DISTILLED ALCOHOLIC BEVERAGE PRODUCTION USING REACTIVE DISTILLATION TECHNIQUES

By

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A DISSERTATION

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

Chemical Engineering – Doctor of Philosophy

2018

ABSTRACT

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The goal of this research was to couple industrial beverage distillation with a chemical reaction to create a flavored spirit without adding anything after the final distillation. Ethanol reacted with butyric acid in the final distillation over Amberlyst® 15 to create ethyl butyrate, which gave the spirit a fruity smell comparable to Juicy Fruit® gum.

It was shown that if a beverage ethanol fermentation having 63 ± 3 g/L ethanol and 1 g/L butyric acid were distilled, the low wine will have 357 ± 32 g/L ethanol and 1.4 ± 0.1 g/L butyric acid. This sets up the low wine to be distilled over the catalyst to create the ethyl butyrate.

For the study, low wine was obtained from a craft distillery. This gave the most accurate representation of how this system would act in the beverage industry. Butyric acid was added to this low wine and distilled on a glass vigreux column with copper wire on the inside to simulate an industrial copper distillation column. The distillations started with a pot ethanol concentration of 30% ABV and varied: the butyric acid starting concentration from 0.5 g/L to 5 g/L, the catalyst loading from 1 g dry / L to 100 g dry/L, and the catalyst position in the column from being in the pot, the bottom of the column, and the top of the column.

All compounds, except butyric acid, followed the ethanol distillate concentration curve and dropped to zero as the ethanol ran out of the system. The butyric acid was not present in the distillate until the ethanol concentration in the distillate started to decreased. As the butyric acid starting concentration increased, the butyric acid in the distillate increased.

The ethyl butyrate concentration was a function of all three variables mentioned above. As starting butyric acid concentration increased, so did the ethyl butyrate. As the catalyst loading increased, the ethyl butyrate concentration increased. When the catalyst was located in the pot, the ethyl butyrate was shown to distill during the entire distillation only to drop with the ethanol. When

the catalyst was in the bottom of the column, ethyl butyrate was present in the beginning but the concentration increased to approximately doubling its starting concentration half way through the distillation. When the catalyst was in the top of the column, the ethyl butyrate was severely delayed in the distillate, only to distill through the tails section and again fall with the ethanol.

During distillation, lower boiling components vaporize and go up the column, making the bottom of the column a higher temperature than the top. Thus, there is more water and more butyric acid at the bottom of the column where the boiling point of the liquid is higher. As ethanol was depleted, the higher temperature water front rose past the catalyst and ultimately to the top of the column where it came out as distillate, bringing butyric acid with it. When this front reached the catalyst, the butyric acid reacted with ethanol to create the ethyl butyrate, which was carried up in the vapor phase by the ethanol and out in the distillate. This unsteady-state system explains why ethyl butyrate presence in the distillate was largely controlled by the location of the catalyst, and butyric acid was present only after ethanol had been depleted.

As the catalyst loading was increased while holding the other variables constant, ethyl butyrate production increased. This show that the system did not reach chemical equilibrium during the distillation.

The reflux ratio in the glassware column was calculated to be 9.4. This value was used to create a simulation on AspenTech® Batch Modeler V10. The model has good agreement with the experimental data.

A provisional patent application has been filed for this process.

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ACKNOWLEDGEMENTS

I would like to thank Dr. Kris Berglund for their guidance as my advisor through my PhD studies. I am grateful for all of their support and allowing me to work with them in their research group and distillery. I would also like to thank Dr. Dennis Miller, Dr. John Linz, and Dr. Richard Lunt for serving on my committee, and Dr. Ramani Narayan for stepping in during my defense. I am grateful to Working Bugs™, LLC and Dianne Holman for providing the low wine used in this study and for allowing me to work in their distillery and gain vast experience and knowledge about the beverage distillation industry.

I want to extend my appreciation to all my former and current research group colleagues Dr. Adam Jaros, Ryan Hendricks, Nicole Shriner, and Yasheen Jadidi for the brain storming, continued learning and late nights in lab. I also thank my industry colleagues Stephen Peabody, Kars Petersen, Dr. Kierstyn Schwartz, Dr. Cordell DeMattei, Dr. Tommy Auchtung, Ari Sussman, and Justin Aden for all that you have taught me, sometimes through trial and error. Thank you also to all of the staff in the MSU CHEMS department and chemistry graduate office for always getting the required paperwork processed in time.

Special thanks to my parents and brothers Richard Rochte, Karen Rochte, Nicolas Rochte, and William Rochte for your unwavering love and support through my entire life and collegiate studies. I thank my grandfather Ralph Brody for always asking the tough questions. And to my beloved wife Amber for supporting me through this trip for Oh, the places we’ll go.

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KEY TO ABBREVIATIONS

C.F.R. —- **C**ode of **F**ederal **R**egulations

HPLC —- **H**igh **P**ressure **L**iquid **C**hromatography

GC —- **G**as **C**hromatography

g/L —- **g**ram per **L**iter (concentration)

% ABV —- Percent **A**lcohol **B**y **V**olume (Ethanol)

RCM —- **R**esidue **C**urve **M**ap

BDL —- **B**elow **D**etectable **L**evel

RIU —- **R**efractive **I**ndex **U**nit

CHAPTER 1

INTRODUCTION

The basic concept of fermentation and distillation to create an alcoholic beverage has remained largely unchanged since its inception, mainly due to tradition. There have been advancements made as knowledge of the process grows. For instance, it is now known why the use of copper is important in a still, as it has a catalytic effect of removing sulfur compounds during distillation.

This research will yield a method for producing an innovative spirit using biological and chemical techniques, namely multiple fermentations and a reactive distillation system. These methods will be combined to create a food grade, flavored spirit while strictly adhering to the standards of identity for distilled alcoholic beverages in the United States.

There are many variables in the production of distilled beverages. This study will focus on using specific organisms to create compounds that are not typically produced by yeast, that will then enter the reactive distillation system, to produce unique flavors and aromas in the final product.

This paper will discuss the materials and unit operations that will be combined to create this overall process and the goal of the proposed research.

1.1 Individual Components and Processes

Unit operations are parts of often complex systems that can be recognized as stand alone systems. These may also be broken down further into more simple processes and components. The major unit operations for a spirits distillery are milling, mashing, fermentation, distillation, and bottling.

1.1.1 Raw Material

One of the most common raw materials for spirit production is grain, the majority being corn. According to the standards of identity for spirits, grain may be used to make whiskey and vodka (27 C.F.R §5.21) [17]. Most distilled beverages made from grain have the same procedure for their production. In the United States, corn is mainly used for whiskey production because of its use in bourbon which legally has to contain at least 51% corn in the mash bill. For this study, 100% yellow dent corn will be used as the mash bill for the spirit because it is easy to ship, store, and process.

Many other materials may be used to make spirits, for example, fruit to make brandy, sugarcane to make rum, and agave to make tequila. These raw materials will be used in future studies with the goal of achieving results similar to those using corn.

1.1.2 Grain Processing

After being delivered from the producer, grain is milled into a flour to expose the starchy endosperm that will be used by the yeast as a metabolite. This process uses a hammer mill, pulverizing the whole grain kernels into small pieces roughly 1-2 millimeters in size, using small hammers that spin at high speeds.

Shortly after milling, the flour meets water on the way into a mash tun. In the mash tun, the grain and water are mixed while enzymes are added to break down the starch that was exposed during milling. Amylase enzymes break down the starch into smaller saccharides, depending on whether it is α-amylase (EC 3.2.1.1), β-amylase (EC 3.2.1.2), or γ-amylase (EC 3.2.1.3) which produce polysaccharides, maltose, or glucose respectively. After mashing, these sugars are available to be used by the microorganism to grow and produce ethanol.

1.1.3 Yeast Fermentation

Yeast are eukaryotic, chemoorganoheterotrophic, single cell facultative anaerobes that are utilized by the brewing, wine making, distilling, and baking industries [4, 11, 13]. They are part of the Fungi kingdom and relatively tolerant to a broad range of environmental conditions, such as pH, temperature, and sugar and ethanol levels, as compared to bacteria. Therefore, bacterial contamination is able to be controlled (by lowering the pH and raising the alcohol content, for example).

The alcoholic beverage industry has many strains of yeast that vary in the type of product they are designed to make. These yeasts tend to give different flavor profiles to spirits by producing slightly different sets of metabolites during their life. Most of these strains are classified under the species *Saccharomyces cerevisiae* or *Saccharomyces pastorianus*. [18] These include commercially available strains as well as proprietary strains used by only a single company. The different yeast strains are sold for different products such as vodka, whiskey, rum, etc., and have been qualified for each product through trial and error. These differences give specific spirits their unique qualities depending on the raw material used, sanitation, and the overall skill of the engineers and operators.

Yeast is used for alcoholic beverage fermentation because ethanol is produced as its primary metabolite from glucose, maltose, and maltotriose. This primary metabolite is a waste product for the yeast cell and is excreted through the cell membrane which makes it easier to recover than if it were retained [5]. Figure 1.1 describes the overall process of fermentation performed by yeast to convert one glucose molecule into two ethanol and two carbon dioxide molecules.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + \text{Yeast} \xrightarrow{\text{Fermentation}} 2 \ \underset{\text{Ethanol}}{CH_3CH_2OH} + 2 \ \underset{\substack{\text{Carbon}\\ \text{Dioxide}}}{CO_2}$$

Figure 1.1: The simplified overall chemical equation of fermentation glucose to ethanol by yeast.

When the yeast is pitched to begin fermentation, oxygen is still present in the mash. This oxygen is important for the growth of yeast biomass through respiration. Yeast reproduce by an asymmetrical form of mitosis called budding, which leaves a mother and daughter cell identical in genetic material [4]. Once the oxygen is depleted by the growing yeast, fermentation begins and thereupon starts the formation of ethanol and carbon dioxide.

1.1.3.1 Sanitation

To avoid spoilage, it is important to keep contaminating organisms out of the fermentation process. These organisms produce compounds that may considerably decrease the yield of ethanol and may contribute an undesirable flavor and aroma. These compounds are usually organic acids such as lactic acid or acetic acid made by species of *Lactococcus* or *Acetobacter*. Anything put into the fermenter other than that needed for the fermentation to proceed as designed is considered a contaminate.

Most facilities have some form of background contamination. Generally, the larger the facility, the more difficult it is to control the development of a background contamination. In fact, some products are characterized by the results of a facilities unique mixture of contaminating microorganisms and yeast during the ferment. If the product is good, that mixture is called a ’house strain’ and regarded as proprietary.

1.1.4 Bacterial Fermentation

There are many different types of bacteria that have varying functions in nature, from breaking down organic matter in the woods to spoiling an ethanol fermentation in a distillery. Although some bacterial fermentations are considered contamination, many cultured bacteria species are used to produce foods and beverages making organic acids as one of their primary metabolites. Some food and beverage genera include *Lactobacillus* (lactic acid bacteria used to make some yogurt and cheeses), *Acetobacter* (acetic acid bacteria used to make vinegar), and *Oenococcus* (used in wine production as the secondary fermentation bacteria).

Unlike yeast, which are facultative anaerobes, there are bacteria species that grow under different oxygen levels. There are some, like *Acetobacter aceti*, that are obligate aerobes and require oxygen to grow and convert ethanol to acetic acid. These organisms are found almost everywhere in soil and industry surfaces, making it difficult to eliminate them from fermentations.

On the other end of the scale, there are bacteria that are obligate anaerobes which die in the presence of oxygen. An example of this would be the genus *Clostridium*, which typically does not pose a contamination threat, as it is killed by the oxygen present in the pre-fermentation mash. *Clostridium tyrobutyricum* is a bacteria that produces butyric acid and could be an organism of interest for this beverages system [9].

1.1.5 Reactive Distillation

Reactive distillation combines the two unit operations of a chemical reaction and a distillation into one. This technique is useful for reactions that need a special condition that can be achieved through distillation. For example, it could be that the equilibrium of the reaction over a catalyst strongly favors the reactants, and the product is more volatile than either reactant. A column could be packed with the catalyst and ran such that the reactants vaporize up to the catalytic section, react, and the product boils off as the distillate, thus removing the product and driving the reaction in the favorable direction.

Combining two processes into one decreases time and energy to produce a desired result. Initial capital cost and maintenance costs are also lowered because the reactor and column is the same piece of equipment. The most common use for reactive distillation is to produce esters. Other than sulfur adsorption onto copper, the alcoholic beverage industry does not use this technique in the production of spirits.

The catalytic property of copper on sulfur compounds is a good example of using reactive distillation in beverage production [7]. Studies have determined that the main compound being removed by the copper is dimethyl trisulfide (DMTS) which has a low odor detection threshold (33 ppt[†] in 20% ethanol) [7].

[†] ppt - parts per trillion

1.1.5.1 Esters

An ester is formed when an acid and alkoxy group join together though a condensation reaction. It can be any acid and any alkoxy, but is usually an organic acid and an alcohol. As this is a slow reaction without the presence of a catalyst, a classic method is to use the Fischer-Speier esterification with a sulfuric acid catalyst. Figure 1.2 below shows the general reaction of a carboxylic acid with an alcohol.

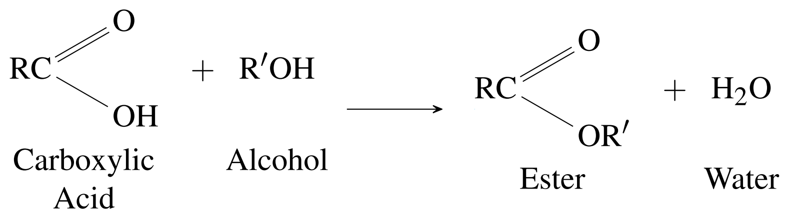
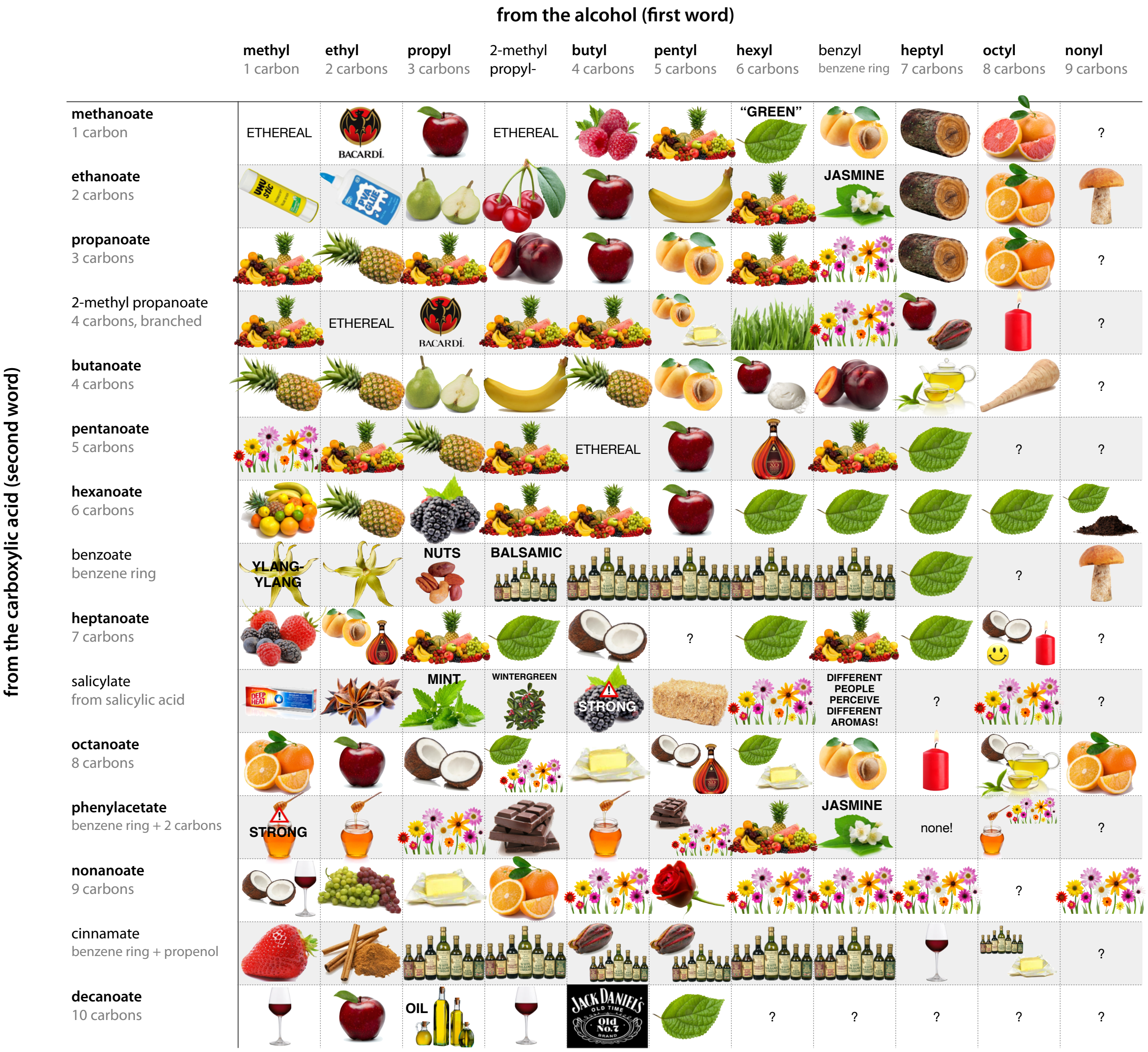


Figure 1.2: The chemical equation for general ester formation, R and R’ are alkyl groups.

Esters are commonly used in flavorings and fragrances because of their pleasant odor. Figure 1.3 shows various combinations of alcohols and organic acids that have certain aromas when combined into an ester. [10] Any of these esters are able to be created if the initial ingredients are present in a mixture.

A common ester used in the fragrance industry is ethyl butyrate which is commonly said to have the smell of pineapple or fresh orange juice.



Produced by James at jameskennedymonash.wordpress.com. Visit website for more infographics. Free to use!

Figure 1.3: A table of esters and their smells produced by James Kennedy, VCE Chemistry teacher at Haileybury in Australia [10]

1.2 Main Objective

The main objective of this research was to develop a distilled beverage spirit with a fruity aroma without having to add a chemical, either artificial or natural, to the product after the final distillation. This character was introduced by combining two industry practices, beverage ethanol distillation and a catalytic chemical reaction. The two compounds of interest were ethanol and butyric acid which, when reacted over a catalyst, form ethyl butyrate and water as seen in Figure 1.4.

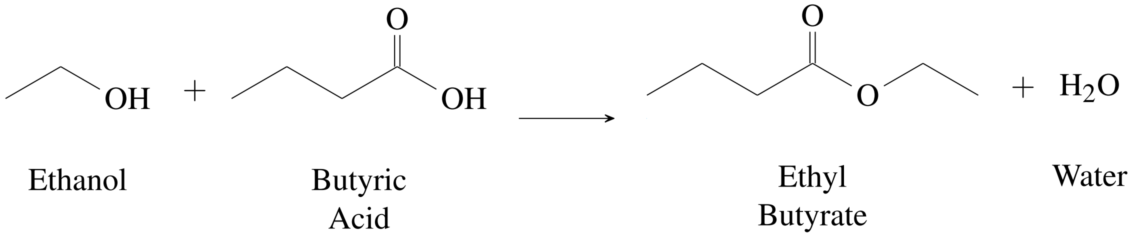


Figure 1.4: The chemical equation for the dehydration reaction of ethanol and butyric acid to form ethyl butyrate and water.

A near complete conversion of the butyric acid in the hearts of the product during reactive distillation is important because butyric acid has an unpleasant odor. It is present in and is one of the distinctive smells in human vomit [8]. At low concentrations, it has a character of buttered popcorn, which is also not desirable with this product. The human odor detection threshold of butyric acid has been reported to be 0.26 ppb[†], so it is important to convert it all to ethyl butyrate in order to avoid a most unpleasant spirit. [3].

1.2.1 Standards of Identity

An important point in this research is to make sure that the standards of identity are followed at all times (27 C.F.R §5.21) [17]. This means that all of the pre-distillation processes must be done according to the standards, along with the distillations. The purpose of this work is to make a product with a unique flavor or aroma, without having to designate it as an imitation spirit.

[†] ppb - parts per billion

1.3 Planned Data Collection

This research will involve lab-scale fermentations that will be monitored for their contents of sugar, ethanol, butyric acid, and other tracer compounds to track the progress of the fermentation. These measurements will be taken primarily using a high pressure liquid chromatography (HPLC) system.

The main factor indicating the completeness of the fermentation will be the amount of available saccharides. When the content drops below two grams per liter (g/L), it will be considered complete.

After the fermentation is complete, the fermented mash will be distilled using the same technique as an industrial beverage distillery. This will involve a stripping run to extract the volatile components and reduce the volume of the product. The outcome of the stripping run is called low wines and is not considered the final consumer product. Low wines are distilled again in a finishing run where the separation of heads, hearts, and tails takes place.

During the stripping and finishing distillations, samples will be taken at intervals to determine the time based composition of the distillate and quantify the effectiveness of the catalyst in the column. These samples will be analyzed on a gas chromatography (GC) system.

1.4 Laboratory Process Equipment

1.4.1 Fermenter

The fermentations and distillations will be performed using standard laboratory glassware along with a New Brunswick™ Bioflo® 310 fermentation system. These systems are able to control agitation, temperature, pH, dissolved oxygen, foam/level, and up to four gas inputs. The Bioflo® 310 keeps the consistency needed for comparing different distillation techniques without varying the fermentation.

1.4.2 Glassware

Figure 1.5 is a picture of the glassware setup used for this research. It consists of a round bottom boiling flask for the pot, a vigreux column with copper wire inside to simulate a copper beverage column as much as possible, and a straight Liebig condenser after a thermometer. The pot is heated with a 270 watt mantle.

1.4.3 Analytical Equipment

1.4.3.1 High Pressure Liquid Chromatography (HPLC)

Fermentation media will be analyzed using a Shimadzu HPLC. Components include a DGU-20A3 degasser, LC-20AT pumping unit, SIL-20A HT auto sampler, CTO-20A column oven, and a RID-10A refractive index detector. The column used was an Aminex® HPX-87H Ion Exclusion Column which was 300 mm by 7.8 mm. The mobile phase used was a 0.005 M aqueous solution of sulfuric acid.

1.4.3.2 Gas Chromatography (GC)

The distilled product samples will be analyzed using a Shimadzu GC-17A equipped with a FID detector. The column used was a Zebron ZB-WAXplus with a 30 m length, 0.25 mm ID, and 0.25 µm film thickness from Phenomenex®. The mobile phase was ultra pure helium supplied by Airgas®.

Calibration standards were run after every distillation was analyzed (approximately 35 samples) to ensure that the calibration was still valid and that the analysis was accurate.

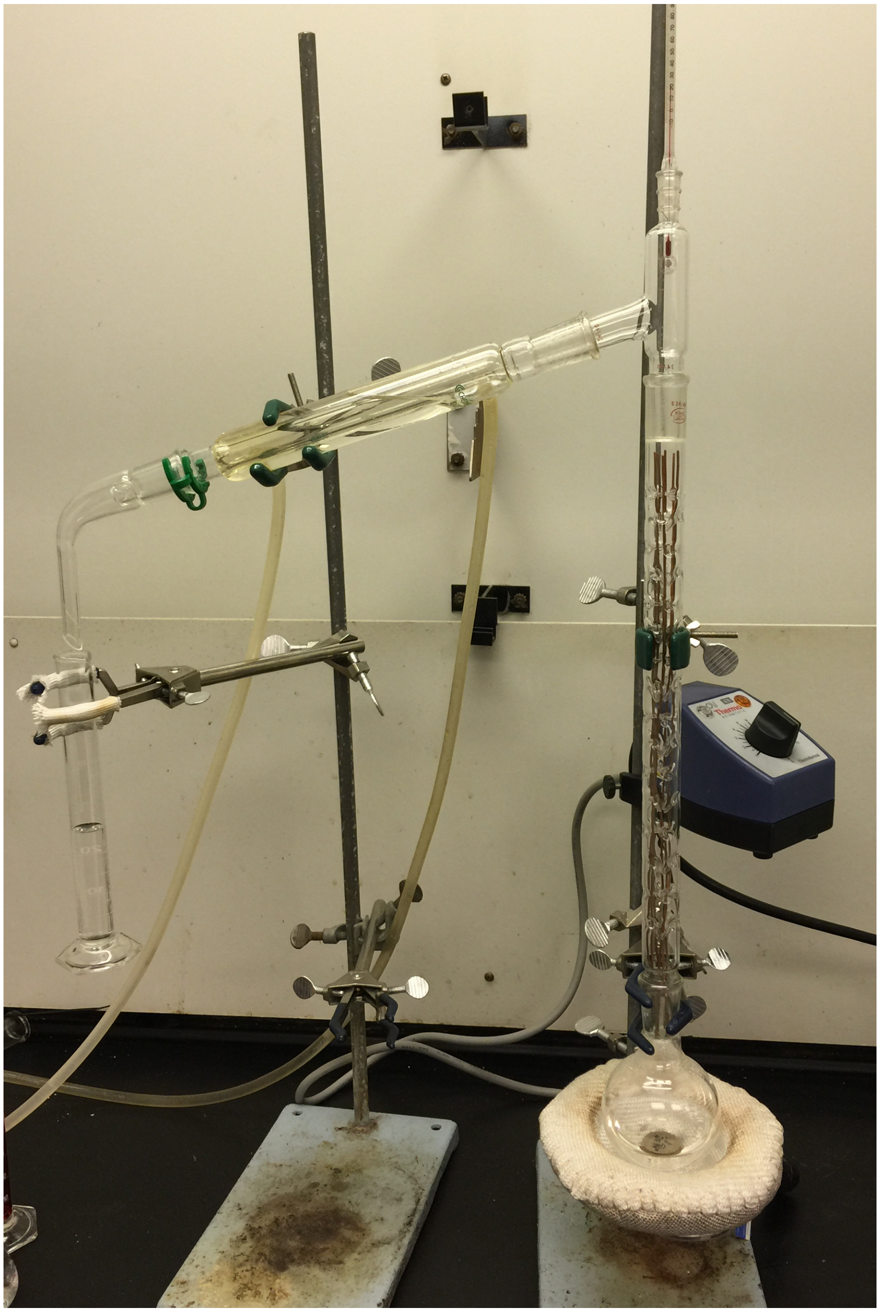


Figure 1.5: The distillation glassware setup used to distill the product.

CHAPTER 2

MODELING

Work was conducted to determine if the proposed research is feasible. A computer simulation was made using Aspen Plus® software by AspenTech for the continuous distillation of water, ethanol, and butyric acid to determine if the butyric acid will be present in the distillate. After the simulation was successful, a fractional distillation was preformed at laboratory scale.

2.1 Ternary Residue Curve Map

The pure boiling points of water, ethanol, butyric acid are 100 °C, 78.4 °C, and 163.5 °C respectively. Ethanol and water have a binary azeotrope which has a boiling temperature at 78.1 °C with a concentration of 95.6%w/w ethanol. Water and butyric acid also have a binary azeotrope at 99.5 °C with a concentration of 18.4%w/w of butyric acid.

Figure 2.1 shows a ternary residue curve map (RCM) of water, ethanol, and butyric acid in weight fraction.[‡] Along with the ethanol/water azeotrope, a binary azeotrope is present between water and butyric acid which boils at 99.5 °C. A separatrix (or simple batch distillation boundary) is drawn in green which divides the diagram into two distillation regions. Residue curves are drawn in light blue with arrows indicating increasing temperature in the pot (or time during the distillation).

The concentrations of water, ethanol, and butyric acid in the pot at the beginning of a run determine the starting point on Figure 2.1 [6, 20]. The residue curves show the concentration of the components in the pot as the distillation proceeds. As an example, if the concentrations of water, ethanol, and butyric acid are 75%w/w, 20%w/w, and 5%w/w respectively, the pot concentration will be 100%w/w water when the distillation is finished with all of the ethanol and butyric acid from the system in the distillate. If the starting point was to the left of the distillation boundary, the pot would eventually consist of pure butyric acid.

[‡] Produced on Aspen Plus®

The presence of these binary azeotropes in this system makes it possible for the high boiling butyric acid to be carried over in the distillate stream by the water during the first distillation of the spirit. This then sets the system up for the second distillation over a catalyst to produce the desired ethyl butyrate in the finished spirit.

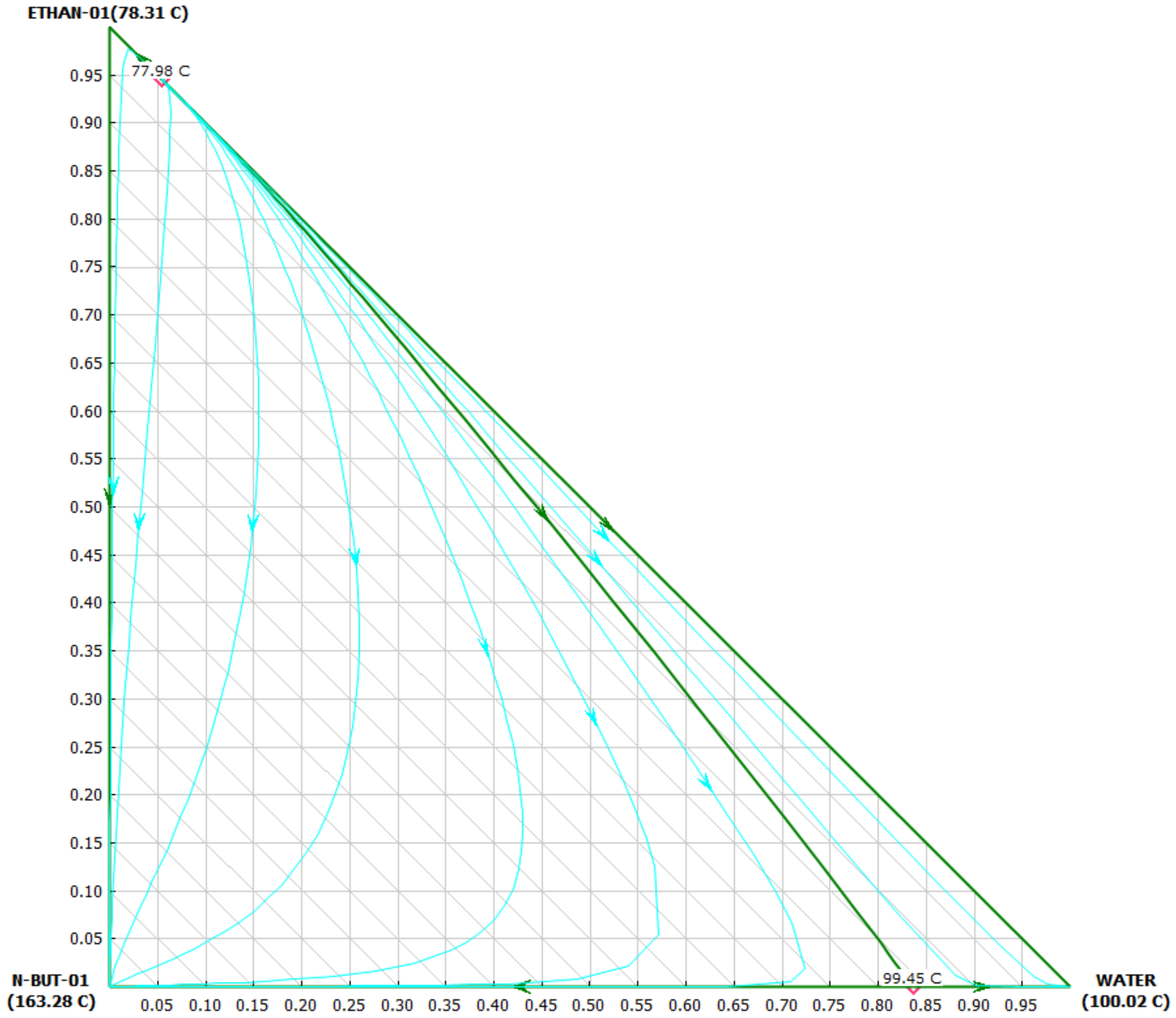
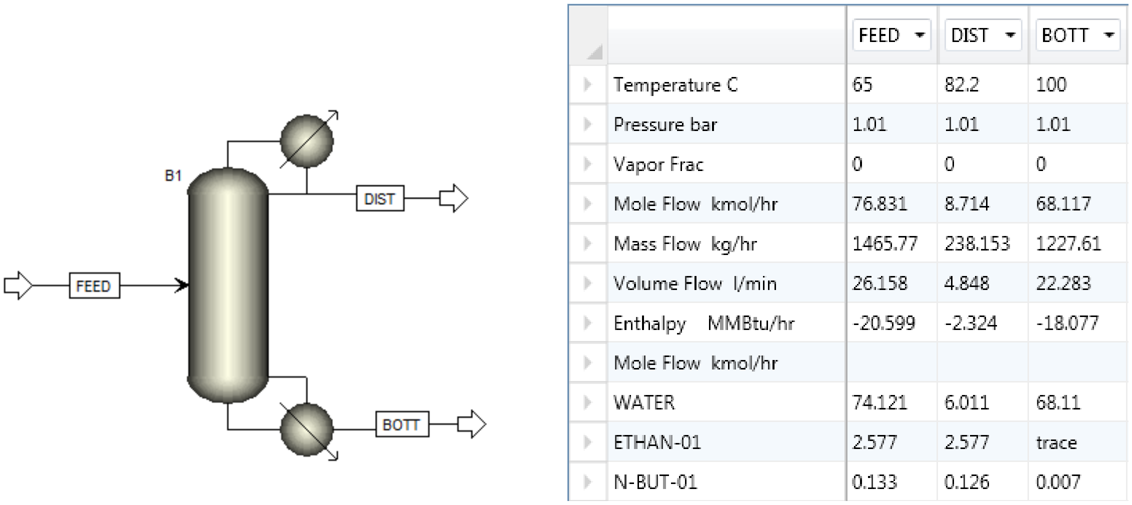


Figure 2.1: A ternary residue curve map of water, ethanol, and butyric acid with separatrix. The separatrix is drawn in green which starts at the ethanol/water azeotrope and ends at the butyric acid/water azeotrope. Residue curves are drawn in light blue. This diagram is measured in weight fraction.

2.2 Aspen Plus® Simulation

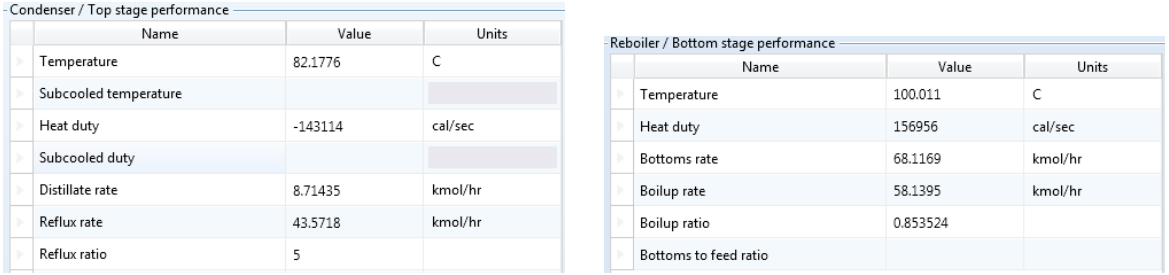
A column was designed in Aspen Plus® to distill a whiskey mash while having butyric acid present in the distillate of the column. The column was designed to have 17 bubble cap trays, stage seven as the feed stage, and a reflux ratio of five. The following figures are screenshots from the Aspen Plus® software used for the simulation.



	FEED	DIST	BOTT
Temperature C	65	82.2	100
Pressure bar	1.01	1.01	1.01
Vapor Frac	0	0	0
Mole Flow kmol/hr	76.831	8.714	68.117
Mass Flow kg/hr	1465.77	238.153	1227.61
Volume Flow l/min	26.158	4.848	22.283
Enthalpy MMBtu/hr	-20.599	-2.324	-18.077
Mole Flow kmol/hr			
WATER	74.121	6.011	68.11
ETHAN-01	2.577	2.577	trace
N-BUT-01	0.133	0.126	0.007

(a) Flowsheet (b) Stream Table

Figure 2.2: Aspen Plus® screenshots of the flowsheet and overall stream table



Condenser / Top stage performance

Name	Value	Units
Temperature	82.1776	C
Subcooled temperature		
Heat duty	-143114	cal/sec
Subcooled duty		
Distillate rate	8.71435	kmol/hr
Reflux rate	43.5718	kmol/hr
Reflux ratio	5	

Reboiler / Bottom stage performance

Name	Value	Units
Temperature	100.011	C
Heat duty	156956	cal/sec
Bottoms rate	68.1169	kmol/hr
Boilup rate	58.1395	kmol/hr
Boilup ratio	0.853524	
Bottoms to feed ratio		

(a) Top Stage Performance (b) Bottom Stage Performance

Figure 2.3: Aspen Plus® screenshots of the performance of the top and bottom stages

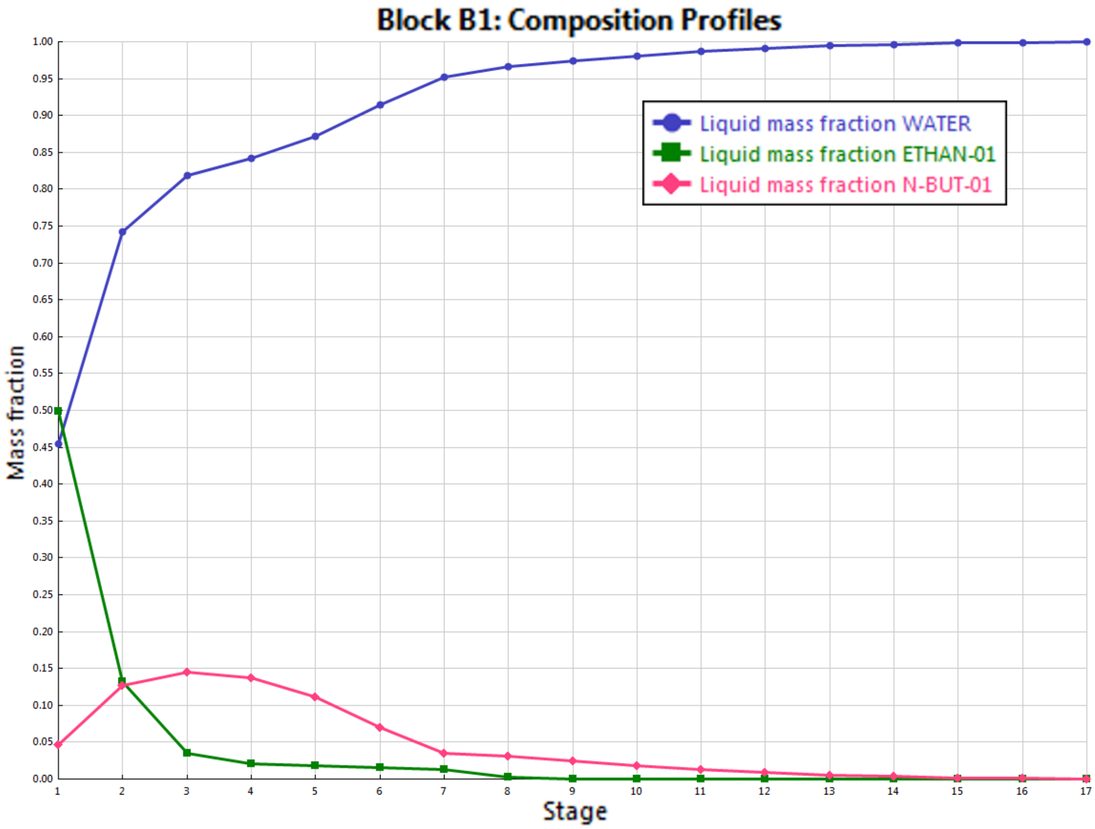
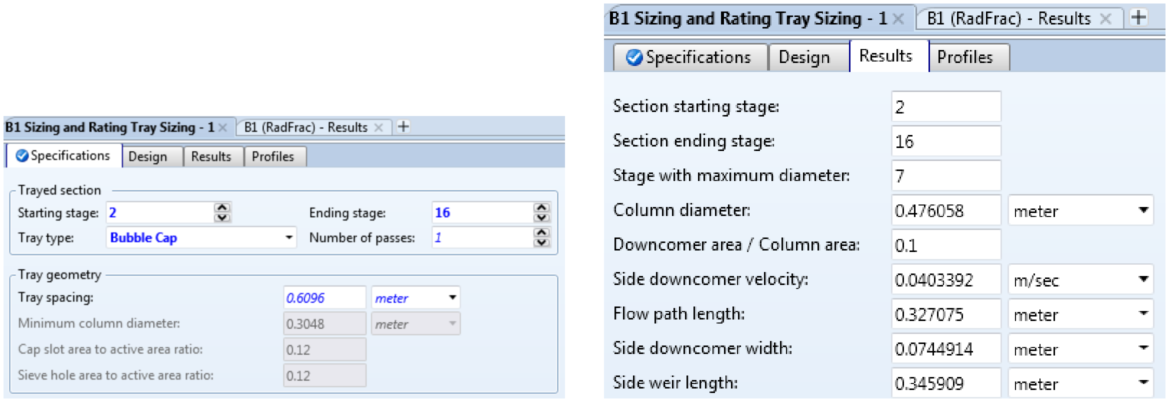


Figure 2.4: A graph of the column tray compositions as produced by Aspen Plus®.



Trayed section
Starting stage: 2
Ending stage: 16
Tray type: Bubble Cap
Number of passes: 1

Tray geometry
Tray spacing: 0.6096 meter
Minimum column diameter: 0.3048 meter
Cap slot area to active area ratio: 0.12
Sieve hole area to active area ratio: 0.12

(a) Tray Sizing Input

Section starting stage: 2
Section ending stage: 16
Stage with maximum diameter: 7
Column diameter: 0.476058 meter
Downcomer area / Column area: 0.1
Side downcomer velocity: 0.0403392 m/sec
Flow path length: 0.327075 meter
Side downcomer width: 0.0744914 meter
Side weir length: 0.345909 meter

(b) Tray Sizing Results

Figure 2.5: Aspen Plus® screenshots for the sizing of the column.

As seen in Figure 2.2b, the distillate stream of the column contains 94.7 mol% of the butyric acid in the system.

2.3 Lab-scale Fractional Distillation

A lab fractional distillation was performed in conjunction with the Aspen Plus® simulation to support its results. The experiment used a 500 mL round-bottom flask, Vigreux column, and a straight condenser setup in a fractional distillation configuration. The flask started with 250 mL of an aqueous solution containing 79.2 grams per liter [g/L] ethanol and 4 g/L butyric acid. Figure 2.6 shows the concentrations of ethanol and butyric acid of the experiment as a function of distillate volume collected.

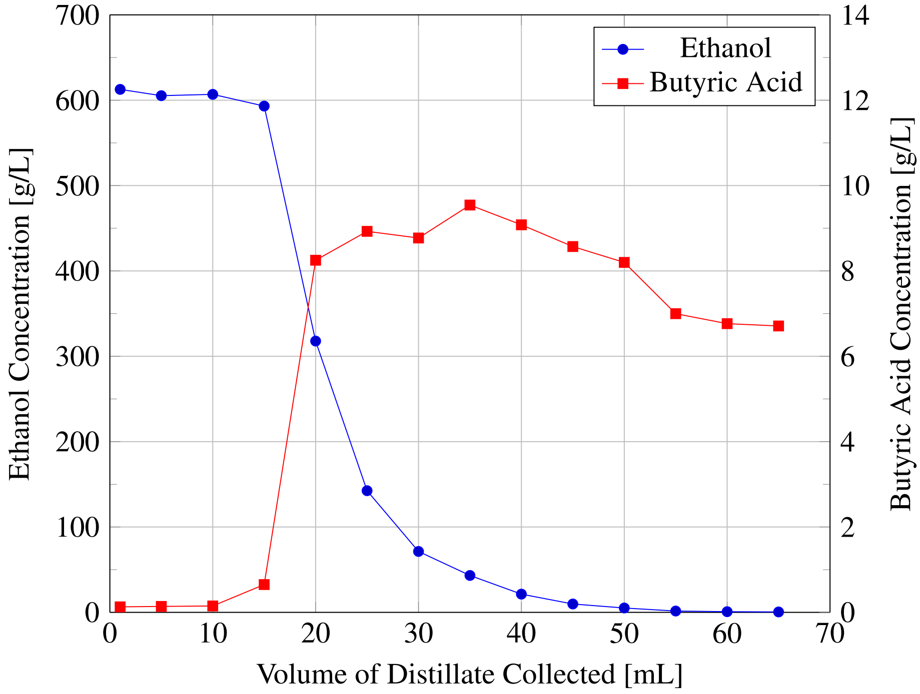


Figure 2.6: Distillate concentrations of ethanol and butyric acid during the lab-scale fractional distillation vs. the amount of distillate volume collected.

A final distillate of 70 mL was collected containing 230 g/L ethanol and 6.2 g/L butyric acid. This experiment coincides well with the Aspen Plus® simulation in Section 2.2.

CHAPTER 3

FERMENTATION

Fermentation is one of the main processes in the creation of alcoholic beverages. This is where a microorganism produces ethanol that will be concentrated in distillation to become liquor. This process is generally anaerobic to produce ethanol. This work will ultimately lead to the use *Saccharomyces cerevisiae* to produce ethanol and *Clostridium tyrobutyricum* to produce butyric acid. *S. cerevisiae* is an facultative anaerobe, so they can live in aerobic and anaerobic conditions. *C. tyrobutyricum*, on the other hand, is an obligate anaerobe which means it will die in the presence of oxygen.

The future goal is to have both organisms grow together to create a mash that has between 50 and 80 g/L (about 6-10% ABV) and has at least 1 g/L butyric acid.

3.1 Ethanol Lab Fermentation

Fermentations were performed using *S. cerevisiae*. The media was composed of 1 part Maltoferm® 10000 liquid malt extract and 3 parts water. Figure 3.1 shows a typical HPLC printout of the fermentation media on day 0.[‡] There appeared to always be a small amount of ethanol and some organic acids in the media when it was diluted with water. This is thought to be due to the media being an industrial product.

[‡] day 0 - Before the media is pitched with a microorganism.

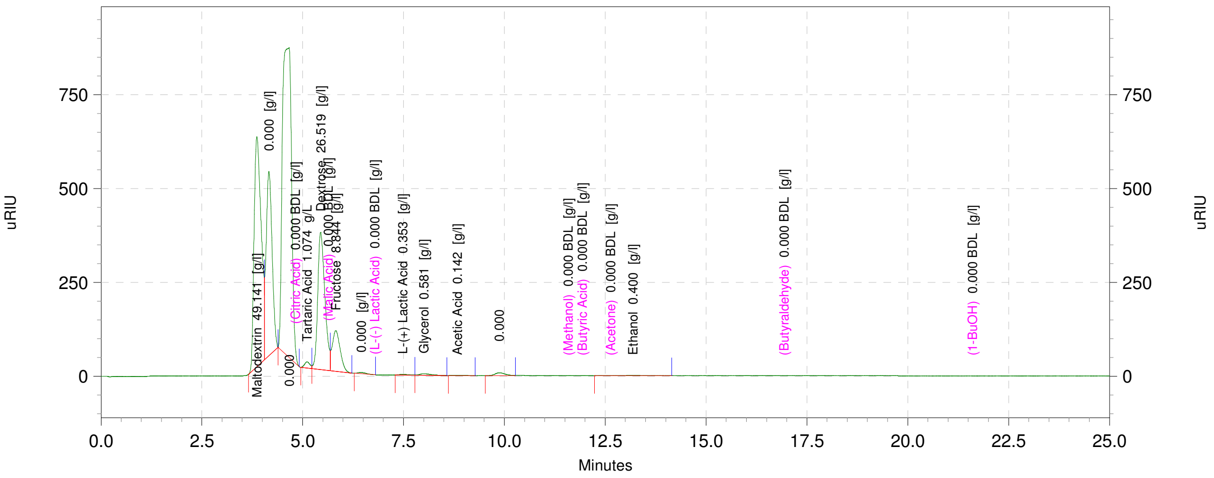


Figure 3.1: HPLC printout of an average control fermentation on day 0.

The fermentations were carried out in the Bioflo® 310 system using 1 liter of media. It was pitched with 0.5 grams of Fermentis SafSpirit™ USW-6 yeast. This strain is produced for the fermentation of bourbon whiskey. The pH of the control fermentations were recorded as 4.50 ± 0.1 and was not controlled during the fermentation. The temperature was controlled at 24 a °Cnd the agitation at 200 rpm.

The fermentations were left to ferment for 3-4 days until the dextrose reading was below the detectable level (BDL) for the HPLC. Figure 3.2 shows a HPLC printout for a control fermentation after 3 days had passed.

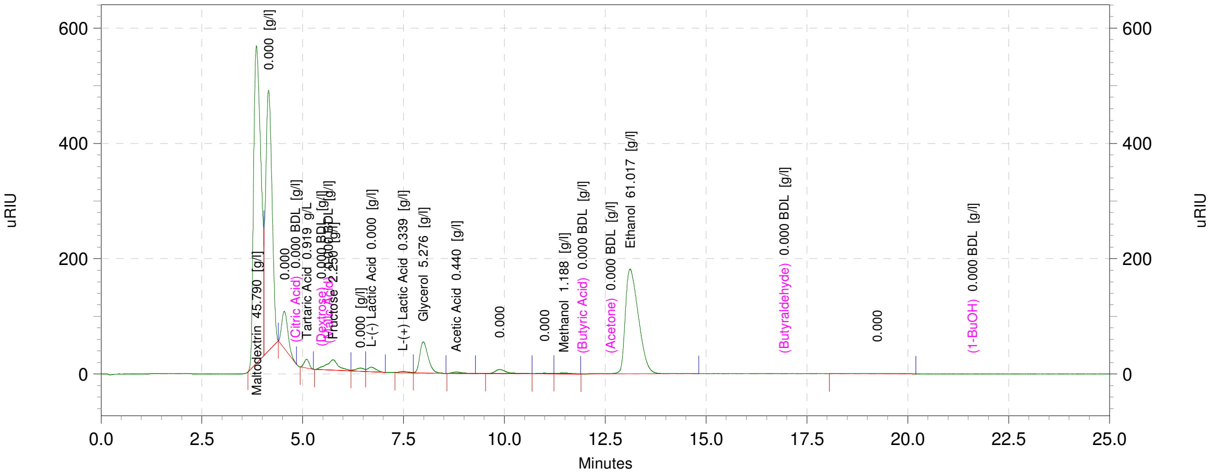


Figure 3.2: HPLC printout of an average control fermentation on day 3.

The control fermentations achieved 63.2 ± 3.0 g/L ethanol. Lab grade butyric acid was added to these fermented mashes and they were stripped as they would be in industry. These distillations are discussed in Section 4.1

3.2 Secondary Fermentation

The goal of fermenting with multiple organisms is to manipulate the contents of the fermented mash without the addition of artificial additives in the product.

CHAPTER 4

DISTILLATION

Distillation is the engineering process that separates chemical components based on their boiling points. This is the main process that defines a spirit in the fermented beverage industry. After fermentation, the mash is distilled in a timely fashion to form a stable intermediate product. This distillate is called low wines and is anywhere from 20-40 % ABV. [12]. Low wines will last for years in an appropriately sealed container, such an intermediate bulk container (IBC) or larger if necessary.

The first distillation is called a stripping run while the the second distillation is typically called the finishing run. The finishing run usually yields the final product used as a beverage, although the product may be distilled as many times as necessary to achieve the desired quality. The higher the number of distillations of a spirit, the less flavor the overall product will have. The number of finishing runs depends on the desired product and the distiller's discretion.

4.1 Lab Distillations

4.1.1 Stripping

When the glucose on the fermentations were BDL, butyric acid was added to simulate the production by *C. tyrobutyricum*. These fermented mashes were distilled on the glassware setup in Section 1.4.2 as a stripping distillation with no catalyst. Samples were collected throughout the run and analyzed on a HPLC for ethanol and butyric acid concentrations. The low wines consisted of 357.7 ± 32.0 g/L ethanol (45.3 ± 4.0 % ABV) with 1.40 ± 0.10 g/L butyric acid. Figure 4.1 is an average HPLC printout of low wines from a stripping run.

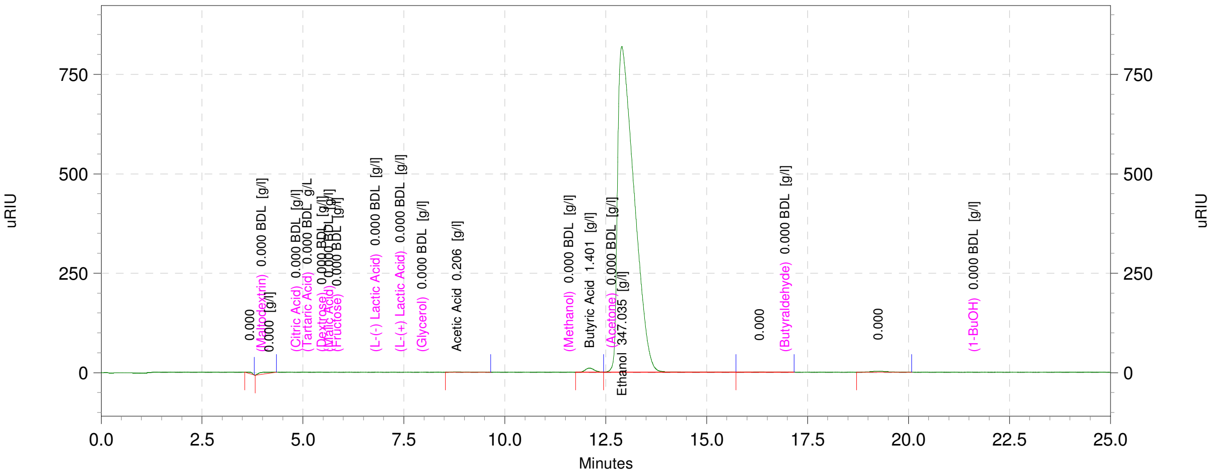


Figure 4.1: HPLC printout of an average control stripping distillation showing the presence of ethanol, acetic acid, and butyric acid in the low wines.

The butyric acid was seen in the distillate only when the ethanol concentration started to fall, as shown in Figure 4.2[†]. This relationship between the ethanol and butyric acid was seen in all distillations throughout this study.

Acetic acid is another volatile organic acid that shows up in the stripping run and will interfere with the aroma and flavor of the final product as it will produce ethyl acetate over the catalyst.

The low wines were collected and mixed together to form a larger quantity, as is common practice in the distilled beverage industry. The collective was then diluted with de-ionized water so that the ethanol was 30% by volume. The percent ABV during dilution was confirmed on an Anton Paar DMA 5000 M density meter.

4.1.2 Finishing

The low wines at 30% ABV were distilled a second time on the same glassware setup as the stripping runs (Figure 1.5). Figure 4.2 shows the finishing run distillate as a function of the volume collected. The pot started with 150 mL of the low wines and no catalyst in the system.

[†] Samples taken during the control stripping runs are not shown.

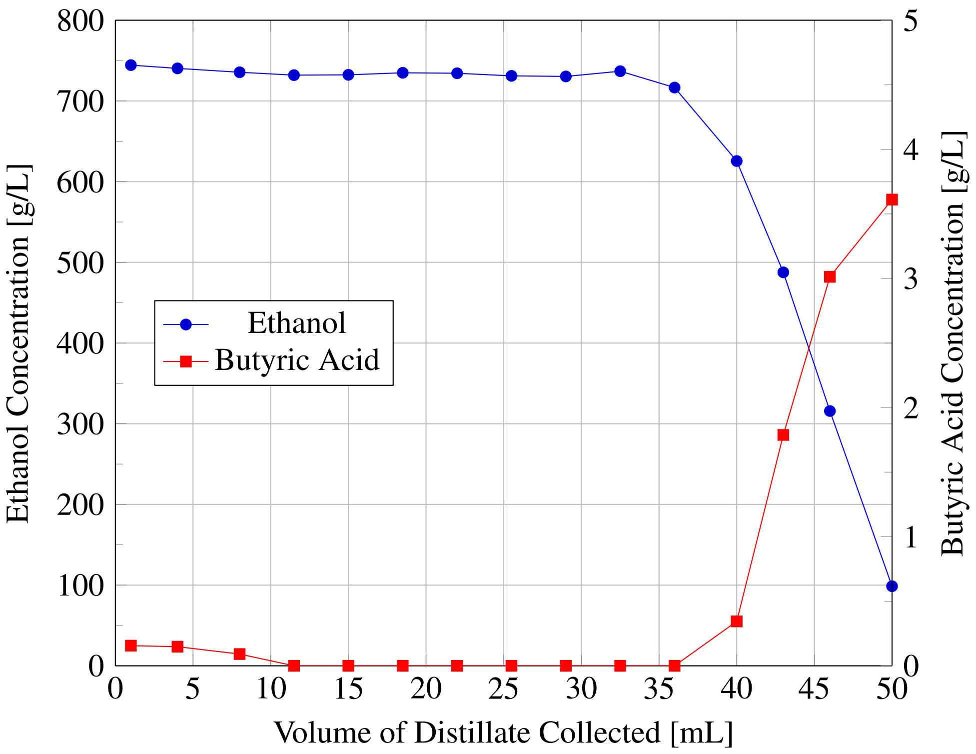


Figure 4.2: Ethanol and butyric acid as a function of volume of distillate collected for the second distillation of the control without adding catalyst to the system.

4.2 Reactive Distillation

After the low wines are distilled, the ethyl butyrate needs to be created over a catalyst. Amberlyst® 15 has been chosen for this system as it is an industry standard for esterification.

This reaction system is different than ethyl butyrate production because pure ethyl butyrate is not the end goal. This system starts with a very high ratio of ethanol to butyric acid, so it does not behave the same way as an even molar ratio.

4.2.1 Minitab

Minitab® is a statistical software used for evaluating and presenting data. It can be used for developing a design of experiment (DOE) which determines how certain variables impact a system.

4.2.1.1 Design of Experiment

A three factor Box-Behnken DOE was made using Minitab®. The independent variables were chosen as: catalyst loading, catalyst position, and starting amount of butyric acid in the pot. The starting ethanol will be constant at 30% ABV (237 g/L). Table 4.1 shows the variables used in the DOE. The position of -1, 0, and +1 represents the low value, midpoint, and high value of each variable, respectively. The units of the staring butyric acid is grams per liter and the units of the catalyst loading is grams of dry catalyst per liter of starting pot volume.

Table 4.1: Variables used for the experiments and their range.

Variable	Low (-1)	MId (0)	HIgh (+1)
Starting Butyric Acid	0.5	1.0	5.0
Catalyst Loading	1.0	50.0	100.0
Catalyst Position	In Pot	Bottom of Column	Top of Column

Table 4.2 shows the experiment order and design from Minitab. The design includes three replicates at the (0,0,0) position. The standard (std) order is different than the run order as to give more randomness so the equipment would be less likely to develop a trend.

Table 4.2: Minitab DOE for Box-Behnken

Std Order	Run Order	Butyric Acid	Catalyst Loading	Catalyst Position
11	1	0	-1	1
2	2	1	-1	0
4	3	1	1	0
13	4	0	0	0
1	5	-1	-1	0
5	6	-1	0	-1
3	7	-1	1	0
10	8	0	1	-1
8	9	1	0	1
15	10	0	0	0
6	11	1	0	-1
12	12	0	1	1
14	13	0	0	0
7	14	-1	0	1
9	15	0	-1	-1

4.3 Starting Materials

4.3.1 Low Wine

The low wine used for these Minitab experiments were obtained from Working Bugs LLC in East Lansing, Michigan. This spirit has been stripped from a 100% corn mash distilled on a 17 tray continuous column. The bulk of the tank from which this low wine was taken was destined to be distilled again into a bourbon that will eventually be put into distribution making this starting material as close as possible to what would be seen in industry. The low wine was measured as 30.45% ABV on an Anton Paar DMA 5000 M density meter.

4.3.2 Butyric Acid

The butyric acid was added from Agros Organics 99+% stock up to the amount specified for each experiment. This will eventually be added during the fermentation by *Clostridium tyrobutyricum* which will distill over into the low wine as described in Section 4.1.1.

4.3.3 Amberlyst® 15 wet

Amberlyst® 15 wet was obtained from MilliporeSigma®. This catalyst has a styrene-divinylbenzene matix with strong acidic sulfonic groups. It is a suitable replacement for the standard liquid sulfuric acid used in esterification. It can be used multiple times and cannot contaminate the distilled spirit with a strong acid.

The catalyst was supported in the pot and column in a mesh pouch. If the catalyst is used in the pot without containment, the system "pops" because there are many smooth beads on the bottom of the pot next to the heating element.

4.3.4 Distillation Apparatus

The setup used the same arrangement of glassware as in Figure 1.5. Between each run, the six copper wires in the vigreux column were rinsed with a 0.1 N solution of sodium hydroxide followed by a 0.1 N solution of citric acid to renew the copper surface and reduce run order variability. This cleaning brought the copper surface back to looking brand new.

The following chapter is a paper written and submitted to *Beverages* (ISSN 2306-5710). It was submitted on April 04, 2018 and is still under review as of this publishing.

The paper is reformatted to fulfill requirements of the dissertation document.

CHAPTER 5

PAPER: PRELIMINARY STUDIES ON THE USE OF REACTIVE DISTILLATION IN THE PRODUCTION OF BEVERAGE SPIRITS

5.1 Abstract

Distilled alcoholic beverages have been produced through fermentation and distillation for centuries but have not purposefully involved a chemical reaction to produce a flavoring. Introducing a microorganism to produce butyric acid along with the typical yeast ethanol fermentation sets up a reactive distillation system to flavor a spirit with ethyl butyrate and butyric acid. The ternary interactions of water, ethanol, and butyric acid allow all three to vaporize in the stripping distillation, thus they are concentrated in the low wines and give a large excess of ethanol compared to butyric acid for better reaction completion. The stripping distillation has also been modeled on Aspen Plus® software and coincides well with a test stripping distillation at the bench scale. Amberlyst® 15 wet catalyst was added to a subsequent distillation, resulting in the production of the desired ethyl butyrate in the distillate, measured by gas chromatography. Primary sensory evaluation has determined that this process has a profound effect on the smell of the spirit with the main flavor being similar to fruity bubble gum. The current results will provide a pathway for creating spirits with a desired flavor on demand without acquiring a heavy capital cost if a beverage distillation column is already purchased.

5.2 Introduction

The basic concept of fermentation and distillation to create an alcoholic beverage has remained largely unchanged since its inception, mainly due to tradition. There have been advancements made as knowledge of the process grows. For instance, it is now known why the use of copper is important in a still, as it has a catalytic effect of removing sulfur compounds during distillation. Studies have determined that the main compound being removed by the copper is dimethyl trisulfide which has a low odor detection threshold (33 parts per trillion in 20% ethanol) [7].

Reactive distillation combines the two unit operations of a chemical reaction and a distillation into one [6]. This technique is useful for reactions that need a special condition that can be achieved through distillation, such as a large excess of one of the reactants, or for removing a product to drive an equilibrium reaction to completion [6].

Combining two processes into one decreases time and energy to produce a desired result. Initial capital cost and maintenance costs are also lowered because the reactor and column is the same piece of equipment. A common use for reactive distillation is esterification. Other than sulfur adsorption onto copper, the alcoholic beverage industry does not purposefully use this technique in the production of spirits.

Introducing esterification into the production of beverages spirits will create a food grade, flavored spirit while adhering to the standards of identity for distilled alcoholic beverages in the United States (27 CFR §5.22). This paper will discuss the materials and unit operations that will be combined to develop this process and create the proposed spirit.

5.2.1 Esters

An ester is formed when an acid and alkoxy group join together though a condensation reaction. It can be any acid and any alkoxy, but is usually an organic acid and an alcohol. As this is a slow reaction without the presence of a catalyst, a classic method is to use the Fischer-Speier esterification with a sulfuric acid catalyst. Figure 5.1 below shows the condensation of butyric acid and ethanol to create ethyl butyrate; this is the reaction that is desired in this beverage research.

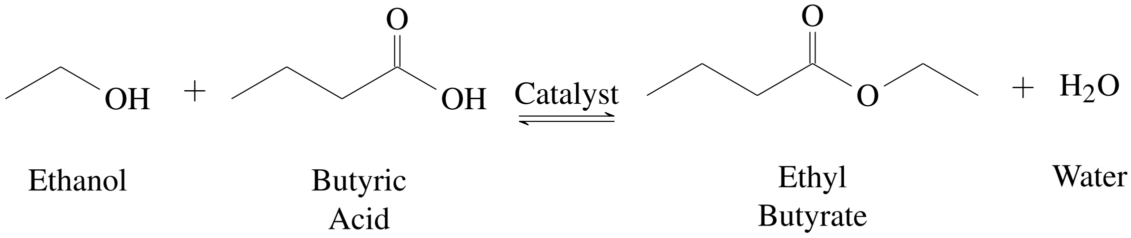


Figure 5.1: The chemical equation for the dehydration reaction of ethanol and butyric acid to form ethyl butyrate and water.

Esters are commonly used in flavorings and fragrances because of their pleasant odor. Ethyl butyrate is commonly used because it has the smell of pineapples or fresh orange juice. [1]

5.3 Modeling

Modeling techniques were used to determine if this study was possible. A ternary residue curve map (RCM) was made with the three main compounds at the corners: water, ethanol, and butyric acid. Aspen Plus® was also used to design a column that shows this system would work for the stripping portion of the beverage distillation process.

5.3.1 Ternary Residue Curve Map

Figure 5.2 shows a ternary RCM of water, ethanol, and butyric acid in weight fraction. Along with the ethanol/water azeotrope, a binary azeotrope is present between water and butyric acid which boils at 99.5 °C. A separatrix (or simple batch distillation boundary) is drawn in green which divides the diagram into two distillation regions. Residue curves are drawn in light blue with arrows indicating increasing temperature in the pot (or time during the distillation).

The concentrations of water, ethanol, and butyric acid in the pot at the beginning of a run determine the starting point on Figure 5.2 [6, 20]. The residue curves show the concentration of the components in the pot as the distillation proceeds. As an example, if the concentrations of water, ethanol, and butyric acid are 75% w/w, 20% w/w, and 5% w/w respectively, the pot concentration will be 100 % w/w water when the distillation is finished with all of the ethanol and butyric acid from the system in the distillate. If the starting point was to the left of the distillation boundary, the pot would eventually consist of pure butyric acid.

The presence of these binary azeotropes in this system makes it possible for the high boiling butyric acid to be carried over in the distillate stream by the water during the first distillation of the spirit. This then sets up the system for the second distillation over a catalyst to produce the desired ethyl butyrate in the finished spirit.

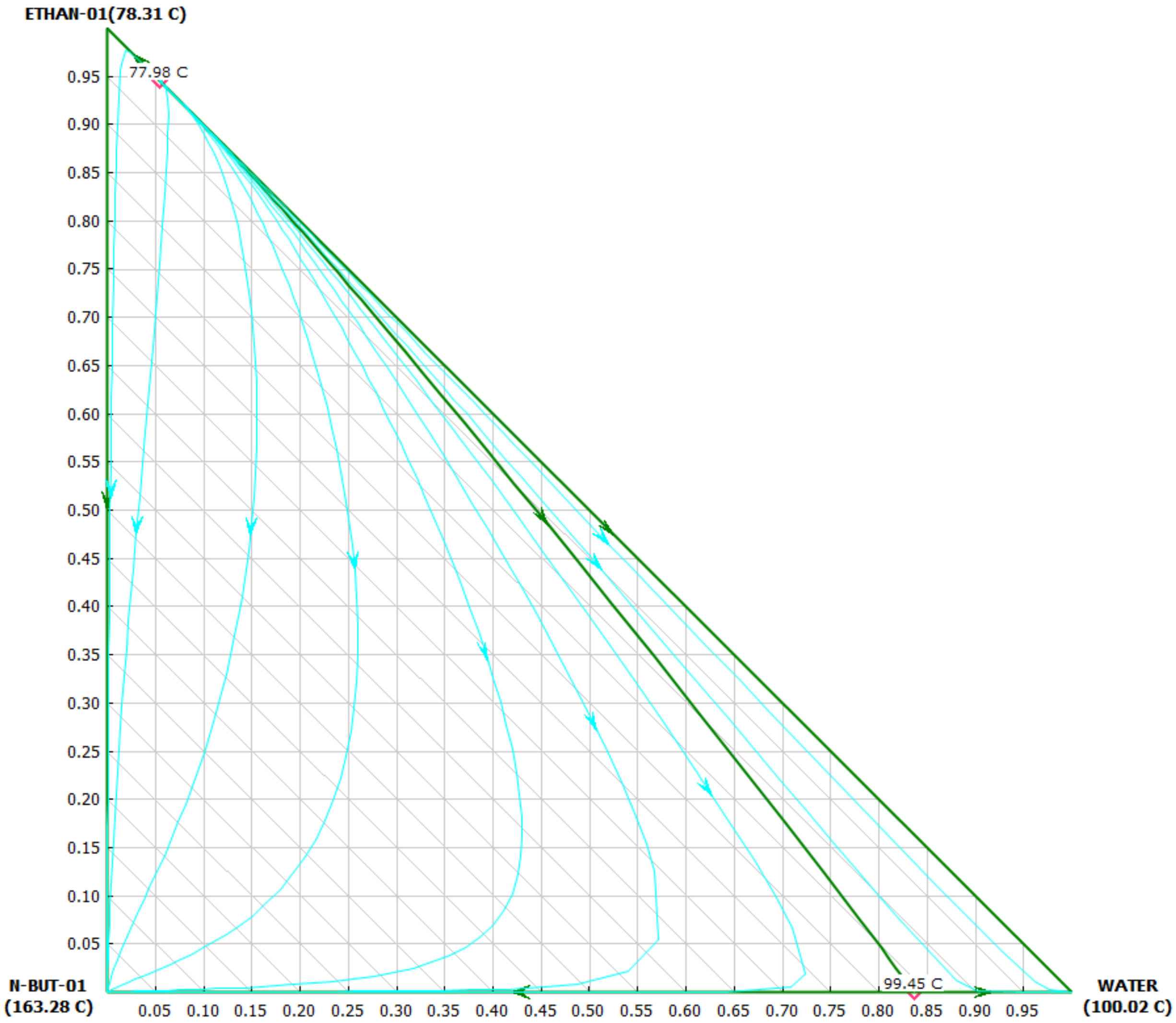
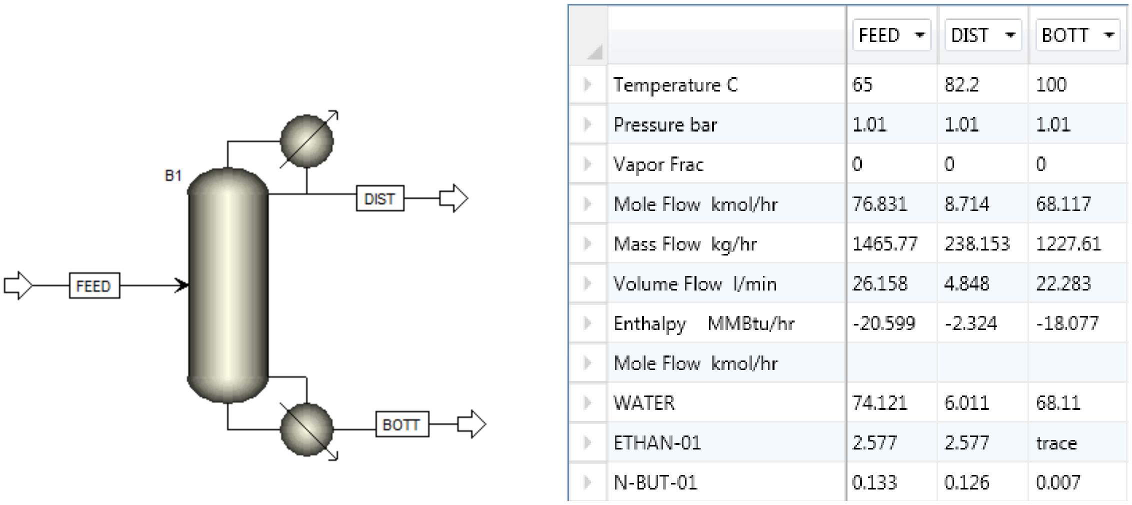


Figure 5.2: A ternary residue curve map of water, ethanol, and butyric acid with separatrix. The separatrix is drawn in green which starts at the ethanol/water azeotrope and ends at the butyric acid/water azeotrope. Residue curves are drawn in light blue. This diagram is measured in weight fraction.

5.3.2 Aspen Plus® column design

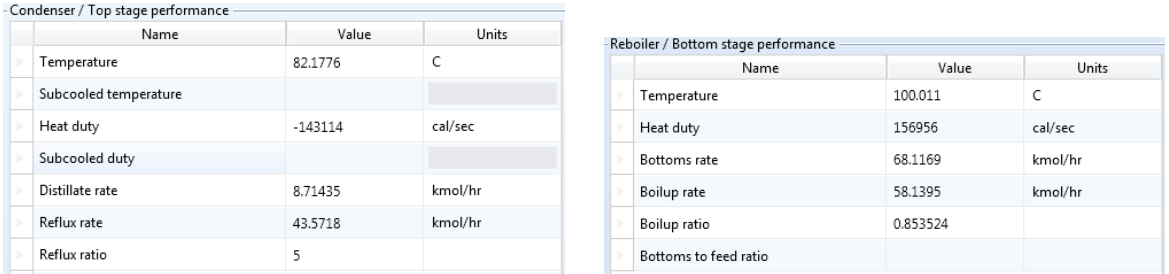
A column was designed in Aspen Plus® to distill a whiskey mash with a requirement to have butyric acid present in the distillate of the column. The column was designed to have 17 bubble cap trays, stage seven as the feed stage, and a reflux ratio of five. The following figures are screenshots from the Aspen Plus® software used for the simulation.



	FEED	DIST	BOTT
Temperature C	65	82.2	100
Pressure bar	1.01	1.01	1.01
Vapor Frac	0	0	0
Mole Flow kmol/hr	76.831	8.714	68.117
Mass Flow kg/hr	1465.77	238.153	1227.61
Volume Flow l/min	26.158	4.848	22.283
Enthalpy MMBtu/hr	-20.599	-2.324	-18.077
Mole Flow kmol/hr			
WATER	74.121	6.011	68.11
ETHAN-01	2.577	2.577	trace
N-BUT-01	0.133	0.126	0.007

(a) Flowsheet (b) Stream Table

Figure 5.3: Aspen Plus$^{®}$ screenshots of the flowsheet and overall stream table



Condenser / Top stage performance

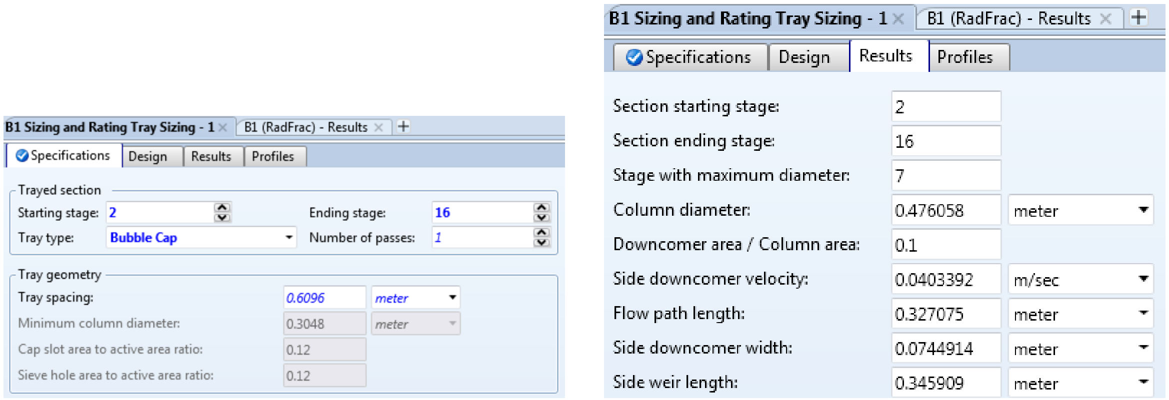
Name	Value	Units
Temperature	82.1776	C
Subcooled temperature		
Heat duty	-143114	cal/sec
Subcooled duty		
Distillate rate	8.71435	kmol/hr
Reflux rate	43.5718	kmol/hr
Reflux ratio	5	

Reboiler / Bottom stage performance

Name	Value	Units
Temperature	100.011	C
Heat duty	156956	cal/sec
Bottoms rate	68.1169	kmol/hr
Boilup rate	58.1395	kmol/hr
Boilup ratio	0.853524	
Bottoms to feed ratio		

(a) Top Stage Performance (b) Bottom Stage Performance

Figure 5.4: Aspen Plus$^{®}$ screenshots of the performance of the top and bottom stages



Trayed section
Starting stage: 2
Ending stage: 16
Tray type: Bubble Cap
Number of passes: 1

Tray geometry
Tray spacing: 0.6096 meter
Minimum column diameter: 0.3048 meter
Cap slot area to active area ratio: 0.12
Sieve hole area to active area ratio: 0.12

Section starting stage: 2
Section ending stage: 16
Stage with maximum diameter: 7
Column diameter: 0.476058 meter
Downcomer area / Column area: 0.1
Side downcomer velocity: 0.0403392 m/sec
Flow path length: 0.327075 meter
Side downcomer width: 0.0744914 meter
Side weir length: 0.345909 meter

(a) Tray Sizing Input (b) Tray Sizing Results

Figure 5.5: Aspen Plus$^{®}$ screenshots for the sizing of the column.

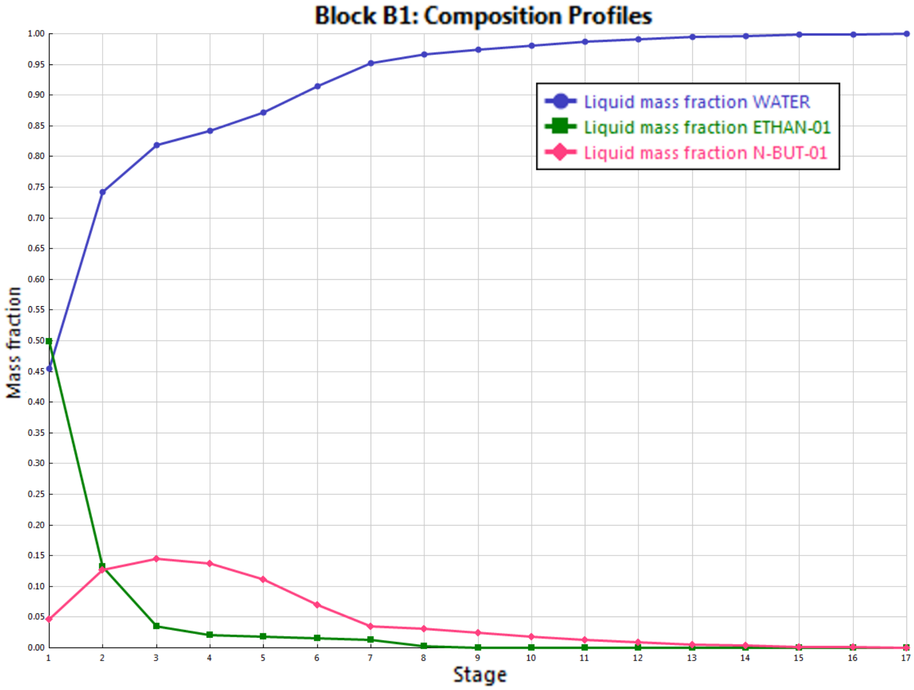


Figure 5.6: A graph of the column tray compositions as produced by Aspen Plus®.

As seen in Figure 2.2b, the distillate stream of the column contains 94.7 mol% of the butyric acid in the system. This simulation shows that the main components will be present in the distillate of the stripping run. The low wines produced from this can then be distilled again using a catalyst to convert the butyric acid into the desired ethyl butyrate.

5.3.3 Lab-scale Fractional Distillation

A lab fractional distillation was preformed in conjunction with the Aspen Plus® simulation to support the results. The experiment used a 500 mL round-bottom flask, Vigreux column, and a straight condenser setup in a fractional distillation configuration. The flask started with 250 mL of an aqueous solution containing 79.2 grams per liter [g/L] ethanol and 4 g/L butyric acid. Figure 5.7 shows the concentrations of ethanol and butyric acid of the experiment as a function of distillate volume collected.

A final distillate of 70 mL was collected containing 230 g/L ethanol and 6.2 g/L butyric acid.

This experiment coincides well with the Aspen Plus® simulation in Section 5.3.2.

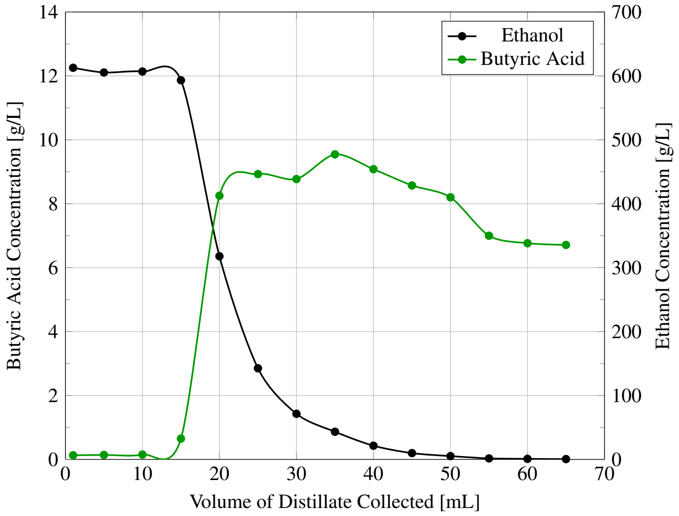


Figure 5.7: Distillate concentrations of ethanol and butyric acid during the lab-scale fractional distillation vs. the volume of distillate collected.

5.4 Materials and Methods

This research was preformed on the bench scale. The mash was stripped 1L at a time in a round-bottom flask. The flask was connected to a 36 cm vigreux column, a 75° distillation adapter, and finally a 20 cm straight Liebig condenser. All connections are ₮24/40. Six strips of 14 AWG copper wire (1.63 mm diameter) were put into the vigreux column to represent the copper in a beverage distillation column.

For each stripping run, the distillate was collected until the ethanol fell below 10% ABV. These low wines were then distilled a second time over Amberlyst® 15 wet catalyst with varying loadings and positions within the column.

5.4.1 Reactive Distillation

Figure 5.8 shows component concentrations in a reactive spirit distillation as a function of distillate volume collected. The distillation consisted of 150 mL of low wine diluted to 30% ABV.

Butyric acid was added to the pot to give a 4.0 g/L starting concentration and 15 g of Amberlyst® 15 wet catalyst was contained in a mesh bag and added to the pot during the distillation; no ethyl butyrate was added prior to the experiment, as seen in Table 5.1.

Table 5.1: Compounds of interest in the reactive distillation system. Concentrations in [g/L].

Sample	Ethanol	Ethyl Butyrate	Butyric Acid
Initial Pot	240.81	0.00	4.02
Final Pot	0.00	0.00	1.64
Total Distillate	349.31	1.29	4.82

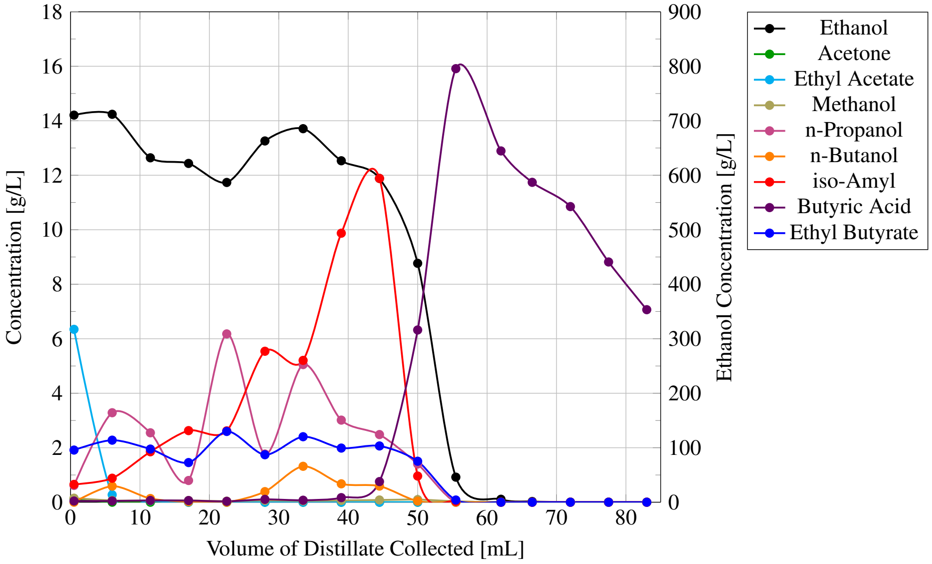


Figure 5.8: Component concentrations in the distillate of a spirit run with 150 mL of low wines at 30% ABV, 4.0 g of butyric acid, and 15 g of Amberlyst® 15 wet catalyst in the pot

As seen in Figure 5.8, the ethanol and ethyl butyrate concentration curves have the same shape and are inverse of the butyric acid concentration curve. During the distillation, butyric acid was reacted with ethanol over the catalyst to form the desired ethyl butyrate. This product was then carried over in the distillate stream by the ethanol.

Note: If creating a spirit, the heads would have been cut after collecting 5 mL, and the tails cut after collecting 40 mL. These cuts would have resulted in the final hearts product being 35 mL in volume and having low ethyl acetate and butyric acid concentrations.

5.4.2 Sensory Evaluation

Four variations of the reactive distillation from Section 5.4.1 were distilled and 35 mL of hearts were collected from each as discussed above. Table 6.2 shows the differences in the four samples. The evaluation sheet asked what the participant could smell in each sample and also if they could tell a difference between samples.

Table 5.2: Difference in the samples used for the sensory evaluation to determine if this process has an effect on the final spirit.

Sample	Butyric Acid [g/L]	Catalyst [g]
1	0	0
2	0	7.5
3	5	0
4	5	7.5

The evaluation showed that samples 1 and 2 were similar with a smell of whiskey and they could be told apart; sample 1 had a stronger whiskey smell than sample 2. Sample 3 had notes of licorice and popcorn, which is expected as there was butyric acid present. Sample 4 was overwhelmingly different than the others having a fruity smell similar to that of banana candy or bubble gum.

5.5 Discussion

For research purposes, food grade butyric acid was added to the fermented mash before the first distillation. Future work will develop a co-fermentation between *Saccharomyces cerevisiae* and *Clostridium tyrobutyricum* to produce ethanol and butyric acid, respectively.

Introduction of ester production in beverage spirit distillations will create a new series of products that have unique smells and tastes. These qualities will give the spirit an increased value and marketability, thus mitigating the reduced ethanol yield from the production of the organic acid in the fermentation.

This research will provide a pathway for creating spirits with a desired flavor on demand without acquiring a heavy capital cost if a beverage distillation column is already purchased. Manufactures would be able to produce a uniquely flavored spirit of their own with only the purchase of the correct catalyst and microorganism.

The code of federal regulations (CFR) has set rules of what can and can not be done when it comes to distilled spirits, specifically 27 CFR §5.

The reaction of ethanol and butyric acid to ethyl butyrate proceeds naturally. The catalyst that is put into the column speeds the reaction rate and drives the reaction more toward the product. i.e. the catalyst is not adding a new reaction, only accelerating an already existing reaction.

CHAPTER 6

RESULTS OF THE REACTIVE DISTILLATION SYSTEM

6.1 Procedure

The setup pictured in Figure 1.5 was assembled and the fifteen runs described in Section 4.2.1.1 were performed. During the distillations, 0.5 mL samples of the distillate were taken every time 5 mL was collected in a graduated cylinder with sample one being the first 0.5 mL of the distillate that came out of the condenser. These samples were analyzed on a GC-17A with FID.

6.2 GC analysis

The samples of the distillate had a large concentration of ethanol which blew out the FID detector as shown in Figure 6.1. The GC analyzed the ethanol peak as 0.000 BDL (Below Detectable Level), which was obviously not correct as there was a large peak with the top cut off. The shape in Figure 6.1 is typical of an undiluted sample of ethanol distillate. The software can be forced to analyze the peak as ethanol, but the area calculated will not be accurate.

These samples had to be diluted and run again to obtain the ethanol content. A solution of 20 µL of the sample with 600 µL of Milli-Q® water was used to create a 31x dilution factor.

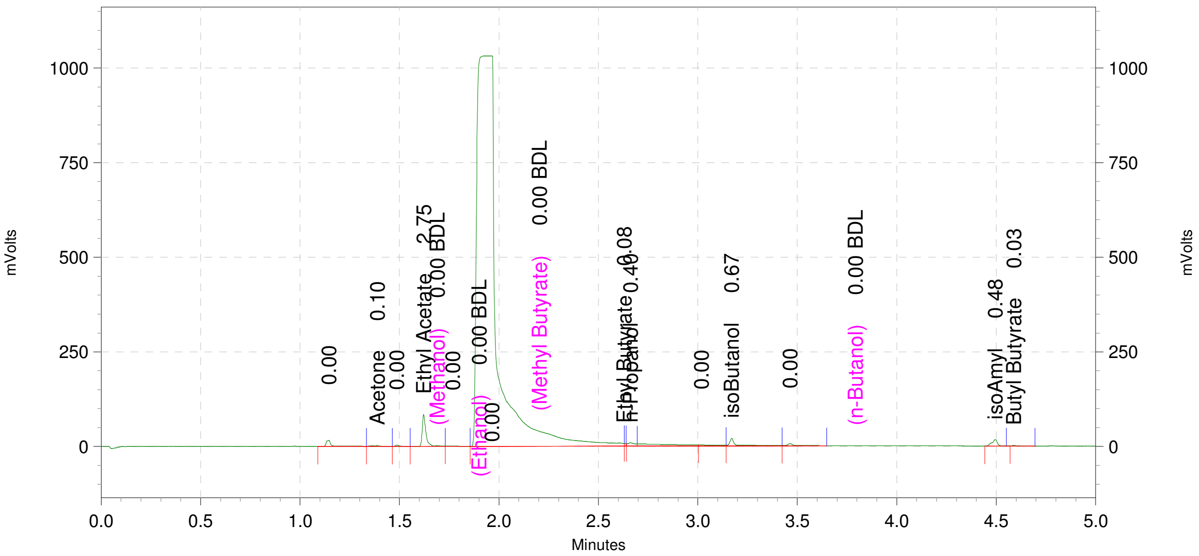


Figure 6.1: GC printout of a distillate sample showing the ethanol peak having a value of 0.000 BDL despite having a large peak with the top cut off.

6.3 Individual Reactive Distillation Example

Figure 6.2 shows component concentrations in a reactive spirit distillation as a function of distillate volume collected. The distillation consisted of 150 mL of low wine diluted to 30% ABV. Butyric acid was added to the pot to give a 4.0 g/L starting concentration and 15 g of Amberlyst® 15 wet catalyst was contained in a mesh bag and added to the pot during the distillation; no ethyl butyrate was added prior to the experiment, as seen in Table 6.1.

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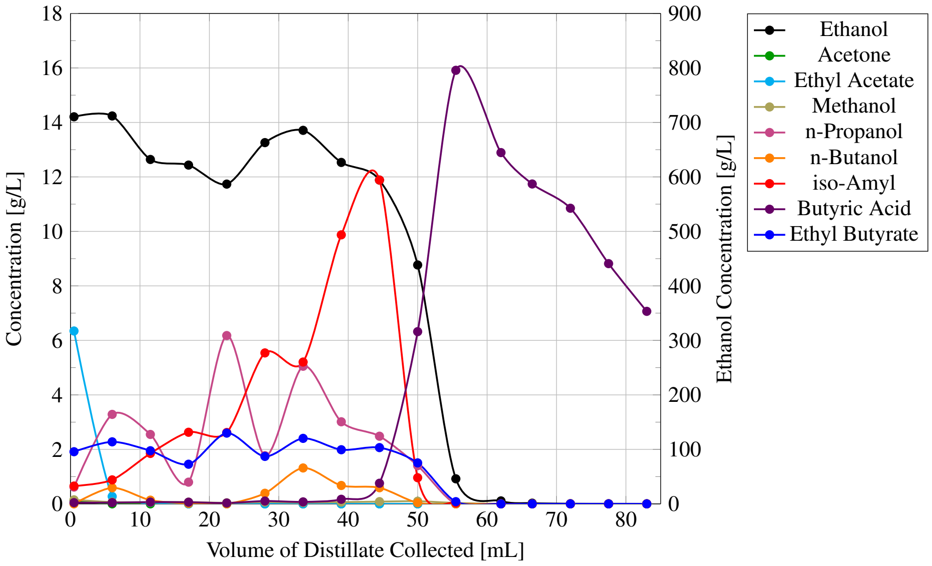


Figure 6.2: Component concentrations in the distillate of a spirit run with 150 mL of low wines at 30% ABV, 4.0 g of butyric acid, and 15 g of Amberlyst® 15 wet catalyst in the pot

As seen in Figure 6.2, the ethanol and ethyl butyrate concentration curves have the same shape and are inverse of the butyric acid concentration curve. During the distillation, butyric acid was reacted with ethanol over the catalyst to form the desired ethyl butyrate. This product was then carried over in the distillate stream by the ethanol.

Note: If creating a spirit, the heads would have been cut after collecting 5 mL, and the tails cut after collecting 40 mL. These cuts would have resulted in the final hearts product being 35 mL in volume and having low ethyl acetate and butyric acid concentrations.

6.4 Individual Component Concentrations in the Distillate

The x-axis (Volume of Distillate Collected) was calculated as 5.5 mL between every sample to take into account the entire distilled volume, 5 mL of distillate in the graduated cylinder + 0.5 mL in the sample vial. The data at 0.5 mL of distillate collected is the first 0.5 mL that came out of the distillation condenser.

6.4.1 Ethanol

The ethanol content of the distillate held a constant value for about 40 mL of the distillate, then decreases sharply as it is depleted in the system. The average ethanol distillate concentration data of all 15 distillations are shown in Figure 6.3. The large error in the data is contributed to error in the dilution of the samples to obtain the ethanol content as discussed in Section 6.2.

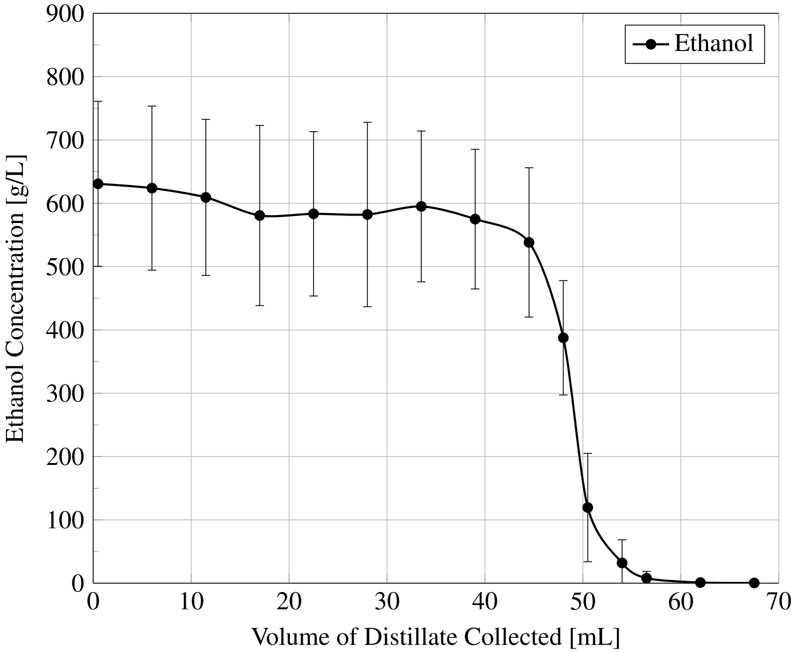


Figure 6.3: Component concentrations of ethanol in the distillate of the runs vs volume distilled. The starting butyric acid concentration, catalyst position, and catalyst loading vary between the data used to create the averages values.

6.4.2 Butyric Acid

As seen in Figure 6.4, increasing the starting pot concentration of butyric acid causes the butyric acid distillate concentration to increase. These butyric acid distillate concentration curves follow an inverted curve of the ethanol distillate concentration, which is associated with the water distillate concentration; this relationship is shown in Figure 6.5 where the ethanol distillate concentration is plotted on the right y axis as a function of distillate volume collected.

These data show that butyric acid in the distillate stream is largely affected by the ABV of the distillate, or the lack thereof.

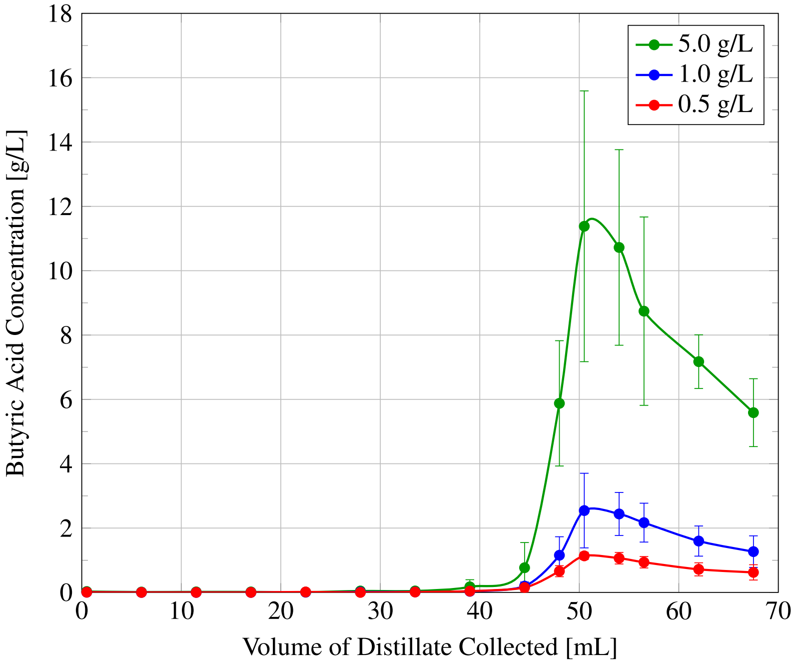


Figure 6.4: Component concentrations of butyric acid in the distillate of the runs vs volume distilled. Each curve represents a different starting concentration of butyric acid in the pot. The catalyst position and loading vary between these data.

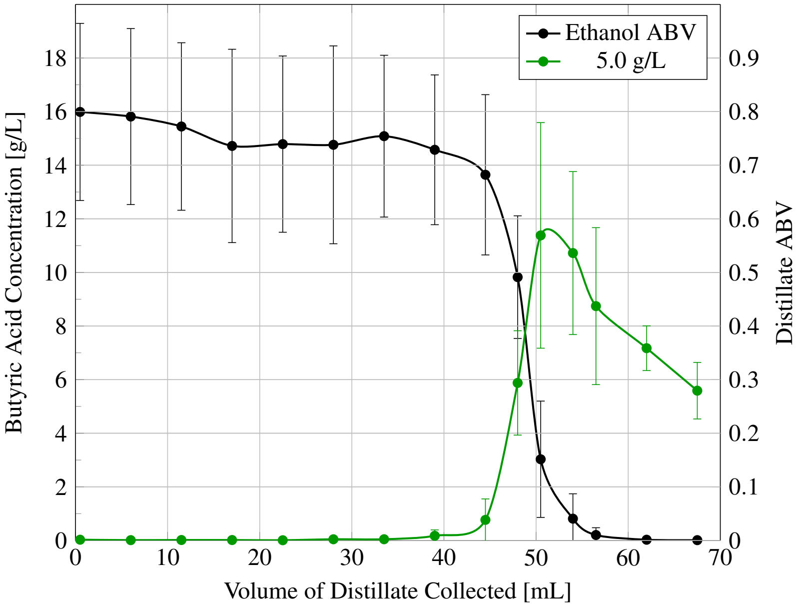


Figure 6.5: Component concentrations of butyric acid in the distillate of the runs compared to the ABV in the distillate. The catalyst position and loading vary between these data.

6.4.3 Ethyl Butyrate

The most important compound of interest is the ethyl butyrate. The initial amount of butyric acid in the pot, the catalyst loading, and the catalyst location in system all affect how much ethyl butyrate is produced and when the compound is present in the distillate. Figure 6.6 shows the ethyl butyrate concentration in the distillate as a function of spirit distilled with catalyst in the pot. Error bars are not present in Figures 6.6 - 6.8 as each curve represents a single distillation.

For this reaction, the forward reaction rate is a function of the product of catalyst weight and reactant concentration. This product of variables is seen in the legend of the following three figures related to ethyl butyrate in the distillate. As this value increases, so does the ethyl butyrate concentration between runs of similar catalyst location.

Comparing Figures 6.6 - 6.8, suggests that ethyl butyrate production is delayed based on how far up the column the catalyst is located. If there is catalyst in the pot, the ethyl butyrate production is not delayed and is present in the distillate throughout the run. If the catalyst is in the bottom of the column, the ethyl butyrate concentration in the distillate is low at first, then increases part way though the run. If the catalyst is at the top of the column, the ethyl butyrate does not come out until the ethanol starts to decrease. Regardless of when ethyl butyrate is present in the distillate, it decreases with the ethanol concentration at the end.

This pattern suggests that the esterification only occurs where the water concentration is rising over time. As the distillation proceeds, a high temperature front moves up the column as the ethanol is depleted. This increase in temperature is correlated with the increased water content in the column which is carrying the butyric acid with it due to their interaction of forming a minimum boiling azeotrope.

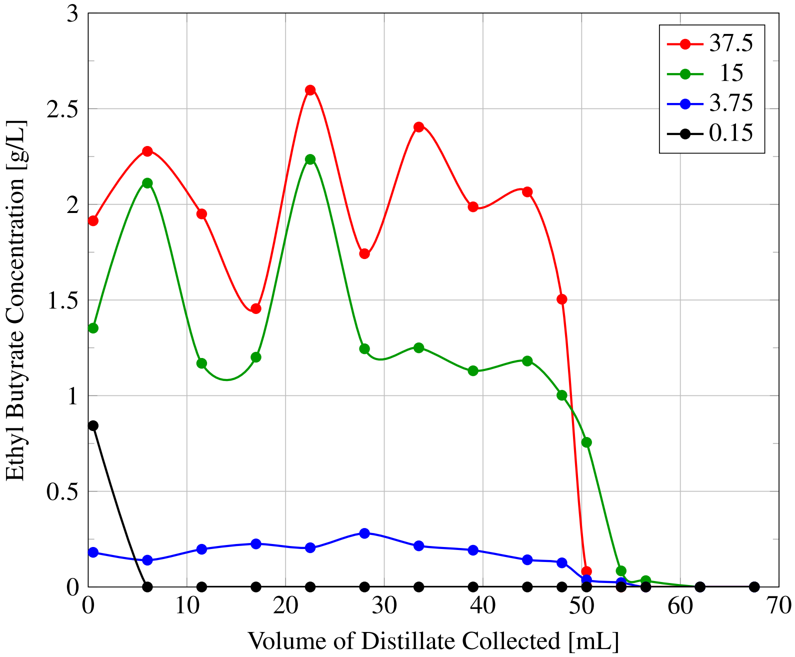


Figure 6.6: Ethyl butyrate in the distillate as a function of volume distilled with catalyst in the pot. Each curve is labeled as the product of the starting concentration of butyric acid in g/L and catalyst loading in grams.

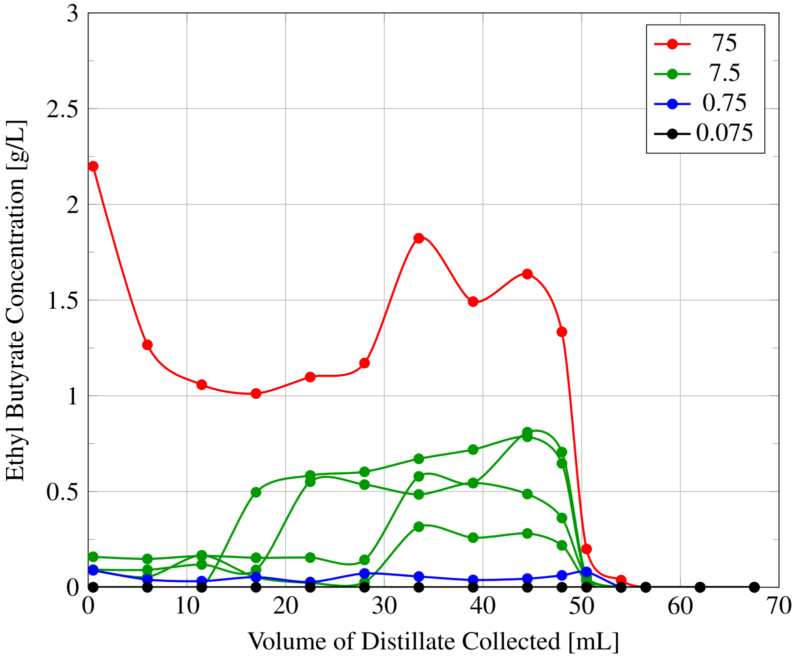


Figure 6.7: Ethyl butyrate in the distillate as a function of volume distilled with catalyst in the bottom of the column. Each curve is labeled as the product of the starting concentration of butyric acid in g/L and catalyst loading in grams.

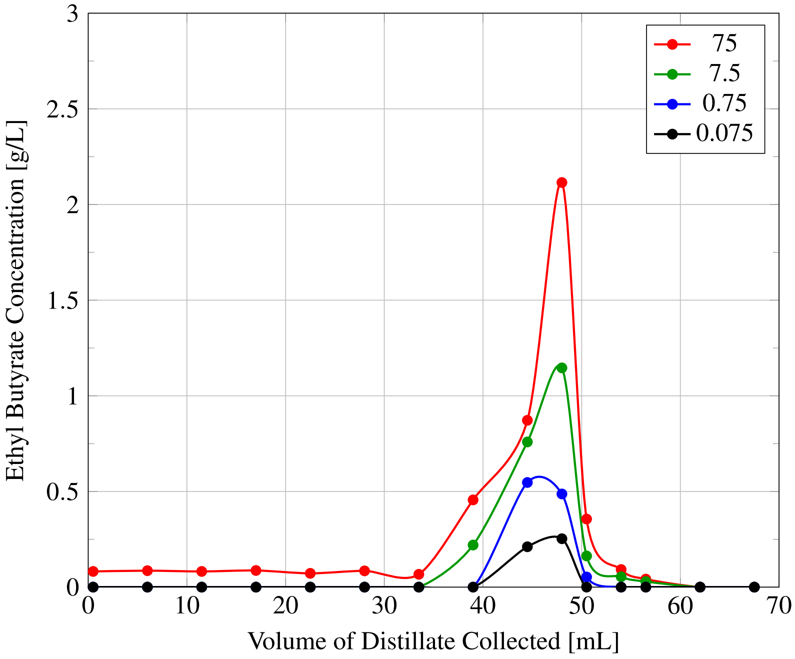


Figure 6.8: Ethyl butyrate in the distillate as a function of volume distilled with catalyst in the top of the column. Each curve is labeled as the product of the starting concentration of butyric acid in g/L and catalyst loading in grams.

6.4.4 Other Compounds

Other compounds measured in the distillate as a function of volume collected include: acetone, methanol, n-propanol, n-butanol, isobutanol, isoamyl alcohol, ethyl acetate, and butyl butyrate. These are plotted in Figure 6.9. The ethyl acetate curve is relatively large in the first sample then falls to zero. The same curve shape is seen for acetone, only on a smaller scale. This is consistent with the pattern seen in industrial beverage distillation as these compounds are removed in the heads fraction.

All of the compounds in the distillation follow the shape of the ethanol curve at the end of the distillation by falling to zero after 50 mL was collected.

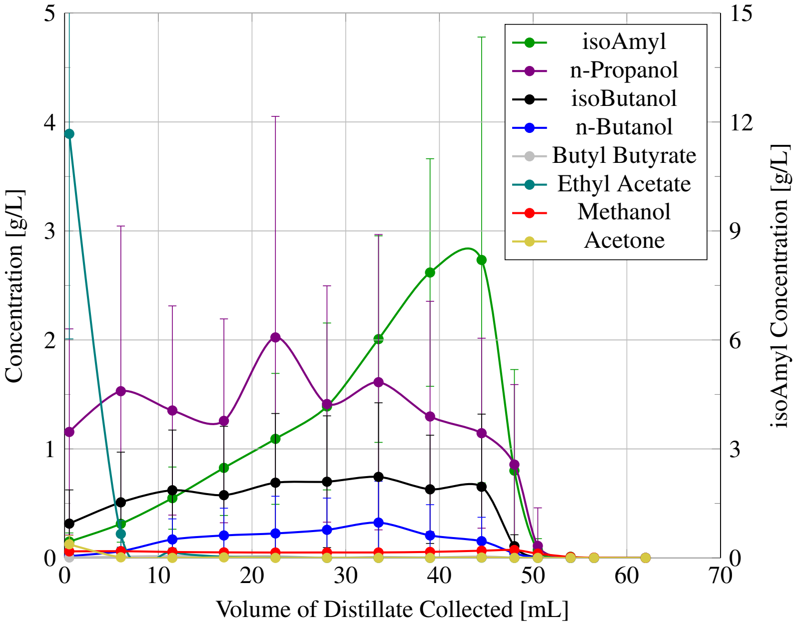


Figure 6.9: Other compounds found in the distillation as a function of volume distilled. The isoAmyl data is plotted on the right axis as it overpowers the others. The curves of butyl butyrate, ethyl acetate, and acetone are on top of each other; most of their values are less than 0.01 g/L.

6.5 Sensory Evaluation

Four variations of the reactive distillation from Section 6.3 were distilled and 35 mL of hearts were collected from each as discussed above. Table 6.2 shows the differences in the four samples. The evaluation sheet asked what the participant could smell in each sample and also if they could tell a difference between samples.

Table 6.2: Difference in the samples used for the sensory evaluation to determine if this process has an effect on the final spirit.

Sample	Butyric Acid [g/L]	Catalyst [g]
1	0	0
2	0	7.5
3	5	0
4	5	7.5

The evaluation showed that samples 1 and 2 were similar with a smell of whiskey and they could be told apart; sample 1 had a stronger whiskey smell than sample 2. Sample 3 had notes of licorice and popcorn, which is expected as there was butyric acid present. Sample 4 was overwhelmingly different than the others having a fruity smell similar to that of banana candy or bubble gum. Results are summarized in Tables 6.3 and 6.4.

Table 6.3: Sample notes from individual sensory evaluations.

Participant	Sample 1	Sample 2	Sample 3	Sample 4
1	whiskey	softer than 1	N/A	juicy fruit gum
2	corn	corn	cheese	licorice/fruity
3	alcohol	alcohol	same as 2	apples
4	corn	corn	corn	bubble gum
5	corn whiskey	corn whiskey	buttered popcorn	buttered popcorn
6	Popsicle stick	less strong, but same as 1	olay bar soap	minty
7	whiskey	bubble yum	soap	sour candy, apple
8	plastic, organic, sweet	less sweet	N/A	popcorn

Table 6.4: Could the participant tell the difference between samples of the sensory evaluation.

Participant	Sample					
	1v2	1v3	2v3	1v4	2v4	3v4
1	yes	no	yes	yes	yes	yes
2	no	yes	yes	yes	yes	yes
3	yes	yes	no	yes	yes	yes
4	yes	yes	yes	yes	yes	yes
5	no	yes	yes	yes	yes	yes
6	yes	yes	yes	yes	yes	yes
7	yes	yes	yes	yes	yes	yes
8	yes	no	yes	yes	yes	yes

CHAPTER 7

DISCUSSION

7.1 Overview

This research studied the production of a beverage spirit with a fruity flavor through the production of ethyl butyrate during the distillation. This process coupled the industrially standard batch distillation for beverage spirits and a chemical reaction. The goal of this research was not to create a pure product, but to add a sensory character to a spirit without adding an artificial chemical after the final distillation.

Ethanol was produced during the fermentation by *Saccharomyces cerevisiae*. The butyric acid in this study was added from lab grade stock. The possibility of butyric acid production during the fermentation has been shown by using *Clostridium tyrobutyricum* [9]. The multiple fermenting organisms can produce the desired reactants without having to add anything other than what is already used commercially.

The ethanol mash was shown to distill with the butyric acid being carried over in the distillate by the water in the system. In the stripping run (with no catalyst) the butyric acid did not come out until the end of the run. This was expected because water and butyric acid form a minimum boiling azeotrope. The phenomena of butyric acid distilling after ethanol has been depleted was seen in all distillation performed.

Amberlyst$^{®}$ 15 wet was used as the catalyst due to its common use in industry for esterification. The position of the catalyst in the column and the catalyst loading were studied. Both of these parameters have a large effect on the production of ethyl butyrate during the finishing distillation. The further up the column the catalyst was located, the later ethyl butyrate was present in the distillate. Also, an increase in the catalyst loading produced more ethyl butyrate in the distillate overall. An increase in the butyric acid starting concentration also led to an increase in ethyl butyrate production.

7.2 Ethanol - Water - Ethyl Butyrate System

After the reaction of ethanol and butyric acid over the catalyst, ethyl butyrate is present with the excess ethanol and water in the system. These three components have unique properties that help this process produce the flavored spirit.

7.2.1 Azeotropes

In the ternary system of ethanol, water, and ethyl butyrate there are three azeotropes present. These are shown in Table 7.1. The pure boiling point of ethyl butyrate is 121.4 °C.

Table 7.1: Azeotropes found in the ternary system of water, ethanol, and ethyl butyrate. Values are in mass percent. These data was obtained from Aspen Properties using the NRTL physical property model.

Temperature [C]	Ethanol	Water	Ethyl Butyrate
78.2	95.6	4.4	0.0
78.2	89.6	5.6	4.7
80.3	0.0	20.8	79.2

Along with the binary azeotrope of ethanol and water, there are two other azeotropes that involve ethyl butyrate. There is a binary azeotrope between water and ethyl butyrate at 80.3 °C with 20.8 % m/m water and 79.2% m/m ethyl butyrate. There is also a ternary azeotrope between all three components that boils at the same temperature as the ethanol and water binary azeotrope. This ternary interaction allows the high boiling ethyl butyrate to be present in the distillate with the beverage distillation temperatures.

7.2.2 Ternary RCM

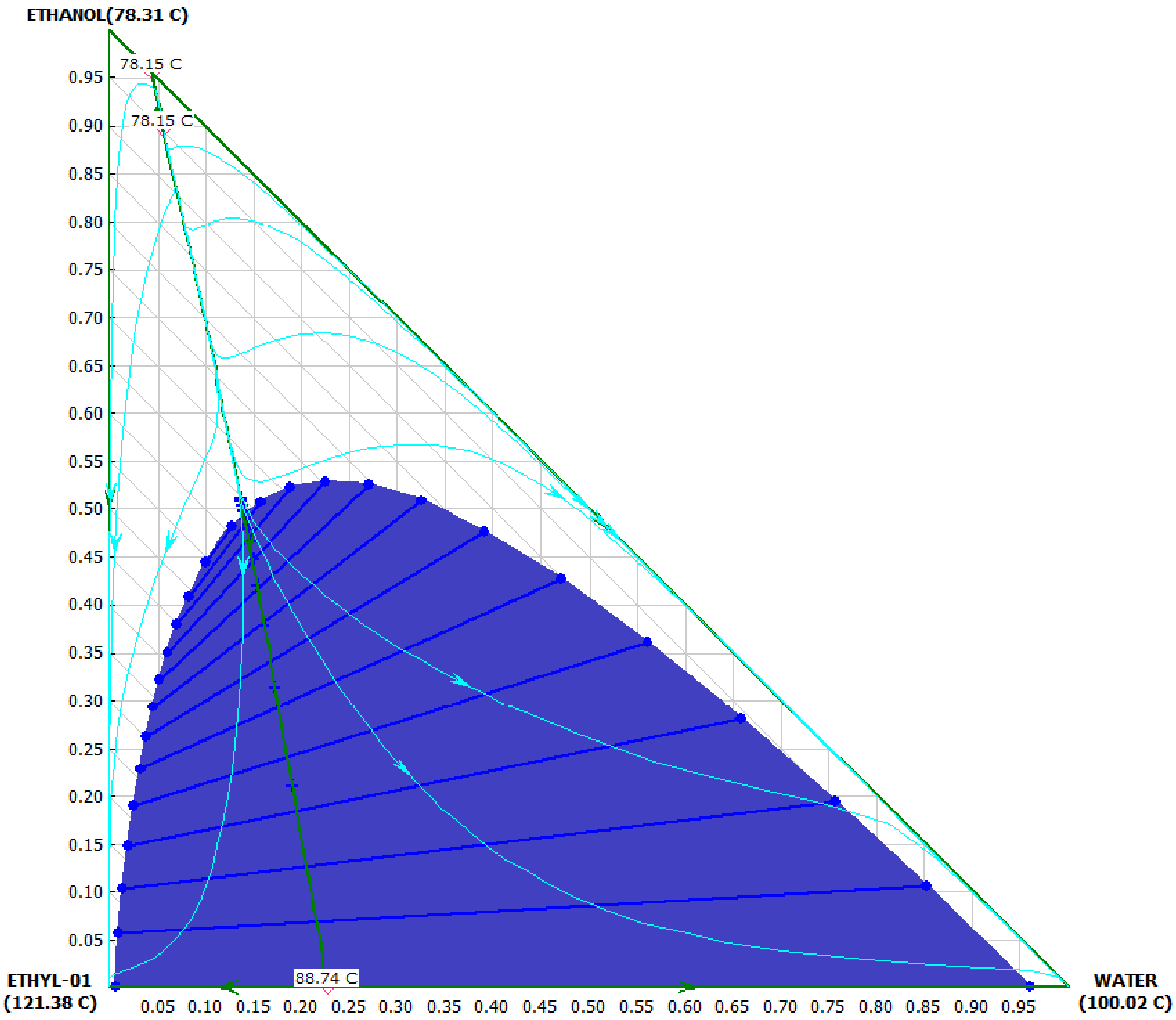


Figure 7.1: A ternary residue curve map of water, ethanol, and ethyl butyrate with separatrix and phase separation envelope. The separatrix is drawn in green which starts at the ethanol/water azeotrope, through the ternary azeotrope and ends at the water/ethyl butyrate azeotrope. Residue curves are drawn in light blue. This diagram is measured in weight fraction.

Figure 7.1 shows a residue curve map of this ternary system. The three azeotropes are labeled, the residue curves are in light blue, the distillation boundary is in green. There is a phase separation between water and ethyl butyrate; That is shown in dark blue with tie lines included. In this distillation system, there is very little ethyl butyrate compared to ethanol and water, so the phase envelope is not entered.

7.3 System Kinetics

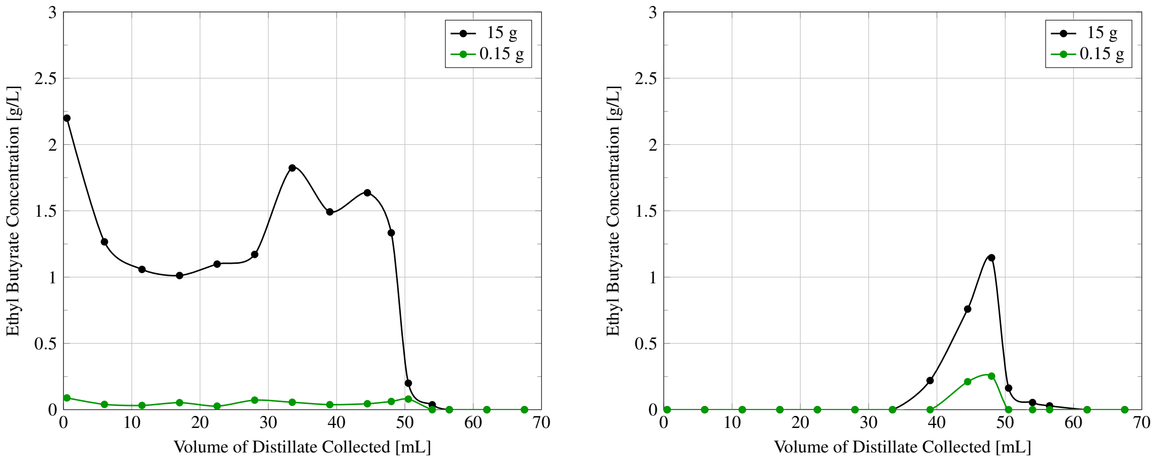
The reaction of ethanol and butyric acid over Amberlyst® 15 is dependent on many factors including molar ratio, catalyst loading, and reaction temperature. These factors in this system have been studied in a batch reactor by Singh et. al. [19]. In a system where the catalyst is in a different phase than the reactants (a solid catalyst in liquid reactants), absorption kinetics have to be taken into account. An Eley-Rideal model states that an adsorbed molecule of ethanol reacts with a molecule of the acid in the bulk liquid. With such a large excess of ethanol, an Eley-Rideal model can be used to describe the reaction kinetics and a pseudo-homogeneous model of the system can be assumed [2, 19].

The system presented in this research had an ethanol to butyric acid molar ratio of 90:1 with the high concentration of butyric acid and 900:1 with the low concentration. This was the ratio present in the initial pot; this value increased in the column as the distillation proceeded until the ethanol in the system was depleted. At the end of the run, the molar ratio was dominated by butyric acid; although the tails of the distillate would have been cut long before this would occur.

During the distillation, the bottom of the column was a higher temperature than the top, thus there was more water and more butyric acid. As ethanol was depleted, the higher temperature water front rises past the catalyst and ultimately to the top of the column where it came out as distillate, bringing with it the butyric acid. When this front reached the catalyst, the butyric acid reacted with ethanol to create the ethyl butyrate, which was carried up in the vapor phase by the ethanol and was present in the distillate. This unsteady-state system explains why ethyl butyrate presence in the distillate is largely controlled by the location of the catalyst, and why butyric acid was present only after ethanol was depleted.

7.3.1 Catalyst Loading

As catalyst increases in the system without increasing butyric acid concentration or the position of the catalyst, the ethyl butyrate production increases as seen in Figure 7.2. The catalyst loading is directly related to the forward reaction rate of the esterification. If the esterification were in equilibrium, the production of ethyl butyrate and forward reaction rate would not be affected by the catalyst concentration. Thus, this system does not reach chemical equilibrium.



(a) (b)

Figure 7.2: These data show increasing ethyl butyrate production with only increasing the catalyst loading in the system while keeping the other variables constant. (a) has the catalyst in the bottom of the column with 5.0 g/L starting butyric acid. (b) has the catalyst in the top of the column with 1.0 g/L starting burytic acid.

7.3.2 Reaction Temperature

Regarding Figures 6.6 - 6.8, there is a slight positive slope on the curves as the distillation proceeds. This is related to the increasing temperature of the distillation system. As the reaction temperature increases, the forward reaction rate increases, creating more ethyl butyrate over the course of the run.

7.3.3 Reflux Ratio Calculation

The glassware setup shown in Figure 1.5 does not have a controllable reflux ratio. The liquid flow down the column is a result of heat loss to the environment around the glass column. Using the energy output of the heating mantle, the vaporization rate of the pot can be calculated along with the reflux ratio. The pot vaporization rate can be calculated by:

$$\dot{m}_v = \frac{q}{\Delta H_{vap}^{pot}} \tag{7.1}$$

Where $\dot{m}_v$ is the vaporization rate out of the pot, q is the heat input from the mantle, and ΔH_{vap}^{pot} is the heat of vaporization of the liquid in the pot.

The heating mantle used had a power output of 400 watts and was used with a heating controller set to a value of 9 out of 10. At the beginning of a run with the ethanol at 25% m/m, $\dot{m}_v^0$ was calculated as 11.4 g/min. When the ethanol is depleted and only water remains, $\dot{m}_v^f$ was calculated as 9.6 g/min. (Superscript 0 (zero) is used to describe a variable at the beginning of the run, a superscript f is used to describe a variable at the end of the run.)

The difference between the pot vaporization rate and the distillate rate is the mass flow rate of the liquid flowing down the column given by:

$$\dot{m}_l = \dot{m}_v - \dot{m}_d \tag{7.2}$$

The distillate flow rate decreased during the run: $\dot{m}_d^0 = 1.1$ and $\dot{m}_d^f = 0.9$.

The reflux ratio can be calculated as:

$$R = \frac{\dot{m}_l}{\dot{m}_d} \tag{7.3}$$

R^0 was calculated as 9.37 and R^f was calculated as 9.44. Thus, the reflux ratio is consistent throughout the run. This high of a reflux ratio explains the large separation of the components in the experimental runs.

7.4 AspenTech® Batch Distillation Model

The system presented above was modeled on the AspenTech® Batch Modeler V10 program. The program simulated a batch distillation column with 10 stages and the reflux ratio of 9.4 calculated in Section 7.3.3. The starting compositions in the simulated pot were initially the same as the experimental distillations. The simulation started at total reflux. The Wilson/Hayden-O'Connell equation of state was used. Wilson-HOC uses an activity coefficient-based property method for calculating relative volatilities. Figure 7.3 shows the simulated distillation of the components in the distillate over time. The left x-axis is in weight fraction of everything except ethanol and water. The right x-axis is weight fraction of ethanol and water.

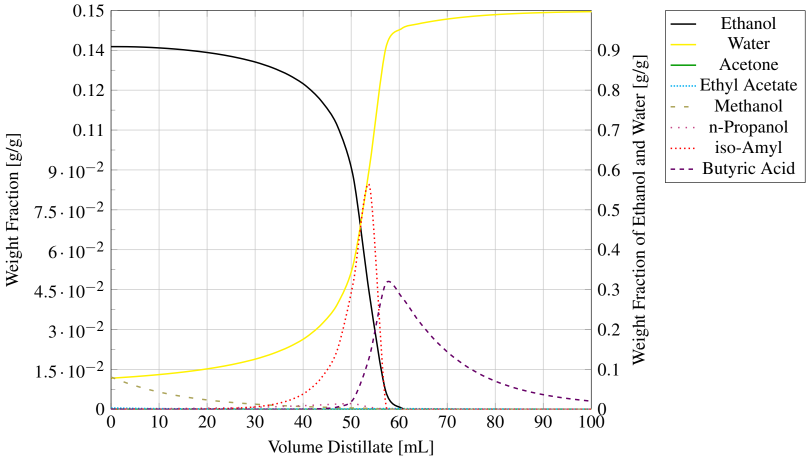


Figure 7.3: AspenTech® Batch Modeler V10 model of the distillation system using the Wilson/Hayden-O'Connell equation of state. Curves are weight fraction of components in the distillate.

If compared to Figure 6.2, each component has the same shape curve during the distillation. The ethanol curve is held at a high percentage and as it is quickly depleted, the butyric acid increases. The iso-amyl alcohol increases during the distillation until the ethanol runs out, then rapidly falls to zero.

This AspenTech® Batch Modeler shows the same curve shapes that are seen experimentally in Section 6.3.

7.5 Commercial Implementation

This process can be easily implemented into an existing commercial distillation facility by modifying the fermentation process slightly and adding the correct amount of catalyst into the distillation column where desired. The product will have to be distilled with close attention to where the ethyl butyrate is expected to distill.

A provisional patent application has been filed for this process.

APPENDIX

APPENDIX

PROVISIONAL PATENT APPLICATION

The following appendix is a provisional patent application submitted on March 23, 2018. Included is the provisional application for patent cover sheet and the provisional patent application document.

PTO/SB/16 (01-18)
Approved for use through 11/30/2020. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET – Page 1 of 2

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. ____________________

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Kris A.	Berglund	Okemos, Michigan
Jacob	Rochte	Lansing, Michigan

Additional inventors are being named on the ____________ separately numbered sheets attached hereto.

TITLE OF THE INVENTION (500 characters max):

REACTIVE DISTILLATION IN BEVERAGE SPIRIT PRODUCTION

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

☒ The address corresponding to Customer Number: 143356

OR

☐ Firm or Individual Name

Address

City	State	Zip
Country	Telephone	Email

ENCLOSED APPLICATION PARTS (*check all that apply*)

☒ Application Data Sheet. See 37 CFR 1.76.
☐ CD(s), Number of CDs ____________
☐ Drawing(s) *Number of Sheets* ____________
☐ Other (specify) ____________
☒ Specification (e.g., description of the invention) *Number of Pages* 31

Fees Due: Filing Fee of $280 ($140 for small entity) ($70 for micro entity). If the specification and drawings exceed 100 sheets of paper, an application size fee is also due, which is $400 ($200 for small entity) ($100 for micro entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).

METHOD OF PAYMENT OF THE FILING FEE AND APPLICATION SIZE FEE FOR THIS PROVISIONAL APPLICATION FOR PATENT

☒ Applicant asserts small entity status. See 37 CFR 1.27.

☐ Applicant certifies micro entity status. See 37 CFR 1.29.
Applicant must attach form PTO/SB/15A or B or equivalent.

☐ A check or money order made payable to the *Director of the United States Patent and Trademark Office* is enclosed to cover the filing fee and application size fee (if applicable).

TOTAL FEE AMOUNT ($) 140.00

☒ Payment by credit card. ~~Form PTO-2038 is attached.~~

☒ The Director is hereby authorized to charge the filing fee and application size fee (if applicable) or credit any overpayment to Deposit Account Number: 13-2855 .

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET – Page 2 of 2

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.

☐ Yes, the invention was made by an agency of the U.S. Government. The U.S. Government agency name is: ______________________

☐ Yes, the invention was made under a contract with an agency of the U.S. Government. The name of the U.S. Government agency and Government contract number are: ______________________

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

SIGNATURE / Steven M. Parks, Reg. #61,889 /
DATE March 23, 2018

TYPED OR PRINTED NAME Steven M. Parks
REGISTRATION NO. 61,889
(if appropriate)

TELEPHONE (312) 474-6300
DOCKET NUMBER 32213/40074

REACTIVE DISTILLATION IN BEVERAGE SPIRIT PRODUCTION

CROSS REFERENCE TO RELATED APPLICATION

[0001] None.

STATEMENT OF GOVERNMENT INTEREST

[0002] None.

BACKGROUND OF THE DISCLOSURE

Field of the Disclosure

[0003] The disclosure relates to a reactive distillation method for beverage spirit production. An additional carboxylic acid is added to a fermentation product reaction mixture along with an esterification catalyst to distill and react the carboxylic acid with ethanol in the reaction mixture to form a corresponding ethyl carboxylate flavor component in the final beverage spirit product.

SUMMARY

[0004] In an aspect, the disclosure relates to a method for beverage spirit production, the method comprising: providing a reaction mixture comprising water, ethanol, and a carboxylic acid (e.g., having 3 or more carbon atoms); reactively distilling the reaction mixture in the presence of an esterification catalyst to (i) react a portion of the ethanol (e.g., a minor portion of the starting ethanol) and the carboxylic acid to form an ethyl carboxylate reaction product, and (ii) form a distillation product (e.g., the distillate) comprising water, ethanol, and the ethyl carboxylate; wherein: the distillation product has a water concentration less than that of the reaction mixture; and the distillation product has an ethanol concentration greater than that of the reaction mixture. The esterification catalyst is not present in the distillation product.

[0005] The carboxylic acid reactive with ethanol to form the corresponding ethyl ester flavor component preferably has 3 or more carbon atoms, for example to prevent formation of (additional) ethyl acetate, such as ethyl acetate that could be formed in addition to a natural amount formed based on levels of acetic acid possibly present as fermentation byproduct in addition to ethanol. Further, cuts of beverage spirit distillate can be selected to eliminate or reduce ethyl acetate from the beverage spirit product (e.g., by appropriate selection of head vs. heart cuts or fractions). In various embodiments, the carboxylic acid can have at least 3 or 4 carbon atom and/or up to 5, 6, 8, or 10 carbon atoms, for example 3 to 6, 6 to 10, or 3 to 10 carbon atoms.

[0006] In various refinements, the carboxylic acid can be an aliphatic (alkyl) carboxylic acid. More generally, the carboxylic acid can include saturated, unsaturated, and/or aromatic hydrocarbon portions in addition to its carboxylic acid (-COOH) functional group(s). In other refinements the carboxylic acid can include linear or branched alkyl carboxylic acid (e.g., where butyric acid is representative), cycloalkyl carboxylic acid, or aromatic carboxylic acid (e.g., where vanillic acid or cinnamic acid is representative). Alternatively or additionally, the carboxylic acid can be a monoacid (e.g., an aliphatic (alkyl) monocarboxylic acid), a diacid (e.g., succinic acid), a triacid (e.g., citric acid), or more to form a corresponding monoester diester, triester, etc. In some embodiments, a single carboxylic acid species is added to the reactive distillation mixture to form a single corresponding ethyl ester as a flavor component. In other embodiments, multiple carboxylic acid species are added to the reactive distillation mixture to form a multiple corresponding ethyl esters as flavor components, for example based on a plurality of different carboxylic acid species having the same or different number of carbon atoms, the same or different number of carboxylic acid functional groups, etc. In addition to its hydrocarbon component and carboxylic acid functional group(s), the carboxylic acid can include other functional groups such as hydroxy groups (e.g., such as in citric acid, vanillic acid) and/or native ester groups (e.g., present before reactive distillation; such as methyl ester groups in vanillic acid or other acids).

[0007] In a particular refinement, the carboxylic acid is selected from the group consisting of propanoic acid (or propionic acid), butanoic acid (or butyric acid), pentanoic acid, hexanoic acid, citric acid, vanillic acid, and combinations thereof. For instance as illustrated in the examples, the carboxylic acid can include butanoic acid/butyric acid.

[0008] In a particular refinement, the carboxylic acid is characterized as having a binary azeotrope with water; a ternary mixture of the carboxylic acid, water, and ethanol is characterized by a separatrix defining a co-distillation region of concentration values in which the carboxylic acid is preferentially distilled with ethanol; and the reaction mixture (initially) has concentration values for water, ethanol, and the carboxylic acid which are in the co-distillation region. In the ternary mixture, water is preferentially recovered (alone) in the bottoms of a distillation process and carboxylic acid/ethanol are together preferentially recovered in the distillate, for example with only minor amounts of the components in the non-preferential distillation streams. The ternary mixture can be further characterized by a concentration region outside the co-distillation region where water/ethanol are preferentially recovered in one stream and the carboxylic acid is preferentially recovered (alone) the other stream. Typical reaction mixtures for beverage spirits will contain more than three (i.e., water, ethanol, and the carboxylic acid) components, but the foregoing reference to a binary azeotrope between water and the carboxylic acid and a ternary mixture of water, ethanol, and the carboxylic acid reflect the properties of the water, ethanol, and carboxylic acid components in combination with each other and other fermentation components. Specifically, the initial reaction mixture component concentrations for water, ethanol, and the carboxylic acid can be selected for the preferential separation between water and ethanol/carboxylic acid even with the other fermentation components in the reaction mixture. In this particular refinement, the ethanol/carboxylic acid mixture is relatively more volatile than water.

[0009] In other refinements, the carboxylic acid need not be characterized as having a binary azeotrope with water. The disclosed method is generally applicable to any system in which the ethanol and carboxylic acid together contact the solid acid catalyst and can be converted to the corresponding ethyl ester.

[0010] In a refinement, the carboxylic acid has a boiling point above that of water. For example the boiling point of the carboxylic acid can range from at least 100, 110, 120, 140, or 160°C and/or up to 120, 140, 160, 180, or 200°C. Representative boiling point values for carboxylic acids of interest are 141°C (propionic acid), 163°C (butanoic/butyric acid), and 187°C (pentanoic acid). The foregoing boiling points can be applicable to carboxylic acids which exhibit azeotropic behavior with water and those which do not.

[0011] In a refinement, the reaction mixture comprises a low wine spirit. The low wine spirit can have an ethanol concentration in a range of at least 5, 10, or 15% and/or up to 30, 35, or 40% ABV. The low wine spirit is generally derived from a mash distillate, for example a stripping product thereof.

[0012] In a refinement, the reaction mixture has an initial concentration for the carboxylic acid in a range from 0.001 wt.% to 2 wt.%, For example, the initial concentration for the carboxylic acid can be at least 0.001, 0.01, 0.02, 0.05, 0.1, 0.2, or 0.5 wt.% and/or up to 0.1, 0.2, 0.5, 1, 1.5, or 2 wt.%. Alternatively or additionally, the distillation product can have a concentration for the ethyl carboxylate up to 2 wt.%. For example, the final concentration for the ethyl carboxylate can be at least 0.000001, 0.00001, 0.0001, 0.001, 0.01, 0.02, 0.05, or 0.1 wt.% and/or up to 0.001, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 1.5, or 2 wt.%. The foregoing concentration can apply to a single carboxylic acid and ethyl carboxylate, or to a plurality of carboxylic acids and ethyl carboxylates, such as when the reaction mixture includes a plurality of added carboxylic acids for forming a distribution of ethyl ester flavor components.

[0013] In a refinement, the reaction mixture has an initial concentration for ethanol in a range from 5 wt.% to 40 wt.%. For example, the reaction mixture can have an initial ethanol concentration at least 5, 10, 15, 20, or 25 wt.% and/or up to 20, 25, 30, 35, or 40 wt.%. Alternatively or additionally, the distillation product can have a concentration for ethanol of at least 30 wt.%. For example, the final concentration for the ethanol can be at least 30, 35, 40, 50, or 60 wt.% and/or up to 50, 60, 70, 80, 90, or 95 wt.%. Alternatively or additionally, the distillation product can have a concentration for ethanol of at least 40% ABV (e.g., at least 40, 50, or 60% ABV).

[0014] In a refinement, the reaction mixture comprises one or more byproducts (e.g., distillation or fermentation byproducts) selected from the group consisting of acetone, acetic acid, methanol, n-propanol, n-butanol, isoamyl alcohol, and combinations thereof. Such additional components can be individually present at levels up to about 0.01 wt.%, for example from about 0.000001, 0.00001, or 0.0001 wt.% to 0.01 wt.%, In some embodiments, corresponding byproduct esters such as methyl butyrate, propyl butyrate, butyl butyrate etc. could be formed and retained in the final distillate product?, which can impart an additional flavor profile to the final beverage spirit.

[0015] In a refinement, the esterification catalyst comprises a solid acid catalyst. The use of the solid catalyst avoids contamination of the liquid beverage spirit product and does not create an additional need to separate the solid acid catalyst from the product (e.g., because it remained in the distillation apparatus). Any solid, food-grade acid can be used, for example including a solid ion-exchange resin with an acidic group (e.g., sulfonic acid group), such as in the AMBERLYST catalysts used in the examples.

[0016] In a refinement, the method further comprises: co-fermenting ethanol and the carboxylic acid in a grain mixture to form a fermented grain mixture comprising ethanol and the carboxylic acid (e.g., aqueous mixture including a grain carbohydrate source, such as a mash mixture); and performing one or more separation processes (e.g., distillation) on fermented grain mixture to form the reaction mixture. In a typical beverage spirit process, a fermented grain mixture or mash is used as the reaction mixture input to the reactive distillation process according to the disclosure.

[0017] In a further refinement, the grain mixture comprises *Clostridium tyrobutyricum* as a fermentation microorganism producing butyric acid as the carboxylic acid having 3 or more carbon atoms. The grain mixture can generally include two microorganisms: *Saccharomyces cerivisiae* for ethanol fermentation and a second microorganism for the carboxylic acid fermentation (e.g., *Clostridium tyrobutyricum* or otherwise). *Clostridium* *acetobutricum* is an example of another suitable fermentation microorganism. Alternatively or additionally, genetically modified microorganisms can be engineered according to general skill in the art to form desired carboxylic acids as their fermentation products. In such cases, as with the used of non-genetically modified microorganisms, the microorganisms are not present in the final beverage spirit (e.g., having been removed from the fermented grain mixture prior to reactive distillation).

[0018] In an embodiment the reactive distillation product is itself or is a component of a beverage spirit selected from the group consisting of vodka, gin, rum, brandy, and whisky. In some cases, the reactive distillation product can be further barrel aged prior to being distributed for consumption as a spirit.

[0019] While the disclosed apparatus, compounds, methods and compositions are susceptible of embodiments in various forms, specific embodiments of the disclosure are illustrated (and will hereafter be described) with the understanding that the disclosure is intended to be illustrative, and is not intended to limit the claims to the specific embodiments described and illustrated herein.

DETAILED DESCRIPTION

[0020] The disclosure relates to the creation of new flavors in situ during distillation of spirits. As an example, butyric acid can be added to the distillation system, for instance as a separate feed to a fermented spirit, prior to the final spirit distillation along with ion-exchange catalyst. The butyric acid could also be created by a parallel fermentation in situ with ethanol formation via fermentation (e.g., with separate microorganisms for each of butyric acid and ethanol). The butyric acid reacts with the ethanol during distillation to create ethyl butyrate in a (final) reactive distillation of the beverage spirit. The resulting product therefore has an additional flavor due to the smell and taste of the ethyl butyrate. For example, the ethyl butyrate can provide a spirit with a fruity smell and taste, similar to banana candy or bubble gum.

[0021] The attached appendices provide further description related to the disclosure, and they are incorporated herein by reference in their entireties.

[0022] Appendix 1 includes a representative reactive distillation process using a low wine alcohol feedstock with added butyric acid reactant and a solid acid catalyst to form ethyl butyrate in the beverage spirit product. A middle hearts cut of the distillate results after elimination of (i) an early heads cut or distillate portion with undesirable distillation components (e.g., ethyl acetate) and (ii) a late tails cut or distillate portion with undesirable distillation components (e.g., unreacted butyric acid or other carboxylic acids) during collection of the distillate. A sensory evaluation of the beverage spirit product indicated that the product had the smell of ethanol and fruity bubble gum.

[0023] Appendix 2 includes a more detailed illustration and description of a reactive distillation method according to the disclosure, also forming ethyl butyrate in the beverage spirit product. In particular, distilled alcoholic beverages have been produced through fermentation and distillation for centuries but have not purposefully involved a chemical reaction to produce a flavoring. Introducing a microorganism to produce butyric acid along with the typical yeast ethanol fermentation sets up a reactive distillation system to flavor a spirit with ethyl butyrate and butyric acid. The ternary interactions of water, ethanol, and butyric acid allow all three to vaporize in the stripping distillation, thus they are concentrated in the low wines and give a large excess of ethanol compared to butyric acid for better reaction completion. The stripping distillation has also been modeled on ASPEN PLUS software and coincides well with a test stripping distillation at the bench scale. AMBERLYST 15 wet catalyst (a solid acid catalyst) was added to a subsequent distillation, resulting in the production of the desired ethyl butyrate in the distillate, measured by gas chromatography. Primary sensory evaluation has determined that this process has a profound effect on the smell of the spirit with the main flavor being similar to fruity bubble gum. The illustrated method provides a pathway for creating spirits with a desired flavor on demand without acquiring a heavy capital cost if a beverage distillation column is already purchased.

[0024] Appendix 3 provides further description of the chemical components, apparatus, and sensory evaluation of the reactively distilled beverage spirit including an ethyl butyrate flavor component.

[0025] Because other modifications and changes varied to fit particular operating requirements and environments will be apparent to those skilled in the art, the disclosure is not considered limited to the example chosen for purposes of illustration, and covers all changes and modifications which do not constitute departures from the true spirit and scope of this disclosure.

[0026] Accordingly, the foregoing description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications within the scope of the disclosure may be apparent to those having ordinary skill in the art.

[0027] All patents, patent applications, government publications, government regulations, and literature references cited in this specification are hereby incorporated herein by reference in their entirety. In case of conflict, the present description, including definitions, will control.

[0028] Throughout the specification, where the apparatus, compounds, compositions, methods, and processes are described as including components, steps, or materials, it is contemplated that the compositions, processes, or apparatus can also comprise, consist essentially of, or consist of, any combination of the recited components or materials, unless described otherwise. Component concentrations can be expressed in terms of weight concentrations, unless specifically indicated otherwise. Combinations of components are contemplated to include homogeneous and/or heterogeneous mixtures, as would be understood by a person of ordinary skill in the art in view of the foregoing disclosure.

What is claimed is:

1. A method for beverage spirit production, the method comprising:

providing a reaction mixture comprising water, ethanol, and a carboxylic acid having 3 or more carbon atoms;

reactively distilling the reaction mixture in the presence of an esterification catalyst to (i) react a portion of the ethanol and the carboxylic acid to form an ethyl carboxylate reaction product, and (ii) form a distillation product comprising water, ethanol, and the ethyl carboxylate;

wherein:

the distillation product has a water concentration less than that of the reaction mixture; and

the distillation product has an ethanol concentration greater than that of the reaction mixture.

2. The method of claim 1, wherein the carboxylic acid has 3 to 6 carbon atoms.

3. The method of claim 1, wherein the carboxylic acid comprises an aliphatic carboxylic acid.

4. The method of claim 1, wherein the carboxylic acid is selected from the group consisting of propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, citric acid, vanillic acid, and combinations thereof.

5. The method of claim 1, wherein the carboxylic acid comprises butanoic acid.

6. The method of claim 1, wherein:

the carboxylic acid has a binary azeotrope with water;

a ternary mixture of the carboxylic acid, water, and ethanol is characterized by a separatrix defining a co-distillation region of concentration values in which the carboxylic acid is preferentially distilled with ethanol; and

the reaction mixture has concentration values for water, ethanol, and the carboxylic acid which are in the co-distillation region.

7. The method of claim 6, wherein the carboxylic acid has a boiling point above that of water.

8. The method of claim 1, wherein the reaction mixture comprises a low wine spirit.

9. The method of claim 1, wherein the reaction mixture has an initial concentration for the carboxylic acid in a range from 0.001 wt.% to 2 wt.%.

10. The method of claim 1, wherein the distillation product has a concentration for the ethyl carboxylate up to 2 wt.%.

11. The method of claim 1, wherein the reaction mixture has an initial concentration for ethanol in a range from 10 wt.% to 40 wt.%.

12. The method of claim 1, wherein the reaction mixture comprises one or more byproducts selected from the group consisting of acetone, acetic acid, methanol, n-propanol, n-butanol, isoamyl alcohol, and combinations thereof.

13. The method of claim 1, wherein the esterification catalyst comprises a solid acid catalyst.

14. The method of claim 1, further comprising:

co-fermenting ethanol and the carboxylic acid in a grain mixture to form a fermented grain mixture comprising ethanol and the carboxylic acid; and

performing one or more separation processes on fermented grain mixture to form the reaction mixture.

15. The method of claim 14, wherein the grain mixture comprises *Clostridium tyrobutyricum* as a fermentation microorganism producing butyric acid as the carboxylic acid having 3 or more carbon atoms.

16. The method of claim 1, wherein the reactive distillation product is or is a component of a beverage spirit selected from the group consisting of vodka, gin, rum, brandy, and whisky.

ABSTRACT

The disclosure relates to a reactive distillation method for beverage spirit production, the method comprising. An initial reaction mixture includes water, ethanol, and a carboxylic acid, for example having 3 or more carbon atoms. The reaction mixture is reactively distilled in the presence of an esterification catalyst to react a portion of the ethanol and the carboxylic acid to form an ethyl carboxylate reaction product, and form a distillation product or distillate including water, ethanol, and the ethyl carboxylate. The esterification catalyst is not present in the distillation product, for example when using a solid acid esterification catalyst in the reaction mixture. In a refinement, ethanol and the carboxylic acid can be co-fermented in an initial grain mixture, which is subsequently reactively distilled according to the disclosed method.

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