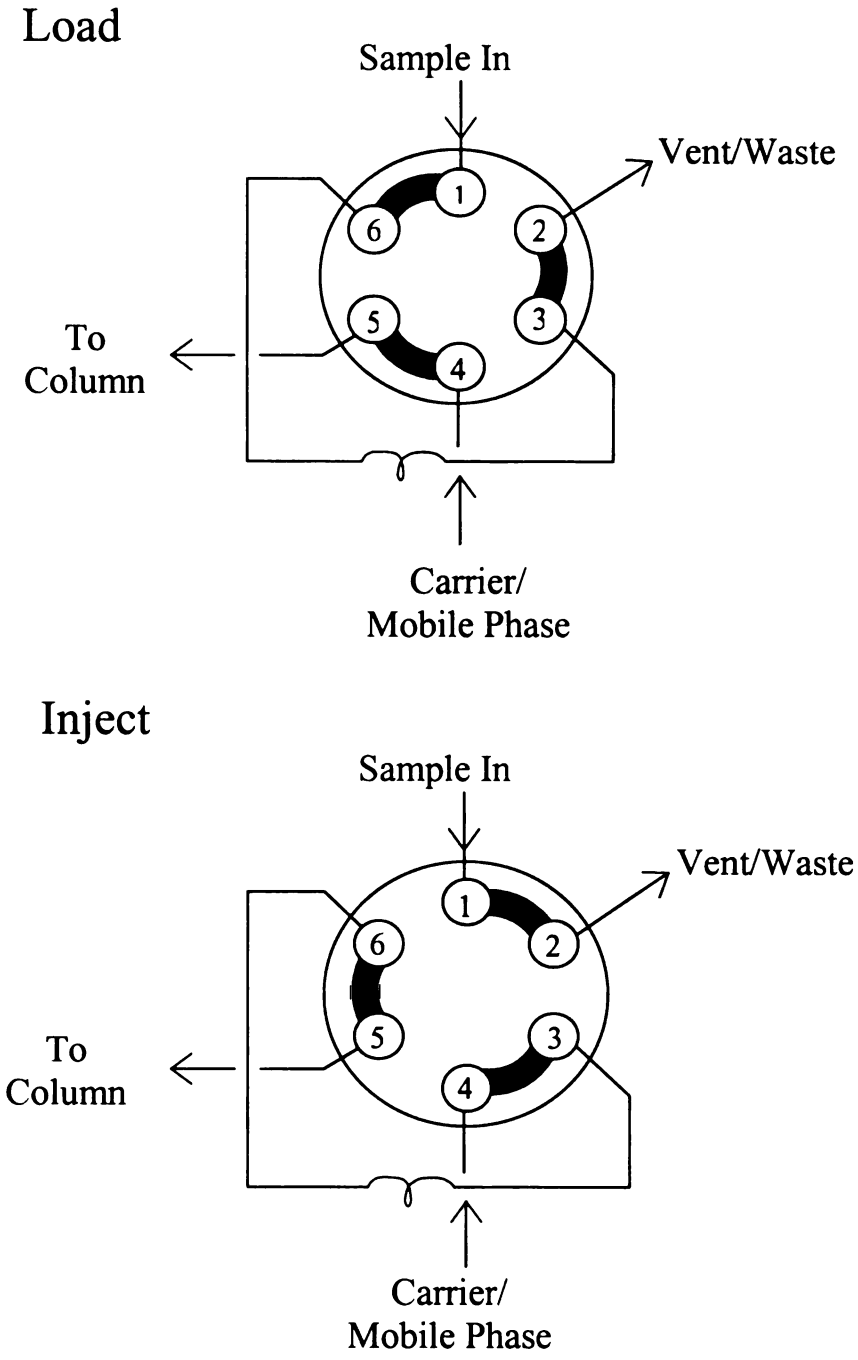


Figure 3.5. A close-up view of the sample loop inside the sampling valve. In the load position, the vapor sample from the still enters through the sample loop. In the inject position, the carrier gas enters the sample loop and tranfers the sample to the transfer line and eventually to the column[4].

and inject positions. To achieve this, the electronic actuator was wired to the SS420 board of the GC computer. GC software was used to generate an external events table that controlled the positions of the valve. The computer simultaneously collected data from the computer by reading signal from the detector and developing chromatograms during the analysis.

Figure 3.6 shows the entire online setup including the still, the headspace sampler assembly, the GC, and the computer. The headspace assembly is connected to the still through the sampling port just above the condenser. With this apparatus, the computer triggers the opening of the injection valve to the load position. Simultaneously, the computer begins data acquisition. While in the load position, pressure from the still transfers vapor sample above the condenser into the sample loop. The sample travels from the sampling port, to the sample loop in the injection valve, and through a heated transfer line. The purge and trap adapter connects this transfer line to the gas chromatograph where the sample travels through the column and detector to be analyzed.

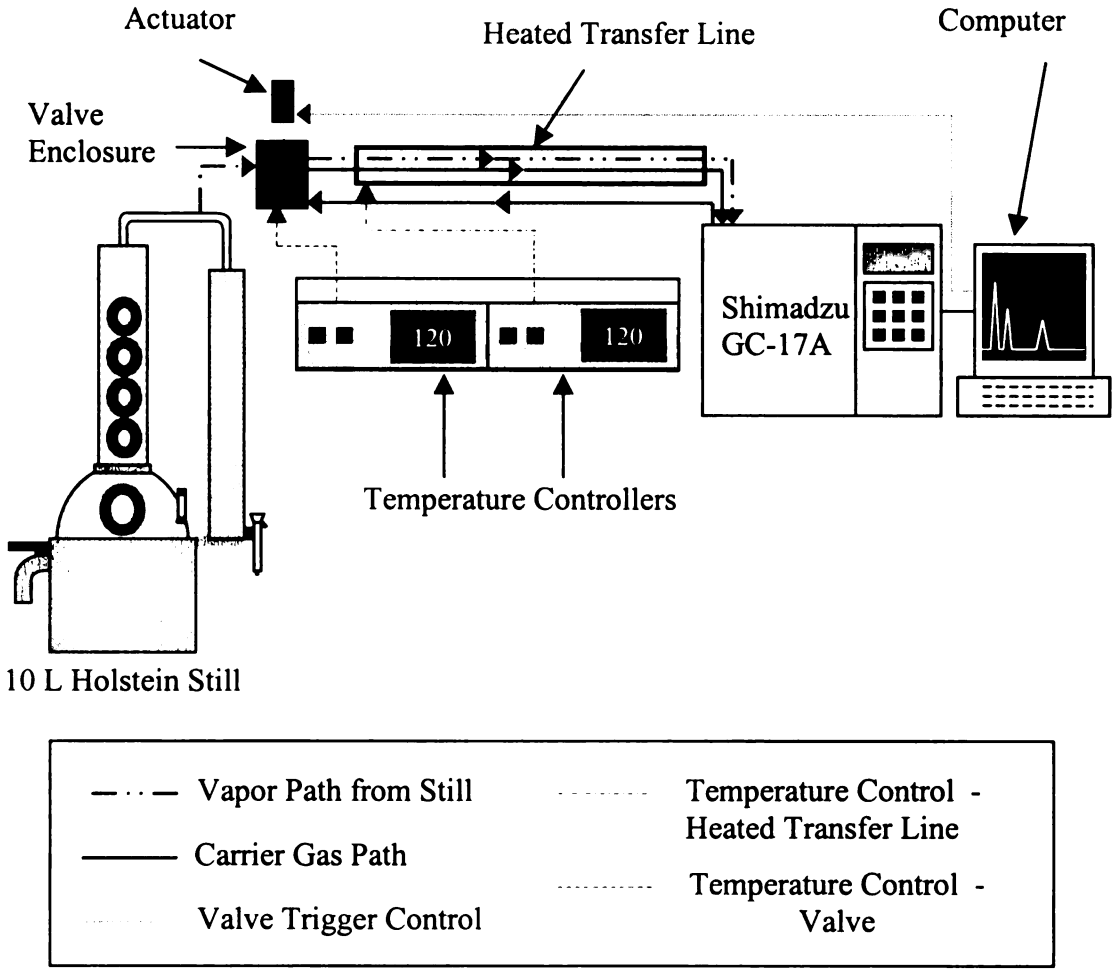


Figure 3.6. Schematic of the headspace sampling system connected to the Shimadzu GC-17A.

Literature Cited

1. Adapted from Chromatofast® GC Accelerator™ Air Sampler User Manual.
2. Adapted from Chromatofast® GC Accelerator™ Fast GC Operation Technical Note.
3. Chromatofast® GC Accelerator™ Air Sampler User Manual.
4. Adapted from VALCO Flow Diagram Technical Note.
5. Shimadzu Purge and Trap Adapter Technical Note.

4. Materials and Methods

4.1 Spirits Production Process

4.1.1 Creation of Standard Solutions

Actual fruit fermentations were not used in performing the online experiments. Fermentations generally take two weeks to ferment, which limits the number of distillations that can be performed in a given period of time. Therefore standard solutions were used to simulate distillation behavior. Creating a mixture that contains a similar amount of congeners as that of a fermentation mash can be done. Solutions were made in 30 mL batches so experiments could be run in triplicate. These solutions consisted mainly of ethanol and water. There are hundreds of congeners that exist in fruit spirits, therefore, only the most prominent ones were investigated. The congeners used and their volume percentages are listed in Tables 4.1 and 4.2. For the experiment with the Accelerator™, the congeners chosen were acetaldehyde, ethyl acetate, ethyl formate, acetone, methanol, n-propanol, and isoamyl alcohol. In the headspace sampling experiment all the congeners were used except for ethyl formate and acetone.

4.1.2 Distillation

Distillation was performed using a 10 L Arnold Holstein still, as shown in Figure 4.1. This still is mainly constructed out of copper and consists of a pot, a steam jacket, three bubble cap trays, a partial condenser, and a total condenser. The pot is where the solution to be distilled resides. It is heated by the steam jacket, which uses electrically heated steam. The bubble cap trays can be opened or closed so that one, two, or all three trays may be activated. Just above the pot is a partial condenser, which can be turned on

Compound	Volume (mL)	Percent v/v Solution
Water	27486	91.62
Ethanol	2400	8.00
Acetaldehyde	15	0.05
Methanol	24	0.08
Ethyl Formate	6	0.02
Acetone	15	0.05
Ethyl Acetate	6	0.02
n-Propanol	24	0.08
Isoamyl Alcohol	24	0.08

Table 4.1. Congener types and volume percentages used in Experiment 1.

Compound	Volume (mL)	Percent v/v Solution
Water	27507	91.69
Ethanol	2400	8.00
Acetaldehyde	15	0.05
Methanol	24	0.08
Ethyl Acetate	6	0.02
n-Propanol	24	0.08
Isoamyl Alcohol	24	0.08

Table 4.2. Congener types and volume percentages used in Experiment 2.

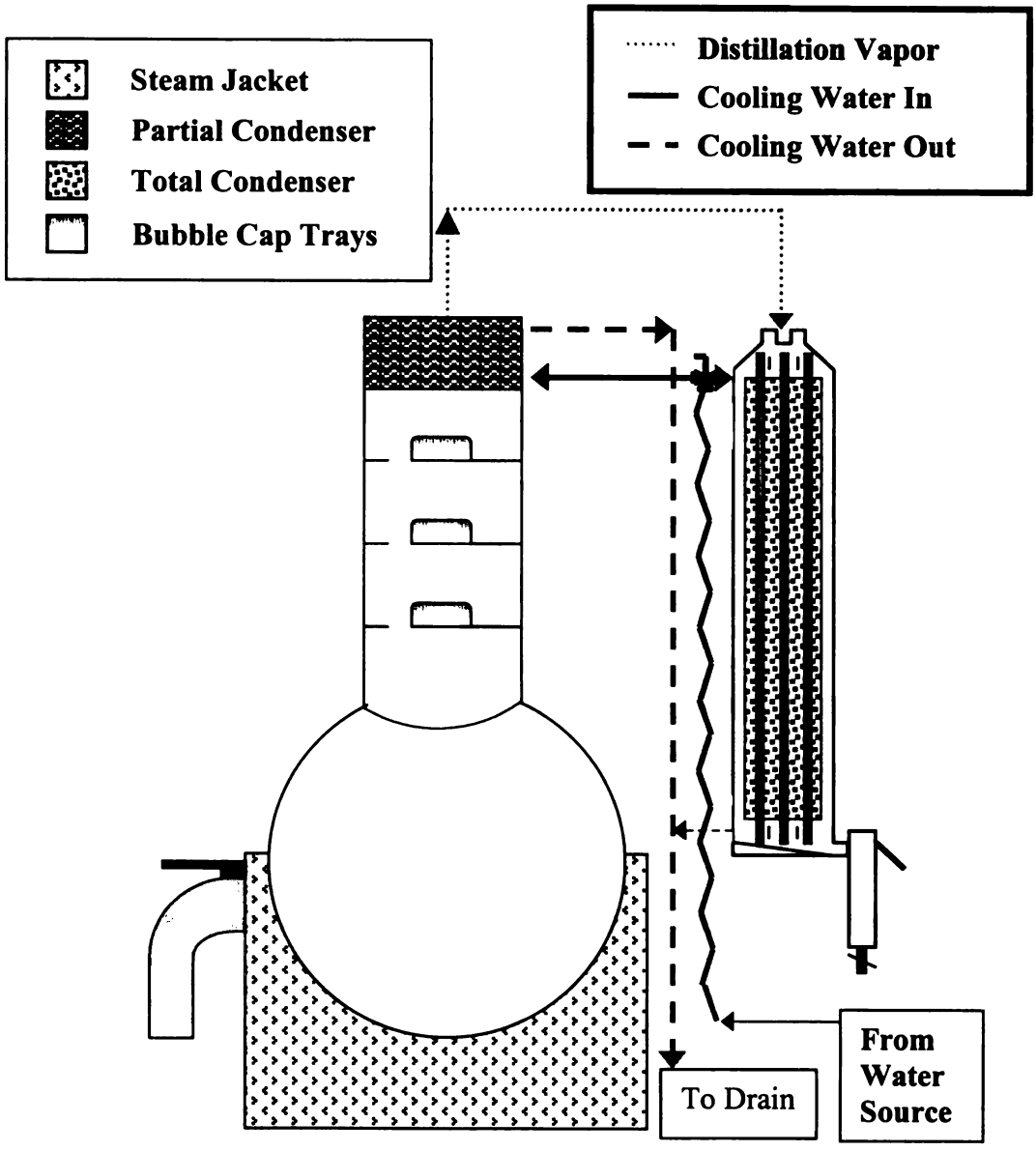


Figure 4.1 Schematic of a 10L Arnold Holstein Still.

or off. The final component of the still is the total condenser, which is constantly cooled by running water in order to condense the vapor to form the resulting distillate. Cooling water is supplied to both condensers by a hose connected to cold tap water. A flow regulator located just behind the total condenser can control the flow of this water manually. This can either increase or decrease the rate of distillate exiting from the still.

Distillation was performed first by adding the synthetic solution. Cooling water should fill the condensing column and the partial condenser if it is used. Rectification is relatively poor because of the small size of the still. Therefore, in order to obtain optimal rectification, the partial condenser was used, and all three trays were closed. The electric heater was turned on in order to heat the steam jacket. The distillation was then allowed to run until distillate appears.

The distillate consists of mostly ethanol and water. Congeners exit the still at different times during the distillation depending on their boiling points. Therefore, depending on the point in the distillation, the distillate will contain different amounts of congeners and ethanol. Normally, the distillate would be broken up into the heads, hearts, and tails portions. However, to keep the analysis consistent, 75 mL cuts were made.

4.2 Measurement of Condensation Time

It was important to understand how fast the vapor condenses when traveling from the top of the condenser to the sampling port below in order to determine how fast a GC analysis needed to be to obtain useful data. This measurement was made by injecting a 1mL sample of methanol into the sampling port above the condenser during an

ethanol/water distillation and recording the time that it takes for methanol to condense and be collected at the sampling port at the bottom. Time was recorded at the moment of injection and cuts were taken every 15 seconds for about five minutes. The cuts were then analyzed with the gas chromatograph to determine at which cut methanol appears. A plot of peak area verses time in Figure 4.2 gives an indication of the time that the methanol starts to appear. It was found to appear at approximately 3 minutes. So in developing an online method, the time it takes to extract the sample and analyze it must be under 3 minutes.

4.3 Analysis

Online analyses were performed using a Shimadzu GC-17A gas chromatograph with flame ionization detection. This particular GC was a base model that did not have tunable pressure and could only perform splitless injections. In addition, the connection between this instrument and the computer did not allow for the analysis software to download GC parameters and to trigger the GC temperature program to run. Therefore, any temperature program had to be entered manually to the instrument using the keypad on the Shimadzu GC. The GC could only be started by manually pressing the start button on the instrument panel as well. This GC was attached to the GC Accelerator™ in the first set of experiments and attached to the headspace sampler for the second set of experiments.

For both the Accelerator™ and headspace experiments, a 12.6 m Quadrex CW-007 Carbowax column was used. This column had an inner diameter of 0.25mm and a stationary phase thickness of 1μm. The temperatures of the injector and detector were

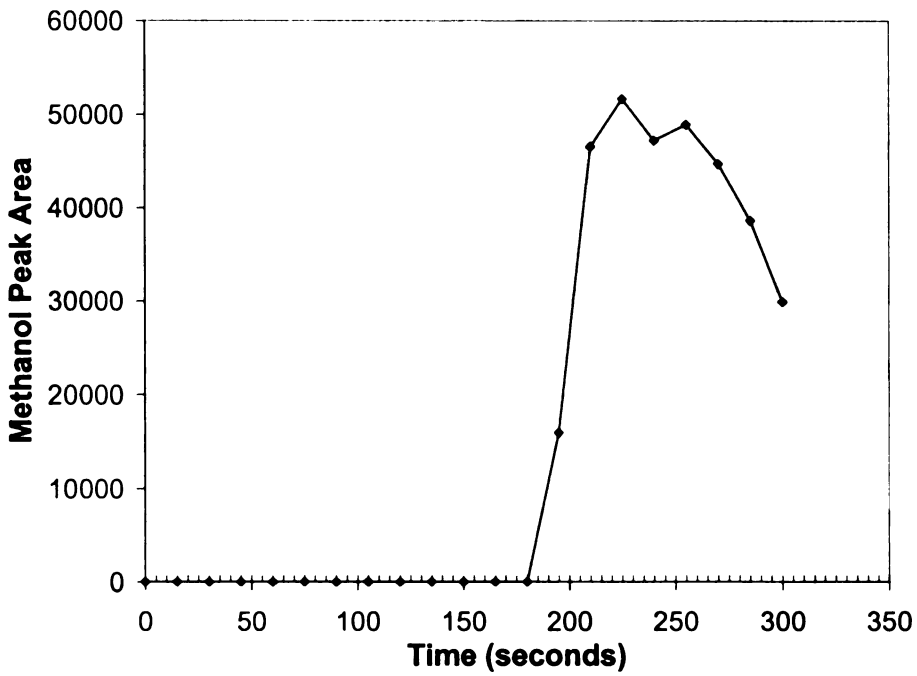


Figure 4.2. **Travel time for methanol condensation from the sampling port above the condenser to the distillate collection port at the bottom. It takes over three minutes before methanol distillate begins to appear.**

240°C and 255°C, respectively, and remained constant throughout the analysis. The temperature and pressure conditions of the column varied depending on the method used. The analysis parameters for each experiment are shown in Tables 4.3 and 4.4.

Acquisition with the Accelerator™ began by turning on the sampling pump and sampling for approximately fifteen seconds. Pressing the start button on the GC and pressing start on the computer manually triggered the GC program. For the Accelerator™ method the GC was run isocratically at 70°C and at a pressure of 38 psi. The elution time was approximately 2.5 minutes. Since this was an isocratic run there was no need for recovery time, so the total analysis time was 2.5 minutes.

For acquisition with the headspace sampling system, analysis began by simultaneously pressing start on the computer and pressing start on the GC instrument. Pressing start on the computer triggered the injection valve to switch from the inject to load position to allow vapor sample from the still to enter the sampling loop. At the same time, pressing start began data acquisition. The sampling loop was programmed to stay open for 9 seconds. Because the sample was vapor and because the pressure from the still was used to transfer sample, it was difficult to determine the exact sample volume that was being injected into the GC. Pressing start on the GC allowed for the temperature program to begin. A pressure of 43.5 PSI was used for this analysis. Separation was only possible with a temperature program for this particular method of sampling. The initial temperature was 40°C and this was held for 0.4 minutes. Next the temperature was ramped 70°C/minute to 115°C. The GC run time was 1.5 minutes. There was a 1 minute recovery time to cool the oven back down to initial conditions. The total analysis time was 2.5 minutes.

Experiment 1	Accelerator Setup
Inlet Pressure	38 PSI
Injector Temperature	240 °C
Detector Temperature	255 °C
Sample Time	15 seconds
Temperature Program	70 °C Isocratic
GC Run Time	2.5 minutes
Recovery Time	0 minutes
Total Analysis Time	2.5 minutes

Table 4.3. GC analysis parameters for the Accelerator™ setup.

Experiment 2	Headspace Setup
Inlet Pressure	43.5 PSI
Sample Time	9 seconds
Injector Temperature	240 °C
Detector Temperature	255 °C
Temperature Program	40 °C held 0.4 minutes. Ramp 70°C/ minute to 115.
GC Run Time	1.5 minutes
Recovery Time	1.0 minutes
Total Analysis Time	2.5 minutes

Table 4.4. GC analysis parameters for the headspace setup.

During the distillation, vapor samples were taken approximately every 150 L for both setups. Compounds were identified by their relative retention times during the runs. These retention times varied depending on the method used. The retention times for the compounds along with boiling points in each experiment will be discussed further in the chapters five and six as part of the results.

Concentration of ethanol was measured after distillation using a standard curve. Samples of distillate cut were run through conventional GC to obtain ethanol concentrations. With this information, ethanol was used as the internal standard. The area percents of the congeners were compared to the area percent of ethanol. Calibration curves were not used in this experiment due to the poor reproducibility in standardization measurements.

4.4 Simple Distillation

Simple distillations were performed in order to test the reproducibility of the headspace sampler. A distillation apparatus, as shown in Figure 4.3[1],was connected to the headspace sampler. This apparatus was like most other simple distillation setups except there was an extra port in the round bottom flask to be used to connect to the headspace sampler to obtain online data.

A 1000 mL brandy type solution with similar percentages to both the Accelerator™ and headspace sampler experiments was used and the composition is shown in Table 4.5. Approximately 150 mL of this solution was placed in a 300mL round bottomed flask and attached to the distillation apparatus. This flask was immersed in a heated silicon oil bath and the distillation was allowed to proceed. Ten milliliter cuts

were collected. Sample injections were made approximately every 2.5 minutes so that there was at least one measurement for every cut. The distillation proceeded until the temperature reached 100°C.

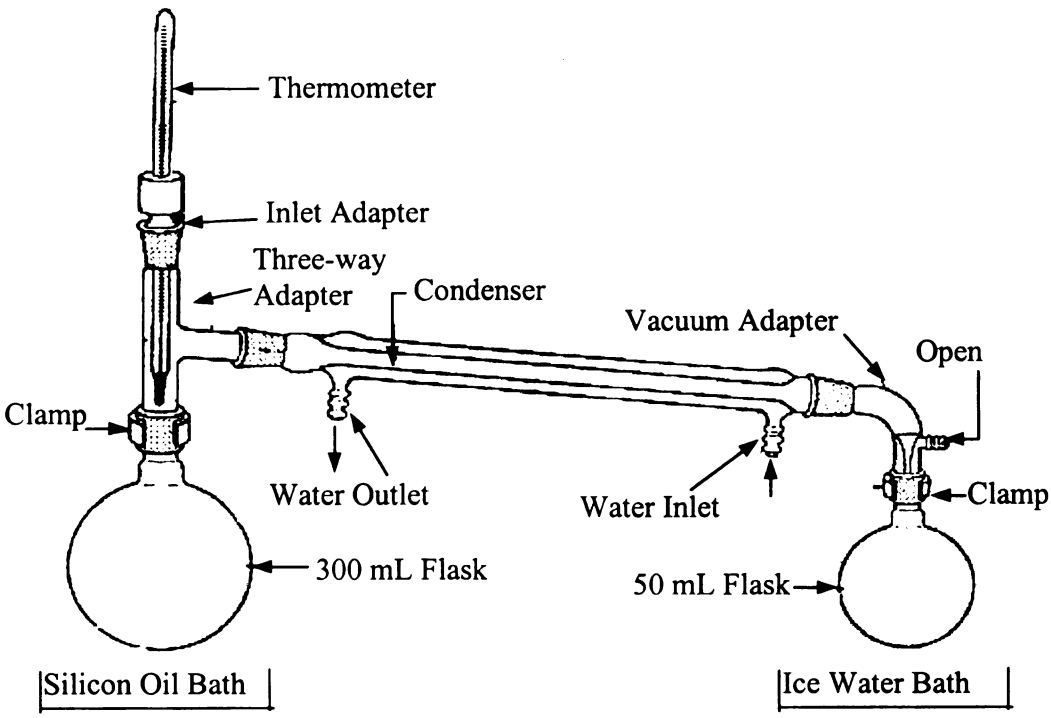


Figure 4.3. A typical simple distillation apparatus. The round bottom distillation flask used is 300mL and contains more than one port. The extra port is needed to insert the sample line of the headspace sampler in an area above the distillation in the flask. The distillate collection flask is 50 mL[1].

Compound	Volume (mL)	Percent v/v Solution
Water	916.9	91.69
Ethanol	80	8.00
Acetaldehyde	0.5	0.05
Methanol	0.8	0.08
Ethyl Acetate	0.2	0.02
n-Propanol	0.8	0.08
Isoamyl Alcohol	0.8	0.08

Table 4.5. Congener types and volume percentages for the simple distillations.

Literature Cited

1) Simple Distillation apparatus. Adapted from

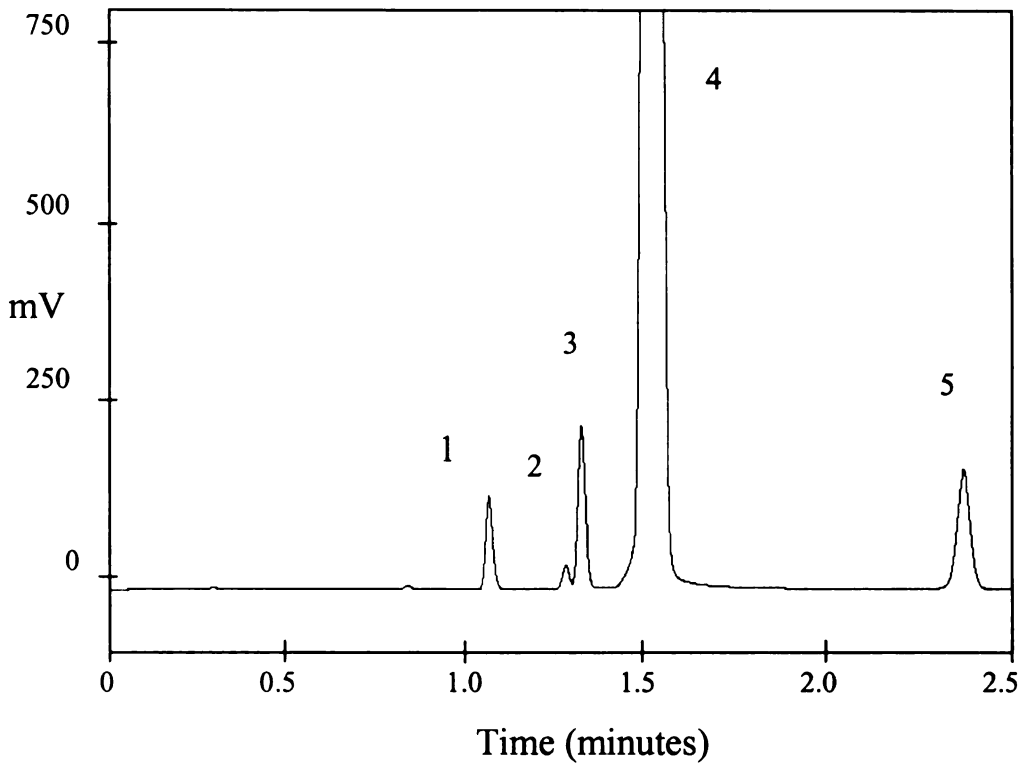
<http://www.ComCapeCanaveral/lab/4444/distillation.html>

5. Results : GC Accelerator

5.1 Method Optimization

The Accelerator™ method successfully collected sample from the still and generated a chromatogram. The next step was to optimize this method. An appropriate sampling and GC program were developed to achieve speed while maintaining adequate separation,. As shown in Chapter 4, the conditions that gave the best separation at the time was an isocratic run at 70°C. An isocratic run allowed for repeated runs without taking time to reset the system. The entire run time lasted about 2.5 minutes. The chromatogram that resulted is shown in Figure 5.1. Figure 5.2 shows a chromatogram of a similar brandy type mixture taken using normal GC injection and method. Comparing the retention times given in the chromatograms to standard retention times of the compounds for both the fast GC and conventional GC methods allowed for the identification of the peaks. The Accelerator™ method proved to be faster in comparison with the conventional GC run. A list of the compounds present and the retention times for both the Accelerator™ and the normal GC run are shown in Table 5.1.

Isoamyl alcohol does not elute within the 2.5 minute run for the Accelerator™ method. The program chosen allowed for good separation and elution of the other compounds. However, isoamyl alcohol eluted much later, beyond the maximum required run time of three minutes. It was decided to run an experiment with this particular program without including isoamyl alcohol. A second experiment was to be run with temperature programming so that isoamyl alcohol could be studied as well. However, the failing structural integrity of the Chromatofast® GC Accelerator™ did not allow for further experiments. This issue will be discussed later in the chapter.



1) Acetaldehyde	2) Ethyl Acetate	3) Methanol
4) Ethanol	5) N-propanol	6) Isoamyl Alcohol

Figure 5.1. **A chromatogram of a brandy type solution taken with the GC Accelerator™ Using a 70°C run. Peaks were identified by comparing the retention times from the chromatogram to a standard set of retention times for each compound. Isoamyl alcohol does not appear due to a much later elution time.**

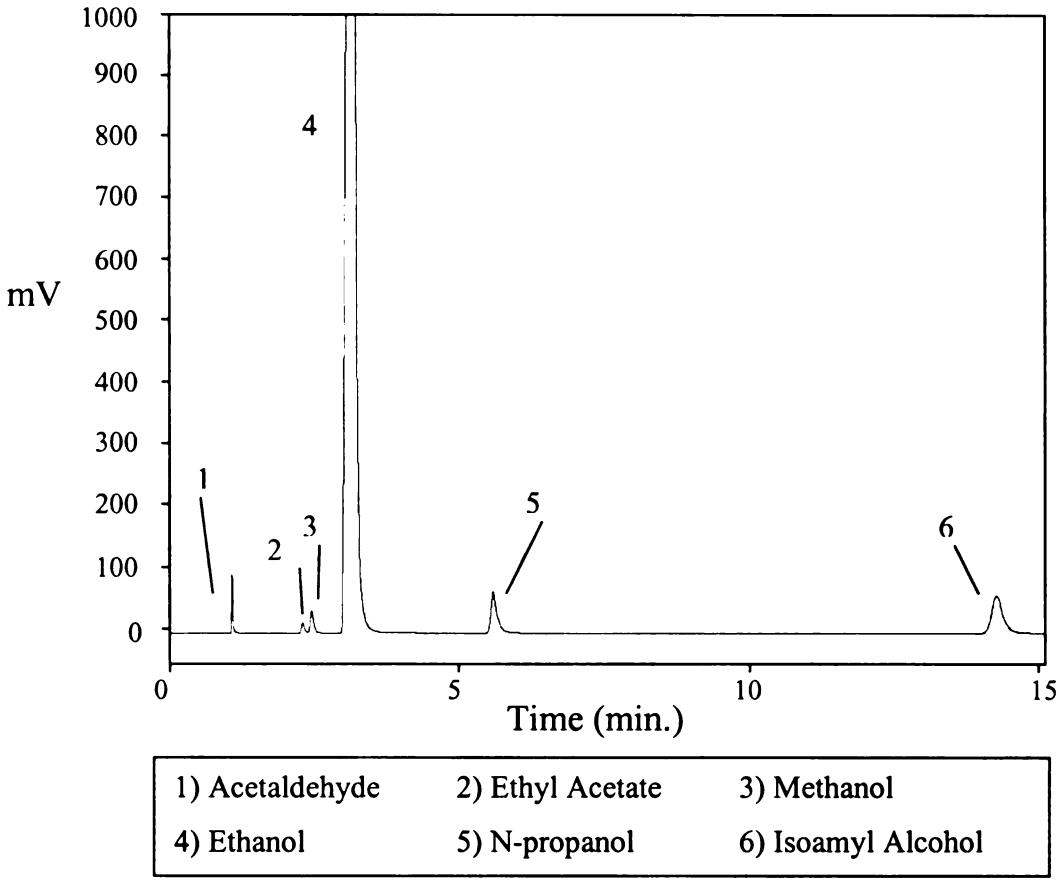


Figure 5.2 **Chromatogram of a sample from a brandy-type solution using a conventional GC. Distillate cuts were taken and analyzed after distillation. Peaks were identified by comparing the retention times from the chromatogram to a standard set of retention times for each compound.**

Compound	GC Accelerator™ (min)	Conventional GC(min.)	Boiling Points (°C)
Acetaldehyde	0.801 ± 0.008	1.451 ± 0.000	20.8
Ethyl Acetate	1.232 ± 0.008	2.667 ± 0.002	77.0
Methanol	1.276 ± 0.008	2.825 ± 0.004	64.7
Ethanol	1.493 ± 0.006	3.563 ± 0.015	78.0
n-Propanol	2.308 ± 0.009	5.996 ± 0.019	97.0
Isoamyl Alcohol	N/A	14.639 ± 0.051	132.0

Table 5.1. A list of the retention times for chromatograms taken using Fast GC with the GC Accelerator™ and also conventional GC. The boiling points for the congeners is also listed.

5.2 Standardization

Standardization with the online setup turned out to be quite challenging. In an attempt to develop a calibration curve for ethanol, standards were created at 40%, 50% 65%, and 85% and placed into 2mL GC autosampler vials. Prior to running the standards through the fast GC, the vials were heated at a temperature of 75°C for at least five minutes to approximate the conditions of the still as best as possible. Headspace above the liquid in the vials was extracted for analysis and a calibration curve was plotted. This plot is shown in Figure 5.3 with the standard deviation between the runs.

From this information it appears that the trends do not follow expected behavior. Typically, peak area increases with an increasing concentration of ethanol; however, the plot obtained from standardization showed a periodic increase and dip in peak area with increasing concentration. This could have been due to the sample vials used to store the ethanol standards. The vials may not have allowed for a consistent pressure to be maintained. So the sample collected from the headspace in the vial could have fluctuated. Inconsistent sampling from the GC Accelerator™ could have also been the problem. Looking at the error, the repeatability of the measurements was actually quite reasonable, falling in the range of 0.48%-1.64%. Therefore the Accelerator™ was most likely not the problem. The problem most likely was due to pressure variations in the sampling vials. This could also be due to the fact that it is difficult to closely imitate the conditions that are present in the still when developing standard samples. Also, the relative concentration of ethanol in the still during the distillation may actually be under 40%v/v rather than being equal to the measure of ethanol in the liquid distillate.

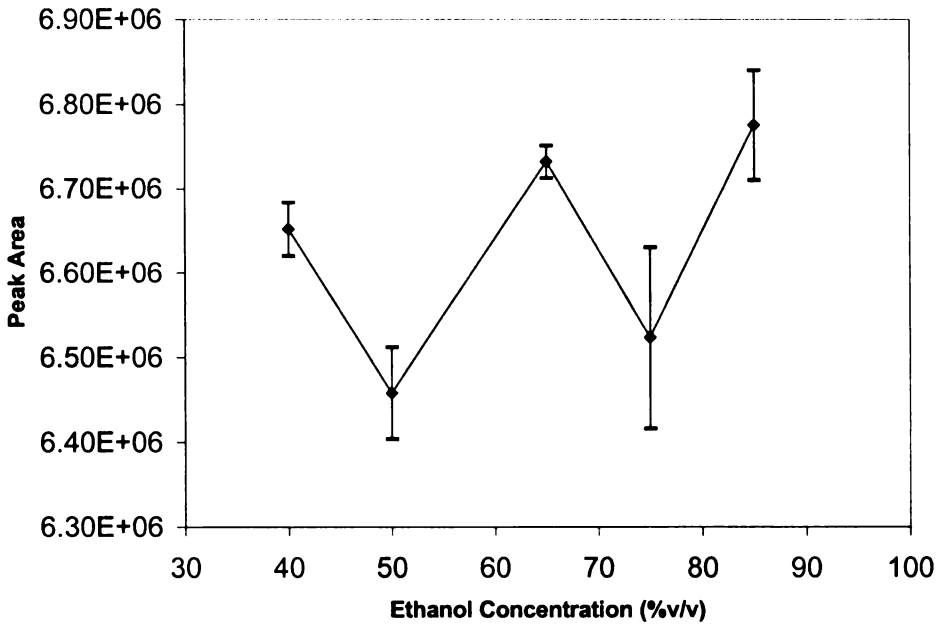


Figure 5.3. **A calibration curve for ethanol using the GC Accelerator™ method. Standard samples were made at 40%, 50%, 65%, 75%, and 85% v/v ethanol. These samples were heated to 75°C for at least 5 minutes. Rather than showing an increase in peak area with increasing ethanol concentration, this curve shows a periodic increase and decrease.**

Studies on the relationship between the vapor and the liquid would need to be done to resolve this issue.

The unusual behavior of the standards made it difficult to actually quantify the amounts of ethanol and congeners that were present in the sampled vapor. So as an alternative, it was decided that ethanol could be used as an internal standard. The amount of ethanol could be measured after distillation using standard curves for conventional GC. Ultimately all of the data would be normalized to make ethanol 40% in order to make a better comparison between runs.

5.3 Distillation Behavior

The behavior of the compounds in the solution was studied during the distillation. Chromatograms were taken using the online system. Peaks were identified by comparing retention times from analysis to standard retention times for each of the congeners. Data was collected for each congener and plots were generated to show trends during the distillation. In addition, samples were collected from each cut that was taken closest to the time of the online analysis.

The major component of the synthetic brandy solutions was ethanol. Ethanol amounts were found after distillation by injecting samples from the distillate cuts into a conventional GC. Ethanol concentrations were found using a standard ethanol curve made for the conventional GC. Knowing this, the peak areas of the other compounds were then compared to the peak area of ethanol in order to obtain relative amounts. The ethanol response by conventional GC is shown in Figure 5.4. Ethanol starts near 80%v/v

and slowly decreases. Closer to the tail end of the distillation, the decrease in percent volume of ethanol becomes sharper.

The major congener to emerge first is acetaldehyde. The behavior of this compound during distillation over time is shown in Figure 5.5. Acetaldehyde starts off with a relatively high concentration and decreases rather sharply as time goes on. This makes sense given acetaldehyde's low boiling point.

Ethyl acetate was studied next. The plot for its behavior is shown in Figure 5.6. Ethyl acetate is another low boiling point compound. So like acetaldehyde, the relative concentration starts out high and quickly drops.

Methanol emerged next. Methanol starts out relatively high in the early part of the distillation and decreases towards the middle. The relative concentration then begins to increase towards the end of the distillation. This behavior is shown in Figure 5.7.

The fusel alcohol, n-propanol was then examined. The behavior pattern is shown in Figures 5.8. N-propanol starts out relatively low and increases as the distillation occurs. This is probably due to the higher boiling point of n-propanol. There is a drop towards the end of the distillation, which is probably a result of decreasing amount of n-propanol in the pot.

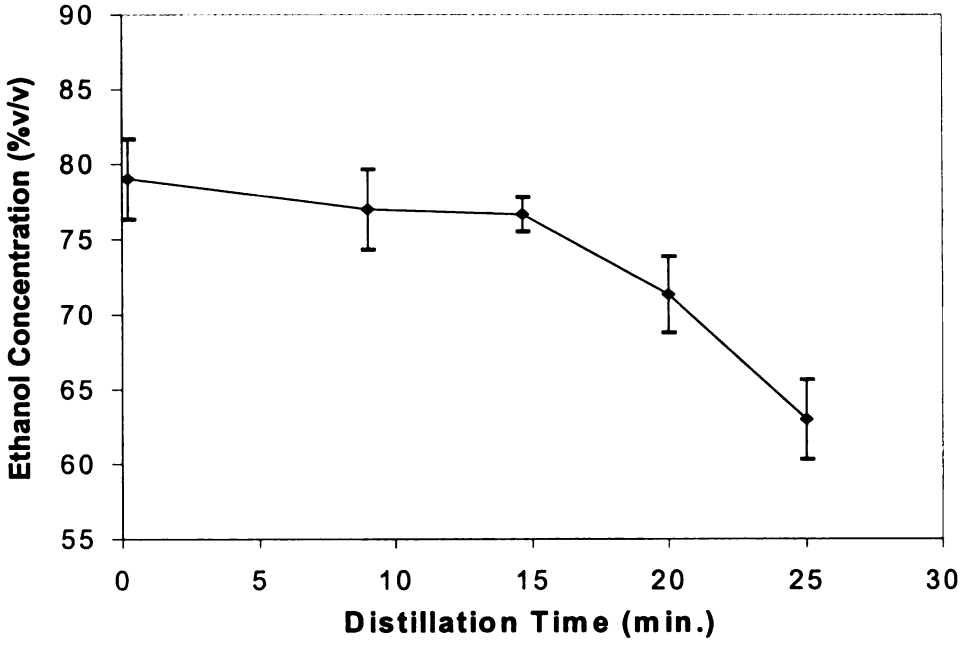


Figure 5.4. **Ethanol concentration measured after the distillation. Samples of the distillate cuts were taken and analyzed using conventional GC. Concentrations were found by comparing peak areas to a standard curve for ethanol.**

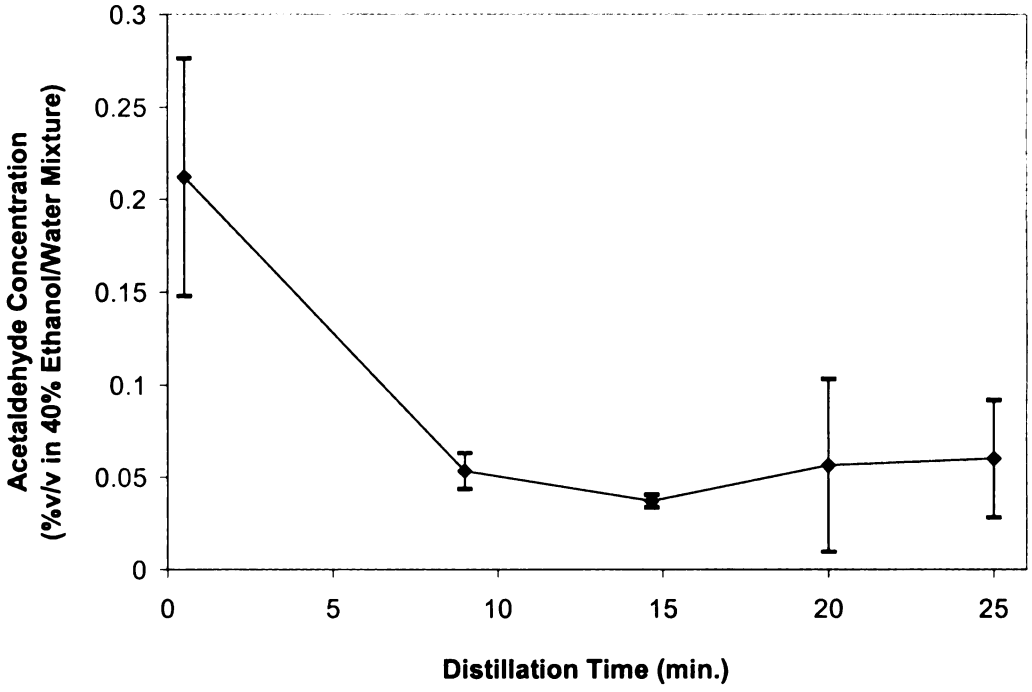


Figure 5.5. **Acetaldehyde concentration in the product as a function of distillation time according to measurements made with the GC Accelerator™. Concentrations are given as percent volume of congener in a 40% ethanol/water mixture.**

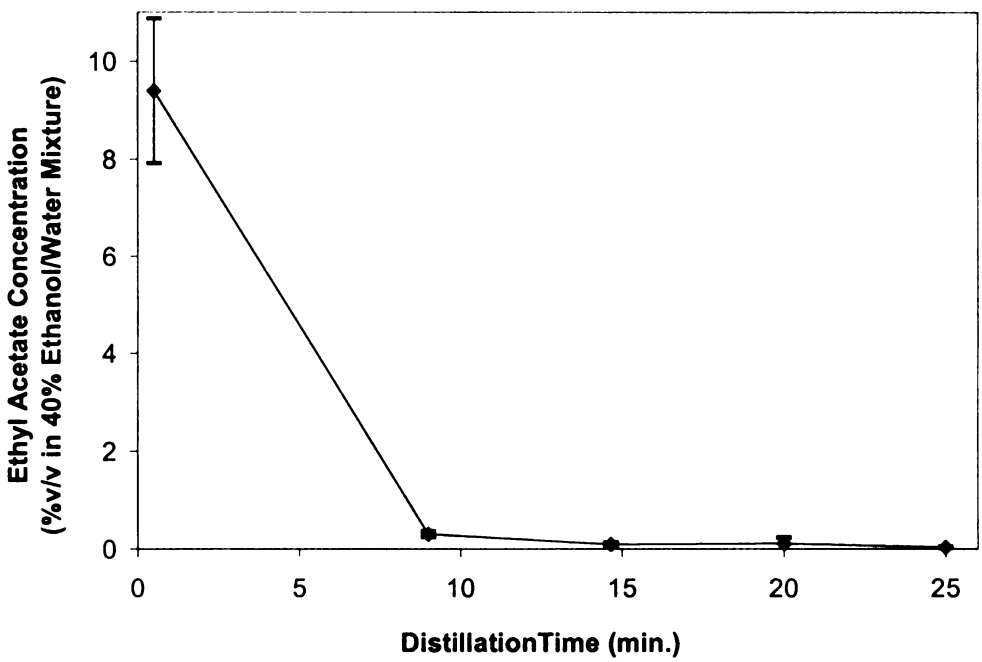


Figure 5.6. **Ethyl acetate concentration in the product as a function of distillation time according to measurements made with the GC Accelerator™. Concentrations are given as percent volume of congener in a 40% ethanol/water mixture.**

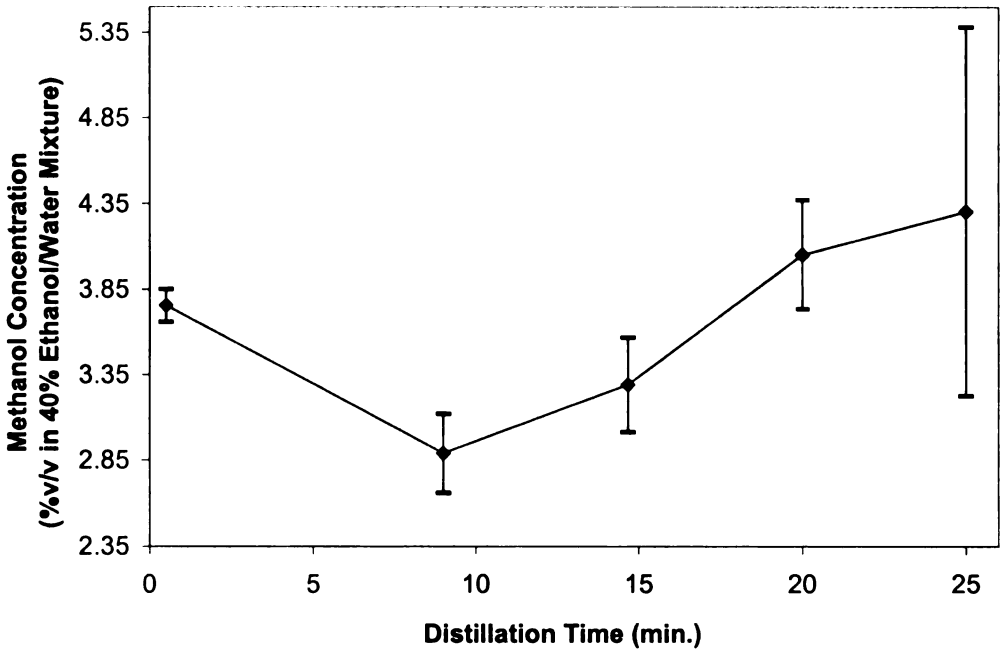


Figure 5.7 **Methanol concentration in the product as a function of distillation time according to measurements made with the GC Accelerator™. Concentrations are given as percent volume of congener in a 40% ethanol/water mixture.**

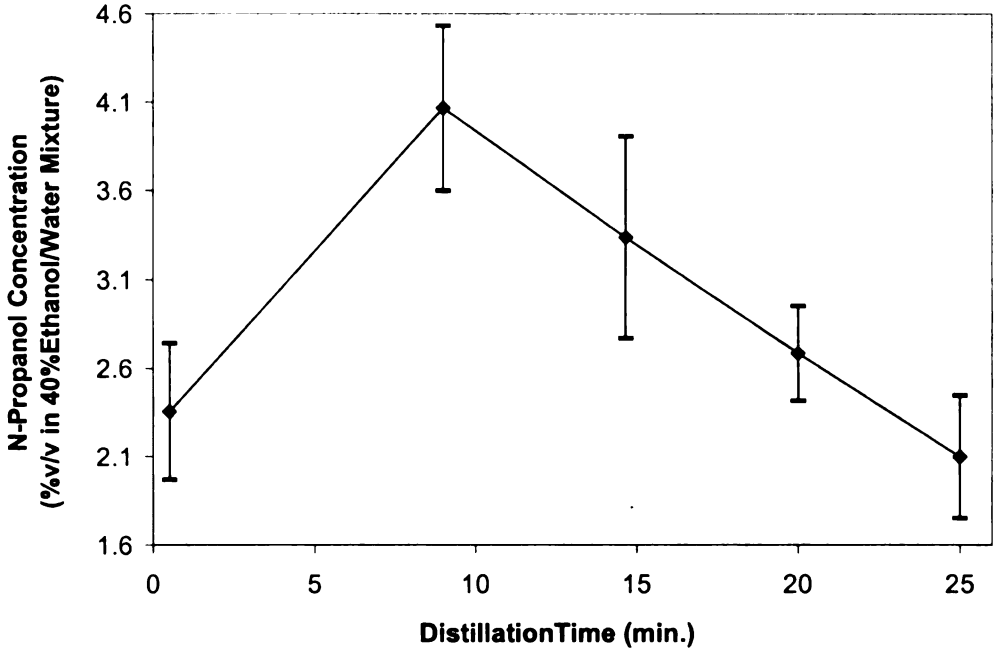


Figure 5.8 **N-propanol concentration in the product as a function of distillation time according to measurements made with the GC Accelerator™. Concentrations are given as percent volume of congener in a 40% ethanol/water mixture.**

5.4 Structural Integrity of GC Accelerator™

The structural integrity is a very important consideration when looking at an online method's ability to monitor a distillation. Robustness is an area of weakness for the GC Accelerator™. It affected the quality of the chromatographic peaks obtained and affected the instrument's ability to even function at all.

One main problem with the GC Accelerator™ was that after repeated measurements, the quality of the chromatograms became poor. Figure 5.9 illustrates what would happen to the chromatograms after several measurements were taken. The formation of poorly shaped peaks was noticed in the online readings. In addition, a very distinct shoulder appeared on the ethanol peak during every measurement.

The formation of shoulders and other poorly shaped peaks was probably a result of the sample not being "plug-like" upon injection into the GC. This could be due to several things. The cryotrap itself may have no longer been efficient in freezing the sample. This behavior could lead to wider injection bandwidths, which could lead to poor efficienc. In addition, inefficient flushing of residual sample in the lines of the Accelerator™ could lead to the appearance of unexpected peaks. If sample from the previous analysis is left behind in the lines, it could be injected along with the new sample from the current run and distort the chromatogram. The solenoid valves may have begun to fail to open and close properly also. This would cause an inefficient transfer of sample and also lead to poor chromatograms.

Another drawback of the GC Accelerator™ was that the liquid nitrogen transfer line often became blocked by ice and would not allow liquid nitrogen to cool the

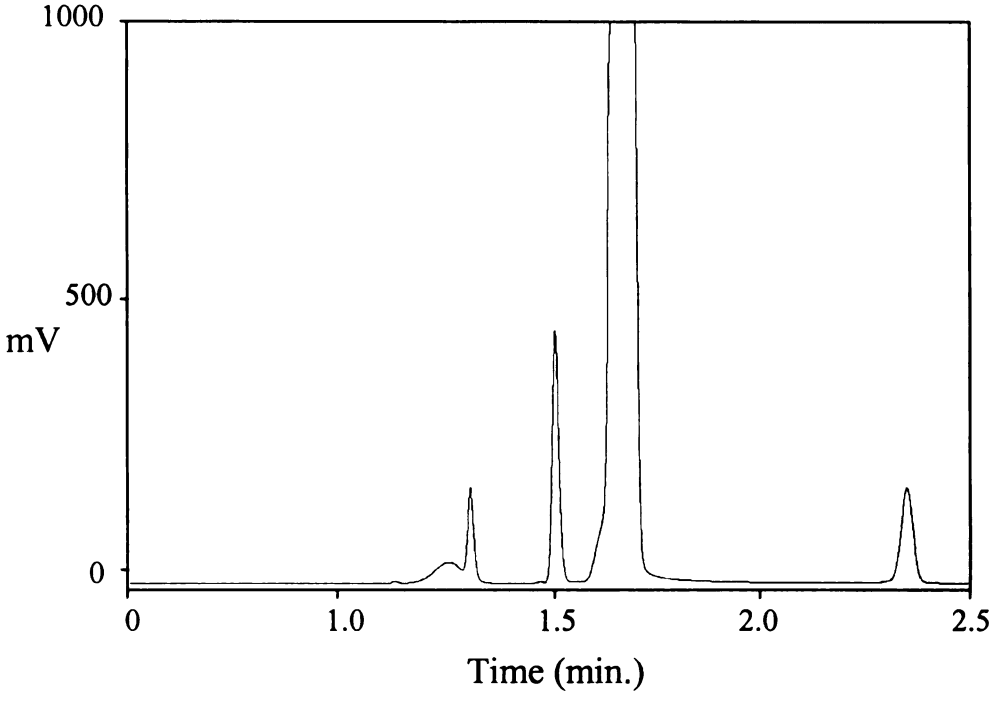


Figure 5.9 **Chromatogram of a sample from a brandy-type solution using the GC Accelerator™. After repeated measurements, the chromatograms would develop poorly shaped peaks, such as in this example. The shoulder on the ethanol peak is most likely a result of the injection volume not being "plug-flow".**

cryogenic trap. The liquid nitrogen was stored in a Dewar and transferred through Tygon tubing into the cryogenic trap. If water was inside this tube, it would freeze upon contact with the liquid nitrogen. The line then became blocked and no more liquid nitrogen could be transferred to the trap to maintain a temperature of –80°C. Once blockage occurred, the GC Accelerator™ was more or less rendered useless until the ice thawed and essentially evaporated, which often took hours.

Finally, the GC Accelerator™ eventually failed to operate at all. The instrument began to produce extremely small peaks or none at all. An attempt to repair the machine was made, however this proved to be difficult. First of all, the instrument itself was very compartmentalized, thus making it difficult to open up and reach the inner workings. Second, the manual that accompanied the instrument was of little aid as far as troubleshooting and instrument diagrams. Finally, Chromatofast® the company is no longer in existence, so there was no hope for receiving technical assistance and repair services.

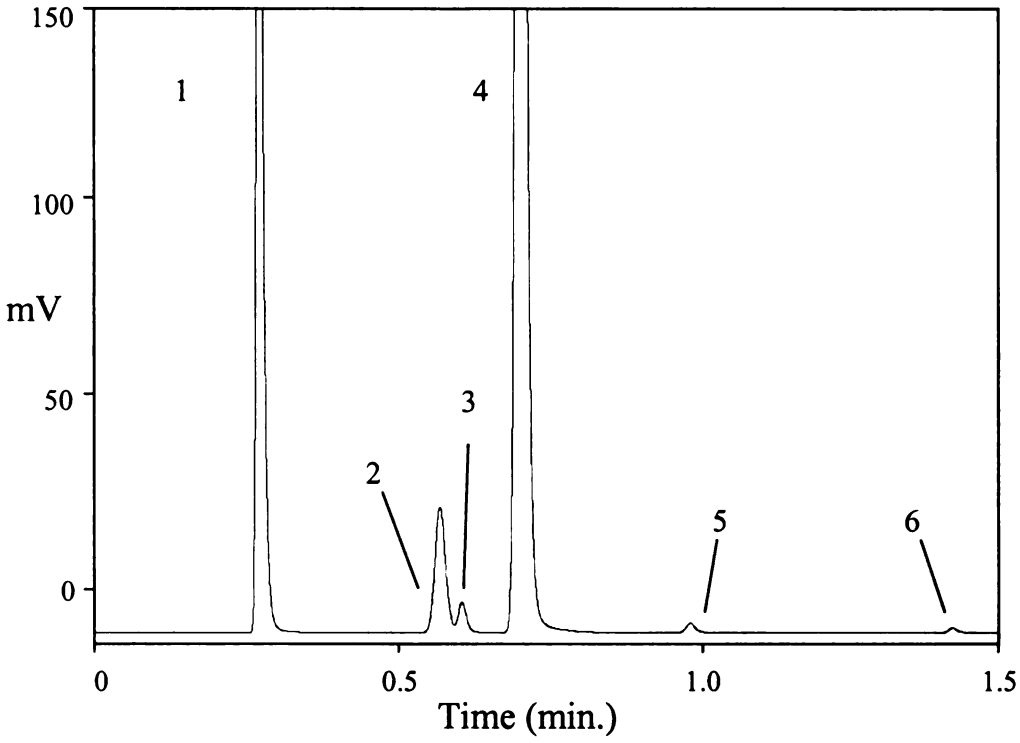
Initially, the GC Accelerator™ achieved online readings. However, the failure of the instrument to continue to operate eliminates it as a viable option for real-time monitoring of a distillation.

6. Results: Headspace Sampler

6.1 Method Optimization

It was found that a special injection technique, such as the GC Accelerator® was not necessarily required to achieve good separation while speeding up analysis. With a short column and faster flow rate, along with the appropriate GC programming, fast, efficient chromatographic readings could be obtained. The only thing that was needed was a method for extracting vapor from the still. So a headspace sampler was constructed to extract sample while using fast gas chromatography for analysis.

The GC program was shown previously in Table 4.4. A temperature program was the best at achieving adequate separation. The elution time was approximately 1.5 minutes. Since a temperature program was used, time was needed to cool down the system to initial conditions. This took approximately 1minute. The total run time of a sample acquisition was 2.5 minutes, which is the same as that for the GC Accelerator®. The chromatogram that resulted from this type of analysis is shown in Figure 6.1. A comparison to a normal GC run of a similar mixture is shown in Figure 6.2. This method definitely proves to be much faster than a normal GC run. The elution is also faster than that of the GC Accelerator®. This can be seen in a comparison chromatogram in Figure 6.3. The top chromatogram shows the elution with the headspace sampler. The bottom chromatogram represents the elution with the Accelerator®. Peaks were identified by comparing the retention times from the chromatogram to standard retention times for each of the compounds. A table with the retention times for all three methods is shown in Table 6.1.



1) Acetaldehyde	2) Ethyl Acetate	3) Methanol
4) Ethanol	5) N-propanol	6) Isoamyl Alcohol

Figure 6.1 **Chromatogram for the distillation of a brandy-type mixture. The sample was collected from the still using the headspace sampler. The program used was the same as in Table 4.4. Peaks were identified by comparing the retention times from the analysis to standard retention times for each of the compounds.**

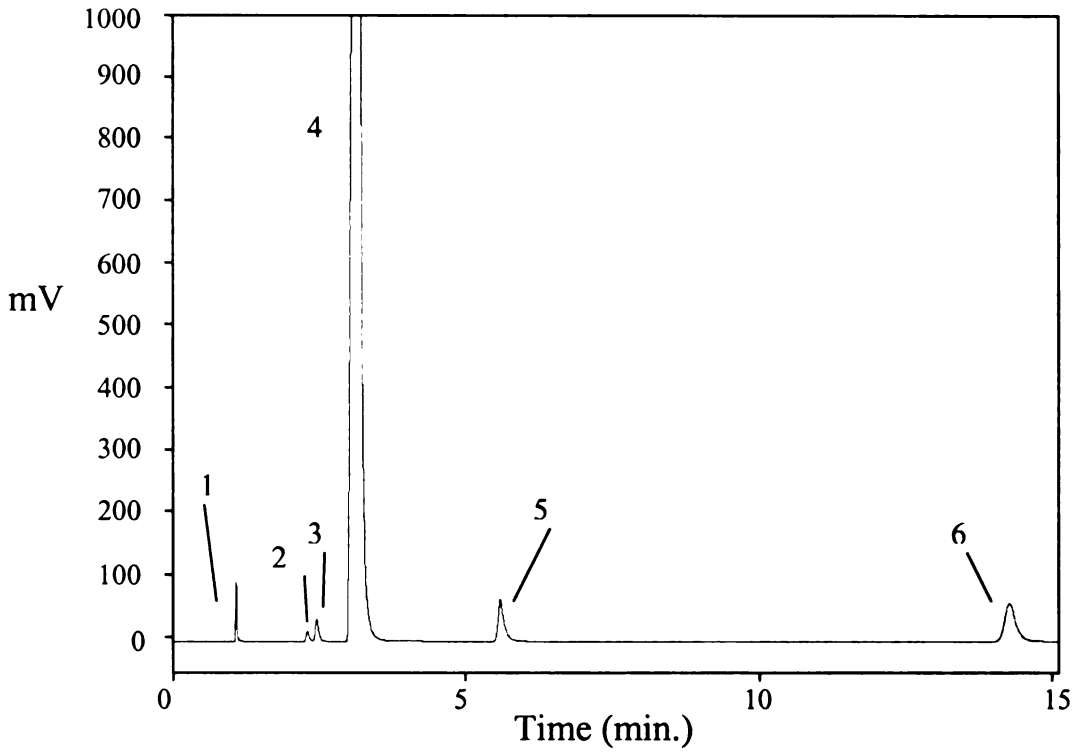


Figure 6.2 **Chromatogram for a sample from a brandy-type solution using a conventional GC. Distillate cuts were taken and analyzed. Peaks were identified by comparing the retention times from the chromatogram to standard retention times for each of the compounds.**

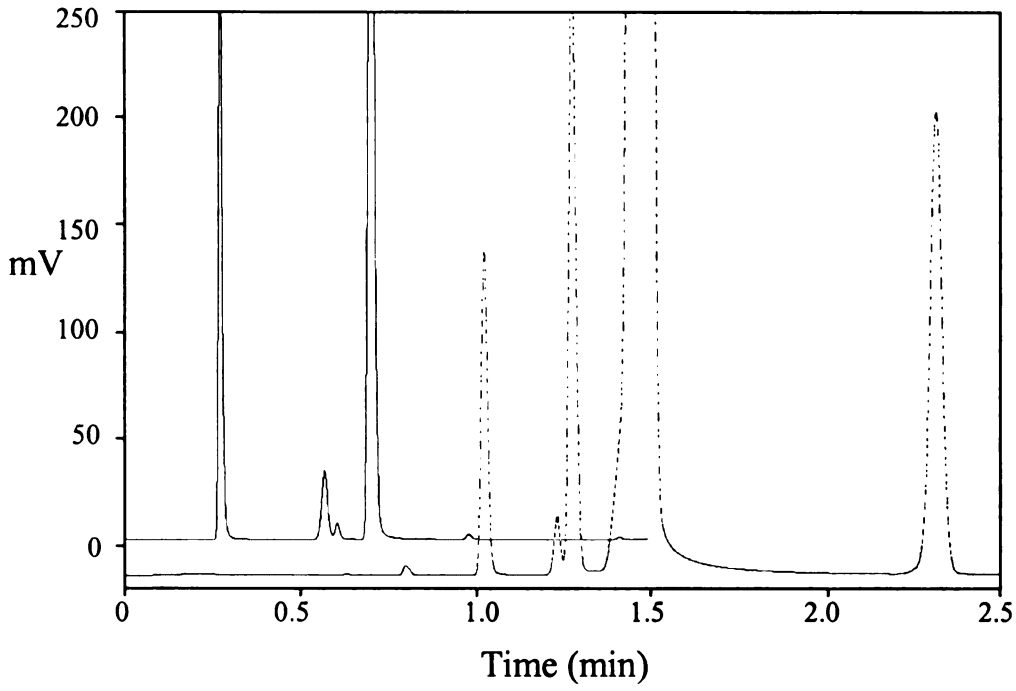


Figure 6.3 **A comparison of the chromatograms for the two methods. The solid curve represents the headspace sampling analysis and the dashed curve represents analysis with the GC Accelerator™. The total elution time with the headspace sampling system is 1.5 minutes whereas the total elution time for the Accelerator™ is 2.5 minutes. Peaks were identified by comparing the retention times from the chromatogram to standard retention times for each of the compounds.**

Compound	Headspace Sampler (min.)	GC Accelerator™ (min)	Conventional GC(min.)
Acetaldehyde	0.276 ± 0.007	0.801 ± 0.008	1.451 ± 0.000
Ethyl Acetate	0.582 ± 0.004	1.232 ± 0.008	2.667 ± 0.002
Methanol	0.620 ± 0.004	1.276 ± 0.008	2.825 ± 0.004
Ethanol	0.719 ± 0.007	1.493 ± 0.006	3.563 ± 0.015
n-Propanol	0.992 ± 0.005	2.308 ± 0.009	5.996 ± 0.019
Isoamyl Alcohol	1.418 ± 0.004	N/A	14.639 ± 0.051

Table 6.1. Retention times for chromatograms taken using Fast GC with the headspace sampler and also conventional GC. Peaks were identified by comparing the retention times from the chromatogram to standard retention times for each of the compounds.

6.2 Standardization

Standardization with the headspace sampler proved to be just as difficult as with the Accelerator™. This can be seen in the attempt to standardize ethanol. Ethanol standards were made at 40%, 60%, 80% and 90% and placed in 2mL GC autosampler vials. They were heated to a temperature of 75°C in order to approximate the conditions of the still as best as possible. Figure 6.4 shows the calibration curve for ethanol and the error between readings. The error range for triplicate runs at the same concentration was 44%-155%. Additionally, the expected trend of increasing peak area with increasing concentration is not followed.

Again it is difficult to standardize headspace samples that have the same conditions as the still. This strange behavior could also be due to the fact that the sampling is not consistent. The headspace sampler relies on the pressure of the still or sample vial to push sample through the sample loop. If the pressure fluctuates in the still or the standard sample vial, the volume that enters the sample loop will be different every time. Therefore, the volume injected into the GC will be different every time, thus leading to irregular peak area readings for each run of a particular concentration.

Since repeatability was poor, quantification was again difficult. Comparing the peak areas of the congeners to the peak areas of ethanol and then normalizing the values to give a 40%v/v ethanol concentration was the method used for finding congener concentration.

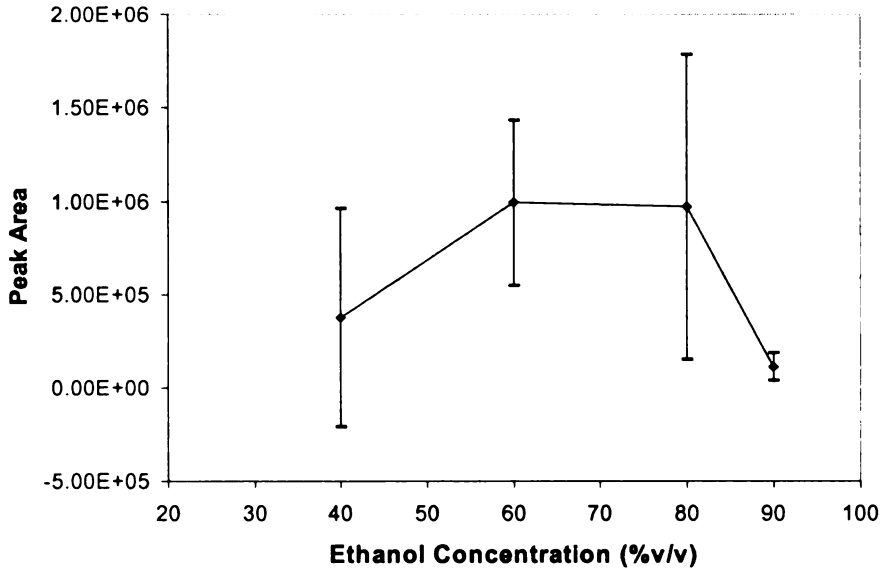


Figure 6.4. **The response curve for ethanol using the headspace sampler. The peak areas do not increase with increasing concentration.**

6.3 Distillation Behavior

The behavior of all of the compounds was studied using the headspace sampler. The concentrations for each of the compounds were calculated by comparing the peak areas of the congeners to the peak area of ethanol. These concentrations were then plotted to show percent volume of congener in a 40% ethanol/water mixture vs. distillation time. A post-distillation analysis was also performed on the cuts of distillate using a conventional GC. This was done in order to compare the behavior and amounts measured by the fast GC to the reliable measurements of the conventional GC.

Ethanol measurements were taken after the distillation using conventional GC. Samples from the distillate cuts were measured and compared to a standard ethanol curve. The behavior of ethanol during the distillation is shown in Figure 6.5. As in the previous experiments, ethanol starts out around 80% v/v of liquid and slowly decreases until it gets closer to the tails portion where the decrease speeds up.

The behavior of acetaldehyde was studied both before and after distillation. Figure 6.6 shows the comparison between online measurements of behavior and post-distillation measurements. Other than the first point in the online measurements, the two plots appear to have agreement in the trends. The amounts calculated according to the online analysis are also markedly different from the amount measured according to the regular GC.

The behavior of ethyl acetate is shown in Figure 6.7. The online and post-distillation trends appear to be similar here. Like acetaldehyde however, the amounts differ substantially. The online measurements give concentration values that are significantly higher than the post-distillation measurements

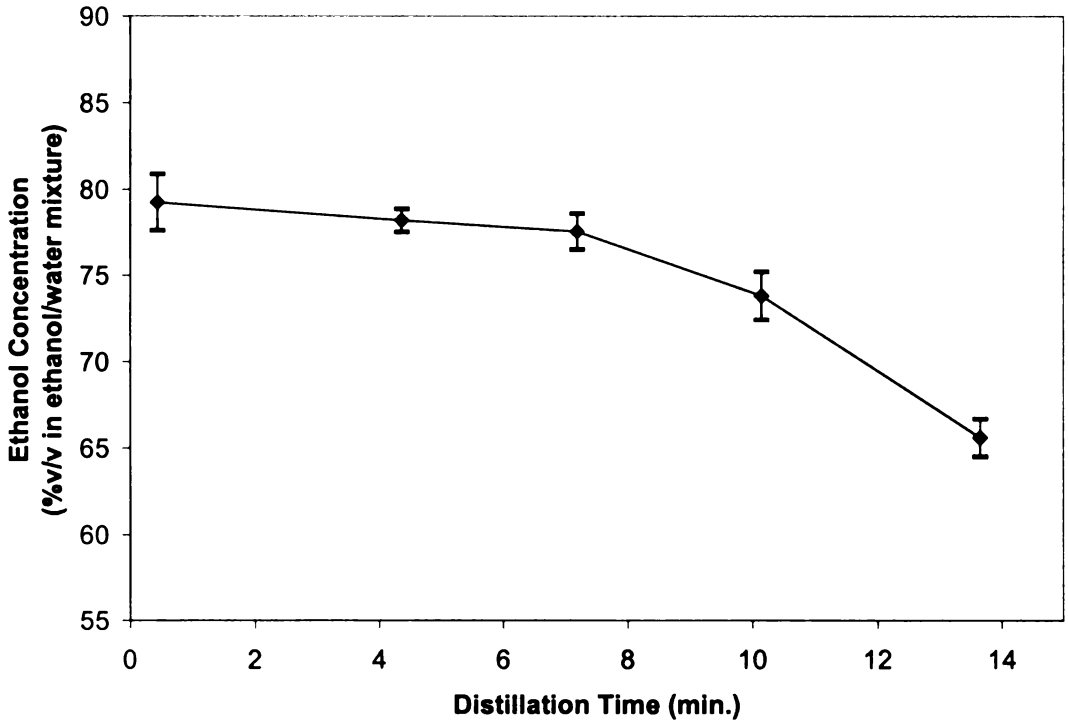


Figure 6.5. Ethanol concentration as a function of distillation time taken after distillation using a standard ethanol curve with conventional GC.

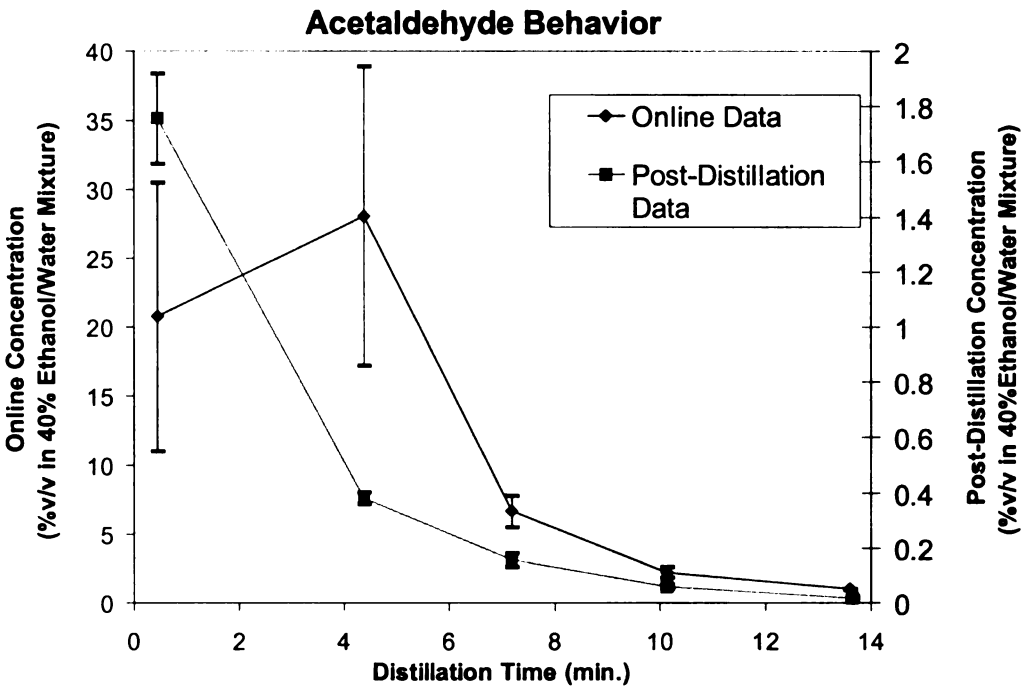


Figure 6.6. **The concentration behavior of acetaldehyde. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

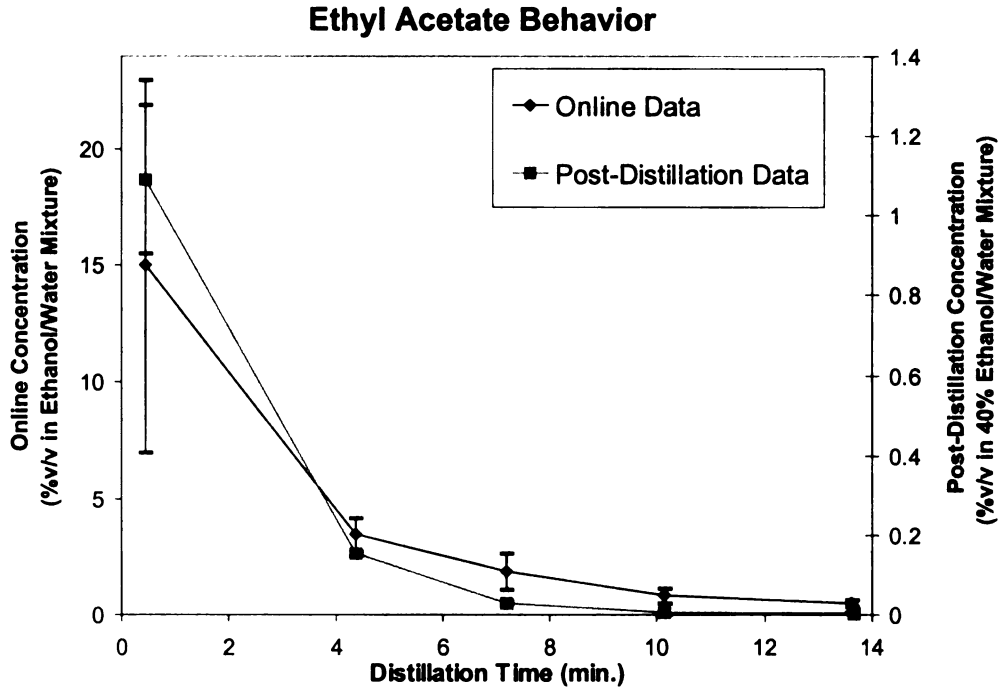


Figure 6.7. **The concentration behavior of ethyl acetate. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

Next methanol was examined. The plots for the behavior are shown in Figure 6.8. The plot according to the post-distillation measurement, shows methanol decreasing slowly towards the middle of the distillation and then increasing towards the end. The plot according to online data shows just a straight increase as the distillation proceeds. Actually it appears that the trends do agree except for the first point of online measurement. The amounts again differ significantly between the two sets of measurements.

Next, n-propanol was examined. The plot for both online and post-distillation measurements is shown in Figure 6.9. The online analysis for n-propanol shows a much different behavior compared to the normal GC analysis. According to the online measurements, n-propanol starts out high and decreases steadily throughout the distillation. This is different from the results from the conventional GC readings. It starts out low and increases as the distillation proceeds and finally starts to decrease as the amount of n-propanol decreases.

Finally, isoamyl alcohol was studied. The strange phenomena that happened with n-propanol also occured here. According to the online plot, shown in Figure 6.10, isoamyl alcohol starts out high and decreases throughout the distillation. The normal GC plot, shown in Figure 6.10 shows it starting out low and increasing until the end where it starts to decrease again. The values between online and post-distillation measurements are very different as well.

On the whole the measurements taken with the online headspace apparatus indicated different behavior compared to the analysis with the conventional GC.

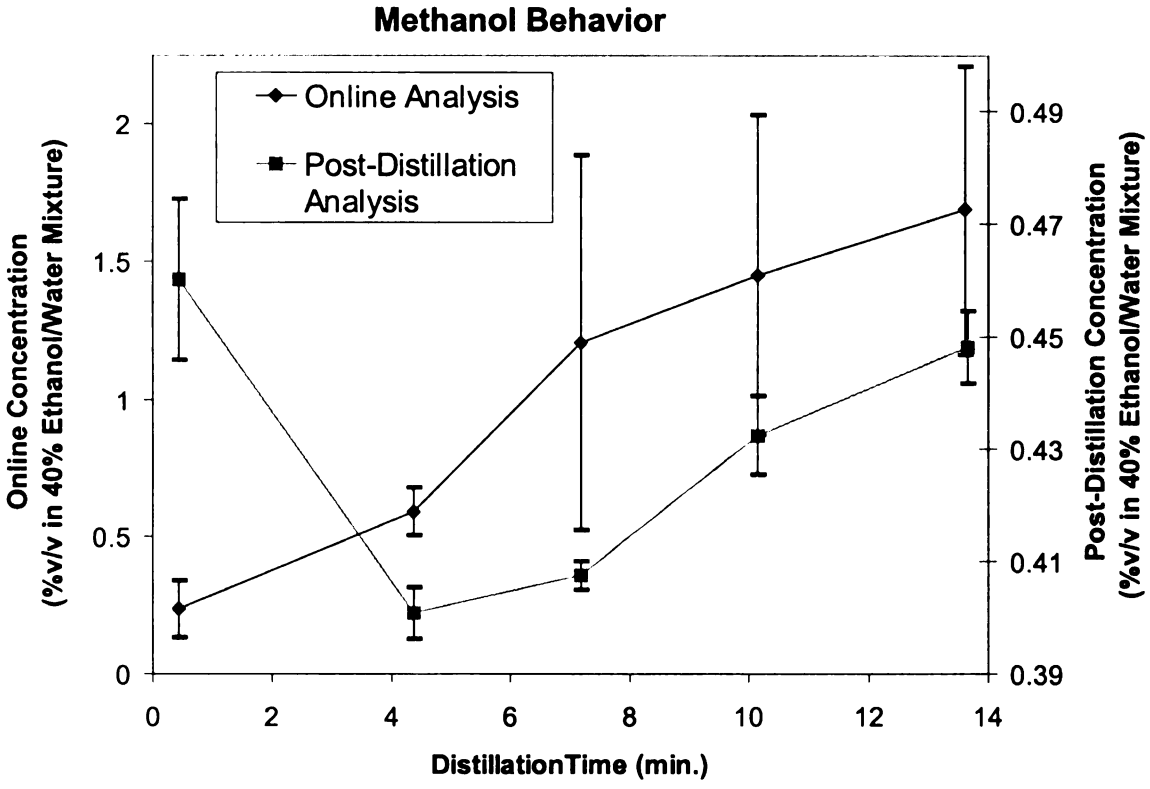


Figure 6.8 **The concentration behavior of methanol. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

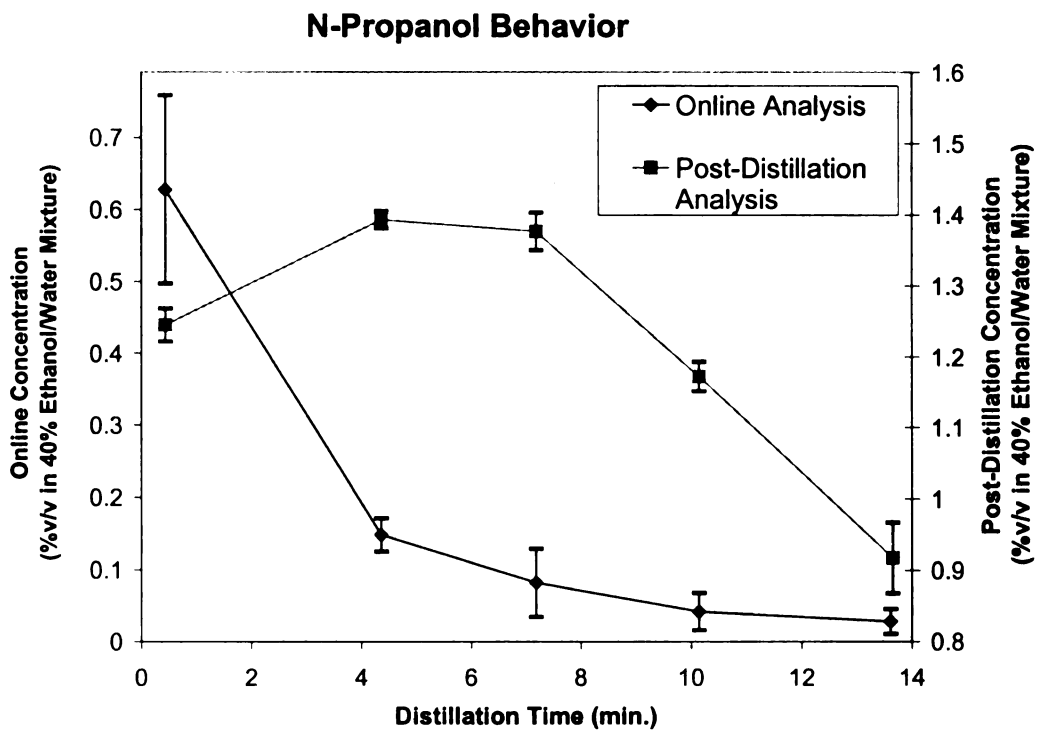


Figure 6.9 **The concentration behavior of n-propanol. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

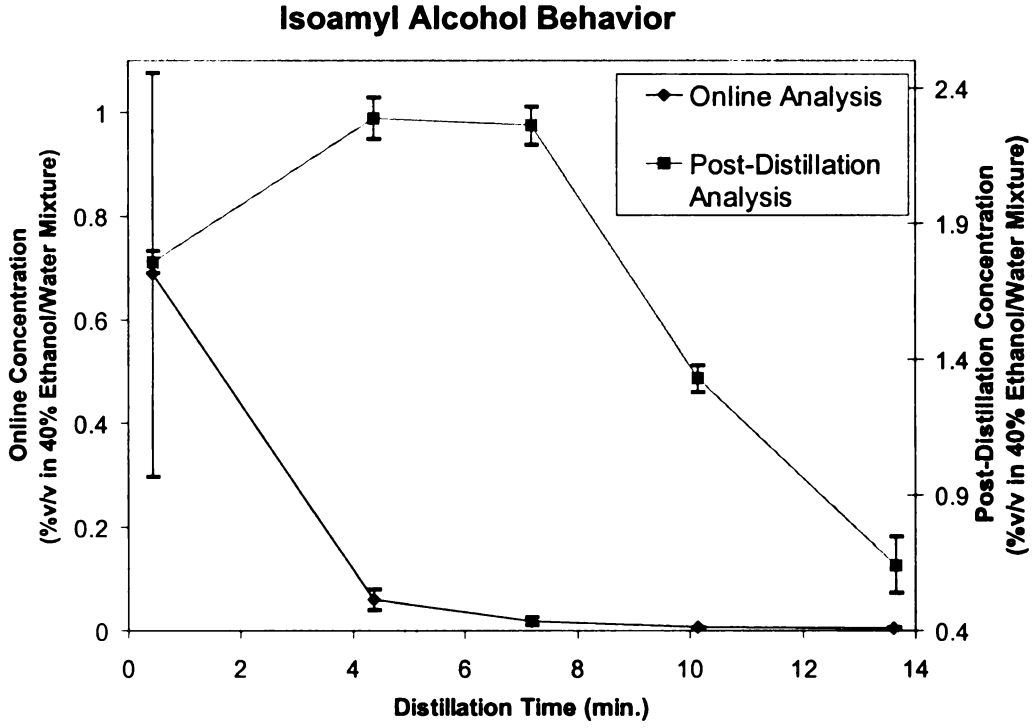


Figure 6.10 **The concentration behavior of isoamyl alcohol. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

One reason could be that this is the actual behavior of the vapor phase at the sampling port above the condenser during the distillation. The distillation behavior itself is inconsistent due to the size and construction of the Holstein still. Another reason could be that the headspace sampler itself samples inconsistently since it relies on the pressure inside the still to transfer the sample. As a result, the sample loop may not be collecting a consistent amount of sample prior to injection, thus leading to sporadic readings from the chromatograph.

Given the evidence so far, it would be more reasonable to conclude that it is the inconsistency of the sampler that causes the behavior of the online readings. Looking at the conventional GC measurements, there is little deviation in the error bars compared to that of the online measurements. This would indicate a relatively constant distillation behavior. Therefore, it is probably the headspace sampler that is causing the poor repeatability. This will be studied further in the next section using simple distillation.

The fact that the amounts measured using the headspace sampler are different from the amounts measured from the distillate in the conventional GC analysis also needs to be examined. This fact could be explained using the McCabe-Thiele diagram. In the sampling port of the still, there exists both liquid and vapor in equilibrium. Looking at the McCabe-Thiele diagram it can be seen that the mole fraction of vapor does not equal the mole fraction of liquid throughout most of the distillation process. So the amount of distillate measured after the distillation is not going to correspond exactly to the vapor sample measured at the top of the condenser. The vapor phase and liquid phase will be related to each other according to their equilibrium properties, but it would take further

studies to determine this relationship in order to figure out actual amounts in the vapor phase.

6.4 Simple Distillation

The headspace sampler was connected to a simple still to see if the behavior measured from the online readings were due to inconsistencies in the still or from the sampler itself. Three distillations were run with a solution similar to the ones made for the previous experiments. GC acquisitions were performed approximately every 2.5 minutes and 10mL cuts were taken. Conventional GC measurements were also performed for the sake of comparison.

Figure 6.11 shows the behavior of the ethanol concentration during the distillations. Figures 6.12 through Figures 6.16 show the behavior of the congeners. Just like the distillation with the 10L Holstein still, there is a difference between the measurements made with the online headspace sampler setup and the post-distillation conventional GC runs. The relative amount of congener and the behavior measured is different between the online and conventional GC measurements. The most pronounced differences in behavior between conventional GC measurements and online measurements seem to appear in methanol in Figure 6.14, n-propanol in Figures 6.15 and, and isoamyl alcohol in Figures 6.16.

The most interesting observation comes from looking at just the online measurements and observing the error bars for the three runs. There seems to be a large inconsistency in both the relative amounts and behaviors between the three runs,

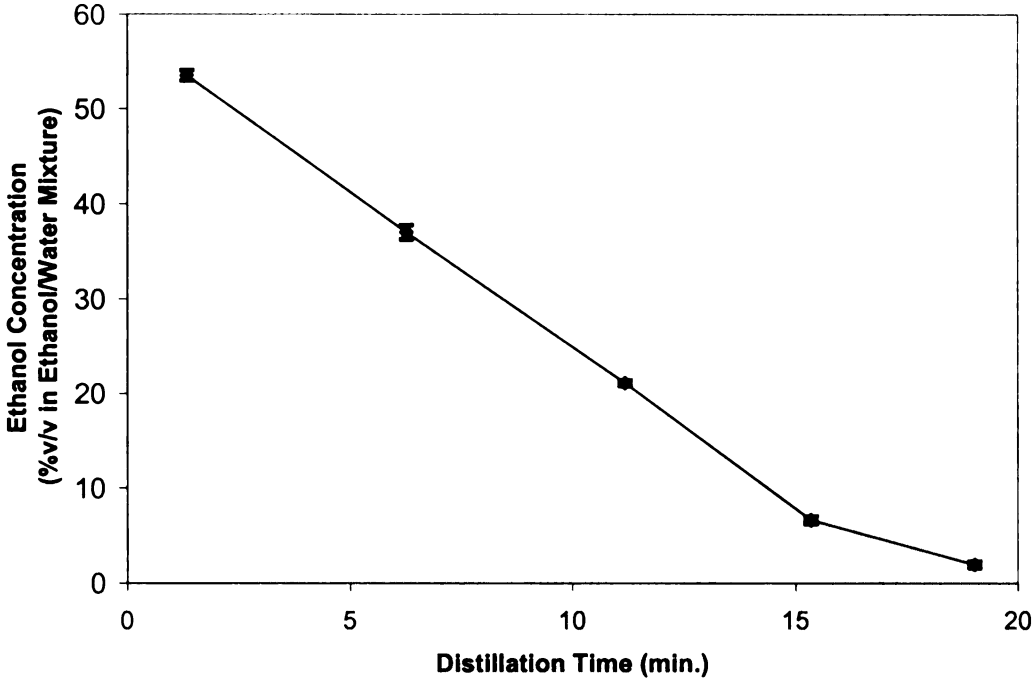


Figure 6.11. Ethanol concentration as a function of distillation time for the simple distillations determined by conventional GC analysis. Ethanol concentration is given in percent volume of ethanol per volume of distillate.

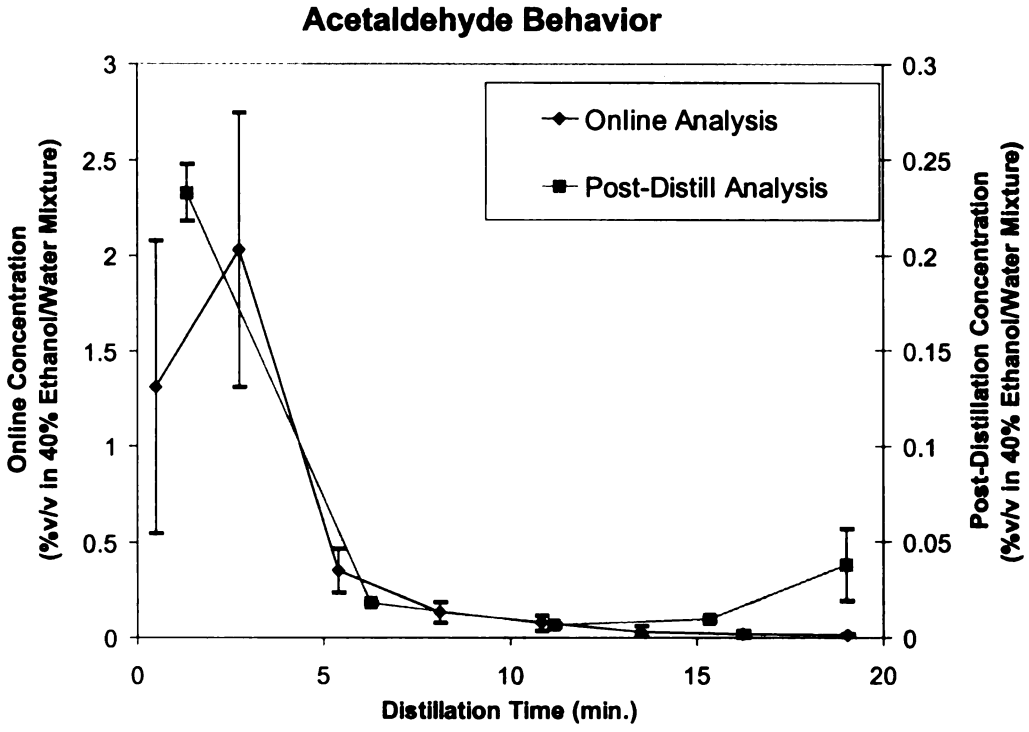


Figure 6.12 **The concentration behavior of acetaldehyde during a simple distillation. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

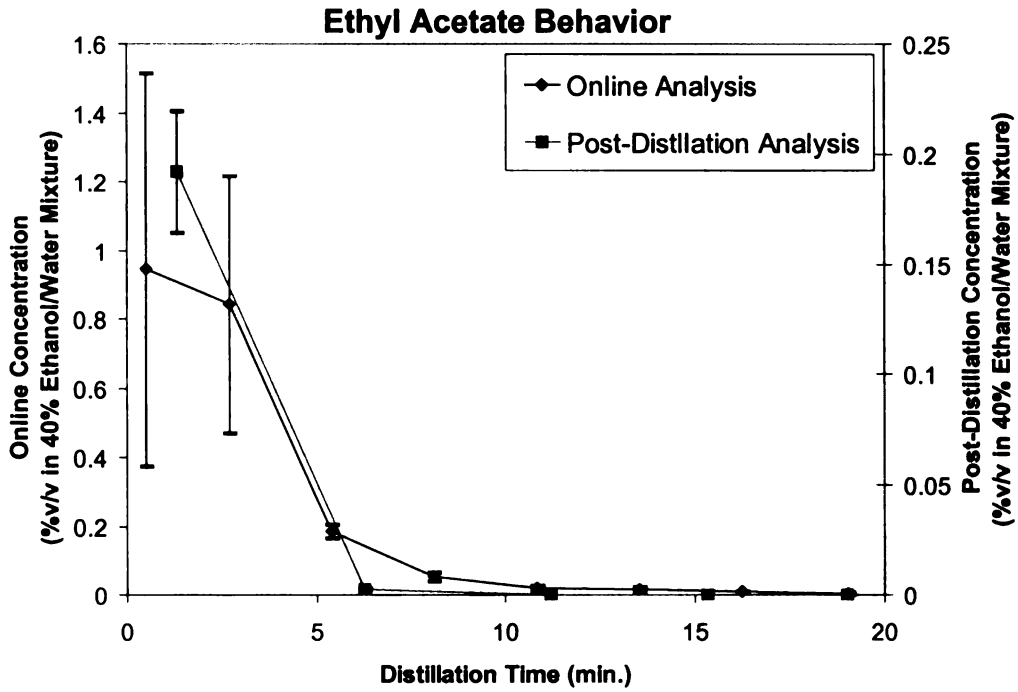


Figure 6.13 **The concentration behavior of ethyl acetate during a simple distillation. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

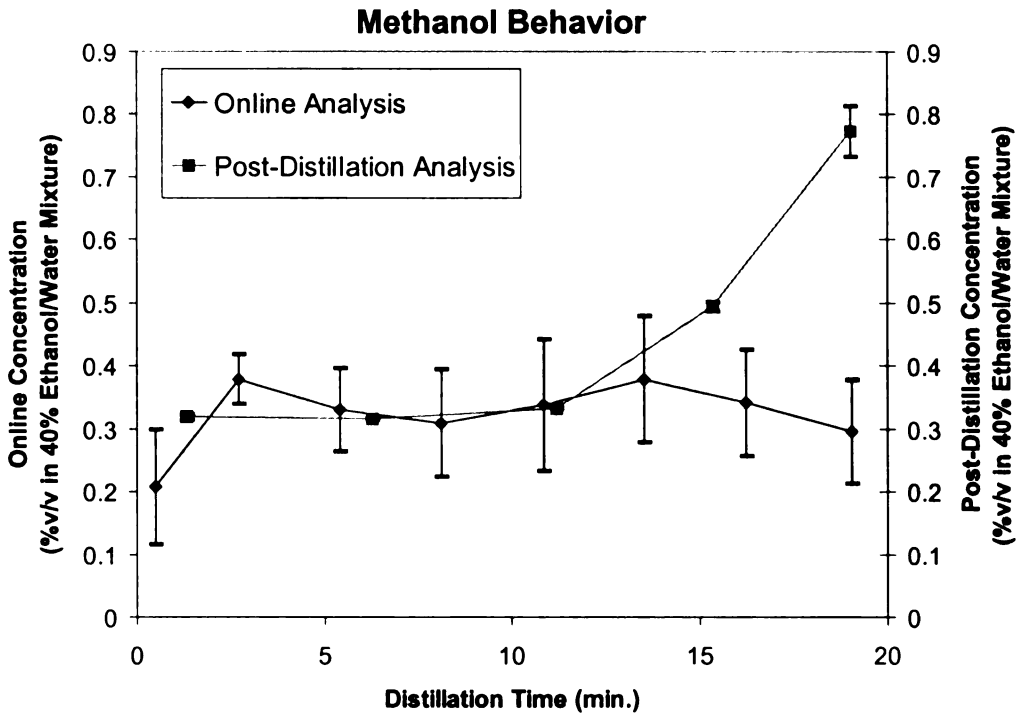


Figure 6.14 **The concentration behavior of methanol during a simple distillation. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

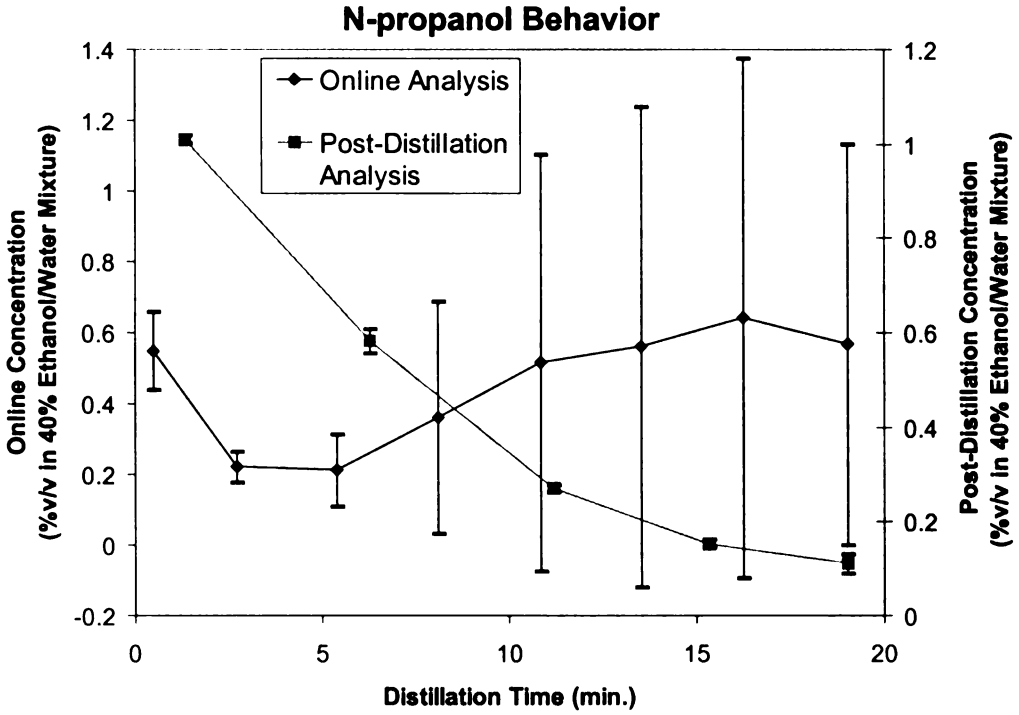


Figure 6.15 **The concentration behavior of n-propanol during a simple distillation. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

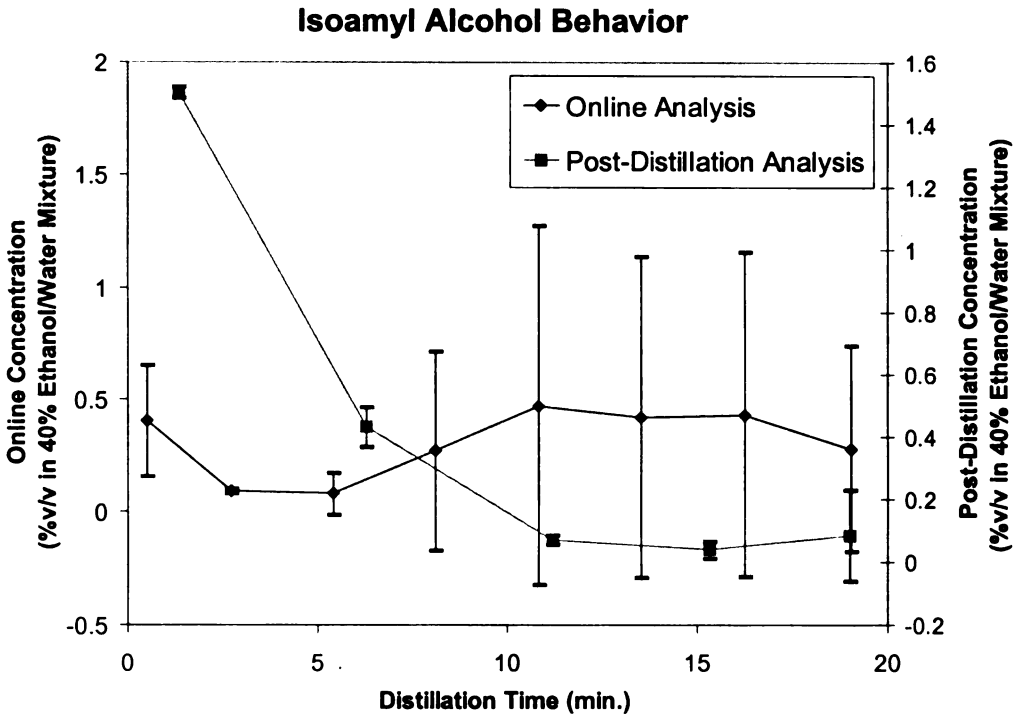


Figure 6.16 **The concentration behavior of isoamyl alcohol during a simple distillation. The online measurement is represented by the diamond plot and corresponds to the left y-axis. The square plot represents the behavior from post distillation measurements and corresponds to the right y-axis.**

especially for methanol, n-propanol, and isoamyl alcohol. This is not the case when looking at the post-distillation measurements. The error bars for all compounds are relatively smaller compared to the online measurements

The measurements with the conventional GC would indicate that the distillation behavior for the simple distillation was fairly constant. Therefore, the inconsistency in the online measurements is more likely a result of the variance in the sampling method. So in order to improve consistency with the online measurements, it is recommended that the focus be on improving the headspace sampling system.

7. Summary and Conclusions

The attempt to obtain online chromatographic analysis while monitoring a distillation with the Chromatofast® GC Accelerator™ was successful with respect to actually achieving analyte separation from a still vapor sample. This method also produced chromatograms in a time much faster than a conventional GC so that measurements could be obtained every few minutes during the distillation. This makes the technique a viable option for use in online monitoring.

Calibration proved to be difficult when measuring samples online. The ethanol calibration curve did not give an increasing peak area with increasing ethanol concentration. It was determined that the repeatability in the sampling of the Accelerator™ was reasonable so it most likely was not the cause of inconsistent data. Rather it was more likely the pressure fluctuations in the standard sample vials causing the problem. In addition, the calibration curve did not seem to correspond to the amounts measured during distillation. This could be due to the inability to approximate still conditions. It could also be due to the fact that there is actually less than 40%-80% ethanol in the vapor phase at the top of the still. Quantification is something that still needs to be studied further.

The behavior of the congeners was also measured using the online setup with the GC Accelerator™. Trends were found for acetaldehyde, ethyl acetate, methanol, and n-propanol. Isoamyl alcohol was not monitored in the online analysis due to its retention time being much longer than 2.5 minutes.

Despite the success in obtaining online data, the poor structural integrity of the Chromatofast® GC Accelerator™ made the process of making repeated measurements

difficult. The use of liquid nitrogen allowed for the possibility of transfer line freezing. In addition, the peak shapes quality worsened over time, most likely because of the failure of the valves to open and shut properly. Finally the Accelerator™ deteriorated to the point where it would no longer collect data. Receiving technical assistance for maintenance and repair on the machine was made almost impossible due to the failure of Chromatofast® Inc. to stay in business. Therefore, using the GC Accelerator™ as an online tool is not practical.

This led to the development of the headspace sampling system. This sampling system was able to extract vapor from the still and inject it directly into the GC. Fast separation of all the major components was achieved.

The chromatograms from the headspace sampling system could be obtained in a much shorter time than both the conventional GC and the GC Accelerator™ method. The headspace sampler also proved to be more rugged than the Accelerator™ as repeated measurements with the headspace sampler produced chromatograms of good quality nearly every time. In addition, the cost of the headspace sampler was much more affordable than the GC Accelerator™.

Despite the advantages, calibration was a problem for the headspace sampler as it was for the previous method. Actually, it appeared to be worse than with the GC Accelerator™. The ethanol calibration curve did not give increasing peak areas with increasing concentration. In addition, the repeatability of the measurements was extremely poor. These difficulties may be due to the inability to measure standards at conditions that are close to the conditions occurring inside the still among other reasons.

As with, the Accelerator™, the behavior of acetaldehyde, ethyl acetate, methanol, n-propanol, and isoamyl alcohol was studied with the headspace sampler online method. In addition, the distillate was studied afterward with conventional GC for comparison. The amounts and the behavior determined from the online measurements did not correspond directly to those of the distillate measured with the conventional GC after distillation. There were inconsistencies in behavior between the three runs for each compound in the online analysis. However the post distillate analysis showed consistent compound behavior between the three runs.

A study of simple distillations was done using the headspace sampling system to compare to the results of the 10L distillation. Again, there was a difference in the behavior and relative amounts of the compounds between the online analysis and the conventional GC analysis. The online analysis also showed inconsistent behavior between the three runs for each compound, while the distillate measurements with the GC showed similar behavior between the three runs.

The reason for the differences in the behavior of the compounds between the online measurements and the measurements taken of the distillate with conventional GC is most likely inconsistent sampling by the headspace sampler. This probably explains the poor repeatability in standardization and the inconsistency between the three runs in distillation measurements as well. The difference in relative concentrations between online vapor sampling and measurement of the distillate with conventional GC may be explained as well. The concentrations of the compounds in the vapor are probably not going to be the same as the concentrations in the liquid. So a relationship between the vapor and the liquid needs to be studied in order to find actual concentrations in the

distillate. Through this, the online data will serve the desired purpose of allowing real-time manipulation of the still to the change the composition of the distillate.

In conclusion, online measurement of a distillation using fast GC appears to be feasible. Fast GC could be achieved with both of the methods studied in this thesis, although the headspace sampling method proved to be more rugged and convenient than the GC Accelerator™ method. Behavior of the compounds chosen could be monitored, however there was a problem with repeatability and finding absolute concentrations of the compounds. With further study these problems could be overcome, therefore making online monitoring with high-speed gas chromatography a useful tool for monitoring distillations.

8. Future Work

One of the major obstacles to overcome with the headspace sampling system is the inconsistent sampling. As mentioned before, the headspace sampler relies strongly on the pressure of the still or the headspace pressure of the sample vial. If the pressures are inconsistent, then the amount of sample will most likely be inconsistent. A solution to this problem might be to connect a pump between the still and the injection valve to obtain a more consistent amount of sample. It might also be helpful to include some sort of pressure regulator to maintain a constant pressure during sampling.

A reliable method for standardization should be found. Perhaps standards should be placed in larger vials in order to better approximate the conditions of the still. In addition, better quality vials should be used to prevent leaks and loss of analyte. Perhaps vials should also be allowed to equilibrate longer when being heated to ensure that they are heated consistently every time.

The other issue, which must be addressed, is the quantification of the compounds. This is also related to the standardization. The inconsistency in sampling contributed partly to this problem. However, there is also the fact that the concentrations of compounds in the vapor probably do not correspond directly with the concentration of the corresponding distillate. So it might be useful to look at the equilibrium behavior of the compounds in question in order to determine the concentration relationship between the vapor phase and the liquid phase.

It may be useful to look at alternatives to the headspace sampler as well. Solid Phase Micro Extraction (SPME) might be a viable option. Using this method, it might be easier to ensure that the volume injected into the GC is more consistent.

This could make it easier to develop calibration curves and obtain better quantitative data. In addition, SPME concentrates samples, which could improve the detection of trace compounds.