Separation of Fusel Oils in Wine

A Project Report for E&J Gallo Winery and Worcester Polytechnic Institute

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Abstract

E&J Gallo (Gallo) currently has access fusel oils through a brandy still side-stream. These materials are being processed and used as an alternative fuel source within the winery, but Gallo wishes to separate the various components of fusel oils to better utilize the chemicals in experiments or production and potentially make a profit. The goal of this project was to develop a methodology that allowed for this separation, and experiments were completed using a bench-scale steam stripper and batch distillation column. While the results from the trials completed were not conclusive, Gallo is now one step closer toward completing its separation goals.

Acknowledgments

Throughout this project, we received a lot of help, but getting ourselves to Modesto required a lot of assistance, and there are so many people that we would like to thank who made this project possible. First, thank you to Alex Kopchik, Professors Kazantzis and DiBiasio, and Laura Robinson at the Gordon Library for helping us through our preparation period. You were all there to help answer our questions and push us to stay on the right track. We would also like to thank Gayatri Kasi for working with us to get both her paper and our paper written. Significant collaboration happened and this report would be nothing without these people.

Once we finally made it to Modesto, we received even more support and friendship than we were expecting. As such, we would like to thank Paige Watson for answering questions and introducing us to pho; Ariana Tway, Thomas Logan, and Thomas Clark for also answering questions and humoring us daily; Joe for being a friend and teaching us how to properly spike wine, Ravi Ponangi for putting a priority on our samples so we could have results; Umesh and AJ for bringing donuts and answering any questions thrown at them; and everyone else at the Cummins Laboratory. This experience would not have been the same without you all. We would also like to thank our driver Chris, without whom we would never have made it to work on time or have listened to Big Boy in the Morning every morning.

Executive Summary

Introduction

This report stems from the cooperation of Worcester Polytechnic Institute and E&J Gallo Winery. The goal of this project was to determine a method of separation for the components of fusel oils. Fusel oils are the byproducts of fermentation collected from the rectifier in the Gallo brandy stills. Fusel oils can give alcoholic beverages an undesirable taste, and are toxic in high concentrations. For the purpose of the experiments completed, three different types of fusel oils were utilized:

- wet fusel oils, taken from the brandy still as is (including water and contaminants)
- dry fusel oils, with excess water removed (specifically for laboratory use)
- lab dried fusel oils, made in lab as an intermediate, (5% by volume of water removed)

Gallo currently uses fusel oils to aid in the degradation of organic waste, and uses the effluent from these reactions as a fuel source. However, if the components of the fusel oils can be adequately separated, the components can be utilized in a profitable way for Gallo.

Distillation was the separation technique used for this project. First the fusel oils were sent through a steam stripper and then a batch distillation column, shown in Figures A and B below.

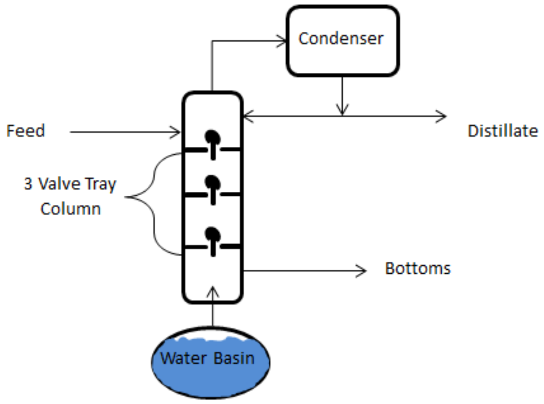

Figure A: Setup of Steam Stripper Column

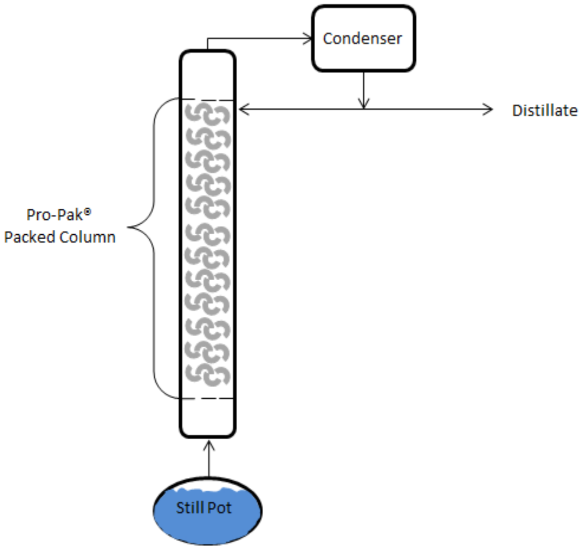

Figure B: Setup of Batch Distillation Column

This method proved to be a good option to utilize the available materials and equipment, both in the laboratory and in the winery. In order to understand how the different columns worked and see their limitations, a multitude of trials including pH and time adjustments were completed before committing to the final methodology. Upon completion of credibility testing, the sequential distillation of steam stripping and batch distillation methodology was implemented.

Results and Discussion

It was found that the equipment, at its current bench scale state, was unable to provide adequate separation. This was due to significant amount of heavy keys present in the distillate. It was determined that pH had minimal effect on the volume of distillate or residual collected from the distillation still, but time allowed for distillation was imperative to final concentration.

The bottoms product for the steam stripped samples contained approximately 71% iso-amyl and 20% active amyl, while the distillate contained approximately 48% iso-amyl and 17% active amyl. The bottoms products from the steam stripping trials were then batch distilled to see the effect of the additional separation. However, the separation obtained was just as mediocre, with approximately 78% iso-amyl and 20% active amyl in the bottoms and 38% and 18% respectively in the distillate. Should more testing be completed in the future, varying the time spent distilling may lead to better separation of active and iso-amyl from the lighter keys in fusel oils, thus removing some of the negative flavor components. See Figure C for the distribution of the components.

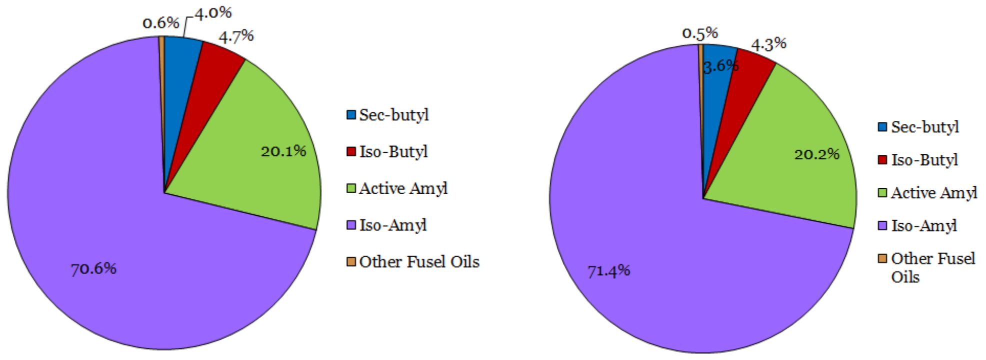

Figure C: Steam Stripped Bottoms for Wet (left) and Lab Dried (Right) Fusel Oils

Active amyl and iso-amyl showed a similar dominant distribution in the steam stripped distillate. However, n-propanol, sec-butanol and isobutanol were more present than before, having compositions of approximately 2.6%, 17.35% and 13.7% respectively. Figure D shows the distribution of the results.

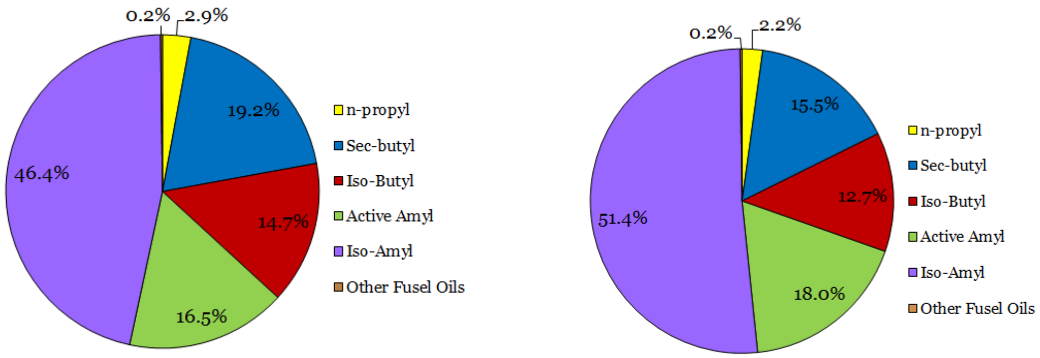

Figure D: Steam Stripped Distillate for Wet (left) and Lab Dried (Right) Fusel Oils

The separations obtained were not as expected, but distillation proved to be an adequate method for the separation of fusel oil components.

There were several setbacks and time restrictions that impacted the findings of this project. The biggest setback was the amount of time it took to run the fusel oil tests (approximately 30-90 minutes for one trial). Unfortunately, almost all samples submitted under this project needed fusel oil composition testing. This analytics testing is very time consuming and difficult to accurately run each time. Additionally, there were equipment limitations that made it difficult to fully control or adjust temperature and pressure during separation. This caused the only independent measurable variable to be time.

Conclusion and Recommendation

Overall, there were several key points and recommendations to be made. The most noteworthy conclusion was that the dry fusel oils showed the best potential for separation of the individual fusel oil components. The dry fusel oils had the most definitive composition value for n-butanol, which was a desirable component. It would be beneficial to have fresh dry fusel oils, to minimize the chances of moisture reabsorption. Drying the fusel oils would require more preparation in the future, but if better products can be obtained, the extra work would be beneficial.

It was also found that separation times of 45-90 minutes or higher resulted in heavy components making their way into the distillate despite there still being light components in the residual. This was unexpected, and it is difficult to explain why this happened, however, it is our belief that with more experimentation this occurrence could be further analyzed. One possible explanation could be that the heavy components present in the distillate had been vaporized with the water that was contained in the fusel oils.

Recommendations

1. Proper Cleaning of all separation columns:
   Both the steam stripper and the batch distillation column required thorough cleaning. This is especially important to reduce fouling. Fouling can reduce the surface area for separation in the column.

2. Continuation of steam stripping and batch distillation with varied parameters:
   Completing both batch distillation and steam stripping trials while testing different components and scales would be beneficial. This will provide a better understanding of the changes that may occur when scaling up the process to production scale, should the process be taken that far. Additionally, different tools may also be considered, such as pressure and temperate probes.

3. Further look into azeotropic distillation
   From azeotropic distillation, the two liquid layers obtained during distillation from what we saw could result in more superior separation, than what is currently being achieved.

The processes designed for this project utilized the equipment already available to E&J Gallo and as such, will not require new equipment, making it more feasible to begin new operations. Even though the separation results obtained were less than satisfactory, they provided a learning opportunity and provided a basis for further experimentation that E&J Gallo can use to continue testing separation techniques involving fusel oils.

Background

History of Winemaking

Wine has been a part of human history since before civilization. According to paleontologists, some form of wine has been around for more than 100,000 years. From Arabs in early Mesopotamia, Egyptian pharaohs, and the ancients Greeks, all the way to today's society, humans throughout history have been consuming wine (Vine et al., 2002). Despite its long history, Christianity is considered by some as the reason that wine has become the developed industry it is today. Christ offering his cup at the Last Supper motivated monks to plant vineyards wherever they settled during the Middle Ages and the Renaissance, and this movement lasted into the New World, with the development of wines in both New York and California, but it wasn't until 1860 with Pasteur's discoveries that people understood the process behind fermentation (Vine et al., 2002). However, the mid 1800s saw an infestation of Black Rot fungus, which caused a lot of discouragement to winemakers. To battle the fungus, a disease-resistant vine was produced in 1854, after 7 years of testing. The cost was $5 per vine, which was an incredibly high price at the time, but the disease-resistant vines brought back the enthusiasm of the winemakers after the fungus epidemic. At the same time, vines from American vineyards were taken to Europe to help combat the *Phylloxera* root louse that was destroying European grapevines. As a result, there are still classic vines in European countries, such as France, that are still grafted on the American roots (Vine et al., 2002).

In addition to the problems caused by rot and fungus the prohibition movement, started in 1846 in Maine, caused significant damage to the wine industry, and resulted in the burning of much of the recorded history of American wine. The prohibitionists worked to strike the word wine from the Bible, claiming it was actually "grape juice," and tried to ban Greek and Roman classic literature that mentioned wine. While some winemakers got around the Volstead Act, which approved prohibition across America, by marketing their wine as medicinal, sacramental, or as cooking wines, many others were forced to shut down their businesses (Vine et al., 2002). Despite prohibition, home winemaking became legal, and allowed each household to produce up to 200 gallons of wine per year for household consumption. Regardless, some winemakers chose to continue production illegally, and became bootleggers, which then became a huge industry for gangster networks, who could get around law enforcement. Finally, in December of 1933, the

Repeal came into effect, and ended the continued destruction to the wine industry in America (Vine et al., 2002). Since the end of prohibition, the wine industry has boomed.

Today, it is estimated that approximately 1 in every 100 people works in the wine industry, whether at the vineyard, the winery, or in the wine marketing sector. Additionally, it is estimated that the French and the Italians consume about 16 gallons of wine per person per year, as opposed to the 2 gallons per person per year in the United States (Vine et al., 2002). As a whole, the wine trade has maintained a sense of stability and proved itself as a lasting industry.

Process of Winemaking

Wine is produced through a chemical reaction called fermentation, which uses the yeast on the grape skins and, if desired, added yeast to create an alcoholic solution from the grapes' juices. The glucose from the grapes reacts with the yeast to form both ethanol and carbon dioxide (Boulton et al., 2002).

$$C_6H_{12}O_6 + \text{Yeast} \longrightarrow 2C_2H_5OH + 2CO_2$$

The process begins with collection during the harvest. Afterwards, the grapes are exposed to approximately 30-100 ppm sulfur dioxide to kill and prevent any further growth of unwanted bacteria on the grapes before undergoing fermentation (Boulton et al. 2002 and Vine et al., 2002). Dry wines can be protected from the bacteria with the low end of 30 ppm sulfur dioxide while wines that have residual fermentable sugar are protected by 100 ppm or more sulfur dioxide (Vine et al., 2002) Finally, the wine is clarified before it is distributed to customers (Boulton et al., 2002).

While the general fermentation processes between red and white wine are essentially the same, the initial process differs. Red wine gets its color from the tannins in grapes (tannins are a material naturally in plants that precipitate protein), so the juice is allowed to stay in contact with the skins during fermentation. White wines, on the other hand, are made by pressing the grapes as quickly as possible and removing the skins, thus reducing contact time. The lower contact time gives less time for the color and tannins to seep, giving a whiter color and different flavor. Additionally, red wines must mature, while maturation is less important for white wines (The Difference Between Red and White).

One of the most important steps of the winemaking process involves the sensory component, generally completed during mixing. For example, red wines are aged in oak barrels so that the oak tannins can be extracted. The oak tannins create a smoky flavor in the wine (Kopchik, 2016 and Vine, 2002). Other factors that play into the overall flavor of the wine are sweetness, acidity, body, and fruit. Sweetness is controlled by how much sugar is left unfermented in the wine, while acidity is a measure of tartness. As a result, a balance between acidity and sweetness must be achieved to obtain an optimal flavor (Vine, 2002). The body of a wine is similar to the mouth feel, or how the wine feels in the mouth, whether heavy or light. Finally, the fruit flavor in the wine has a huge impact on how the wine is perceived by tasters. The intensity of the fruit flavor varies with the alcohol content; the pH; and the aging material, as some wines are aged in oak barrels while others are aged in steel containers (Vine, 2002).

Sensory Evaluation

While the sensory components of wine are adjusted during the winemaking process, there are several different aspects that affect the tasting process. Some of these aspects include the physiological standings of the taster--hunger, fatigue, ability to smell and taste, et cetera (LaMar, 2001). Others involve both the shape and size of the wine glass, as different sizes affect the collection of wine volatiles (Mansfield, 2010). The combination of these attributes, along with a tasting process, allows a person to thoroughly experience and taste a wine.

The tasting process includes four elements: smell, taste, feeling, and seeing. A person’s sense of smell is about 1,000 times more sensitive than their sense of taste, and as a result, smell is one of the most important elements in wine tasting. In fact, the flavor a person tastes is greatly influenced by smell, with about 75% of the flavor coming from smell, or olfaction, and the other 25% coming from taste, or gustation. With these facts in mind, the first step of the tasting process is to swirl the wine in the glass and smell the aroma. Doing this can give the taster an indication of the alcohol level in the wine. If the smell is similar to rubbing alcohol, the alcohol content is too high for the type of wine. Additionally, if upon tasting, the wine as a hot sensation, it is possible again that the alcohol content is high. However, if the wine “feels thin and unsatisfying on the palate,” then the alcohol content is on the low side (5 Key Wine Components, 2012).

The combination of smelling, tasting, feeling, and seeing lead to a taste process that is thorough and thoughtful. To start tasting, about one-third or less of a wine glass should be filled, as this allows the vapors to stay in the glass. The wine should then be swirled in the glass to bring some of the vapor molecules into the air and increase the surface area for vapor to move. Next, one should smell the wine to play to the olfactory senses. This prepares the brain for the flavor to come. After smelling the wine, a sip should be taken and swirled around the mouth. This allows the taster to experience the mouthfeel of the wine. Slurping while drinking aerates the wine, volatizing it, which increases the intensity of the smell and flavor (LaMar, 2001). The taste testing process is an important part of analyzing the wine flavors produced during ingredient development and can be used to help ensure that a wine will be liked by consumers.

Fusel Oils at E&J Gallo

Fusel oils are congeners that are formed during fermentation as the yeast changes the sugars from the grapes to ethanol and carbon dioxide, among other compounds. Fusel oils are responsible for bringing a “hotness” to wine that, to some, can be undesirable. Additionally, they can be toxic in higher concentrations (Total Wine & More, 2016), and if inhaled, can cause a range of negative side effects including nausea, vomiting, dizziness, and even unconsciousness (NPC Alcohols, 1996). However, they add a so-called flavor complexity to wines, and without fusel oils, wine and other fermented beverages would be more bland (Ingraham, 2010).

To E&J Gallo, these oils are referred to as “bad alcohols.” The term “bad alcohols,” comes from the rough translation of fusel, a German word meaning “bad spirits” (Ingraham, 2010 and Kopchik, 2016). Fusel oils are called oils, because they separate from the alcoholic mixture during the distilling process and form an oily layer on top of the plates in a continuous still housing 100 to 135 proof alcohol (Ingraham, 2010). These oils are a mixture of several alcohols that are composed of more than two carbons (except in the case of methanol), causing them to have higher molecular weights and boiling points than ethanol (Kopchik, 2016). While yeasts appear to always form some type of fusel oils, aeration has also been found to stimulate the creation of fusel oils. As a result, restricting air in the fermentation process should reduce the amount of fusel oils produced (Ingraham, 2010).

While some components of fusel oils may be undesirable within wine, isoamyl alcohol is considered by some as the most undesirable in wine, causing a burning sensation, even in low quantities (Ingraham, 2010 and Kunkee et al., 1983). However, despite their flavor influencing properties, the undesirable fusel oils may still prove valuable to E&J Gallo. Various reactions can take place to turn the fusel oils into more usable materials, such as aldehydes, which are important sensory components in wine (Liu S.Q. and G.J. Pilone, 2000). The separation of wanted and unwanted fusel oils can occur through steam stripping and distillation. By completing separation on the fusel oils, the more desirable fusel oils can be used in other production processes at E&J Gallo and the undesired fusel oils can continue to be used in organic waste removal and further reacted to be used for fuel (Kopchik, 2016). The smell and flavor components in fusel oils can be seen in Table 1. The bolded components are considered valuable in this project for their fruity flavor.

Component	**Boiling Temperature (^{o}C)**	**Molecular Weight (g/mole)**	**Vapor Pressure (20^{o}C-25^{o}C)**	**Flavor/Smell**
Active Amyl (g) (2-Methyl-1-Butanol)	127.5	88.148	0.400 kPa	Whiskey, Roasted Odor, Banana
Methanol (g)	64.7	32.04	13.02 kPa	Sweet (Toxic)
n-Propanol (g)	97-98	60.095	0.020 kPa	Rubbing Alcohol
n-Butanol (g)	**118**	**74.122**	**0.800 kPa**	**Fruit**
iso-Butanol (g)	107.89	74.122	1.200 kPa	Scotch
sec-Butanol(g)	**98-100**	**74.122**	**1.67 kPa**	**Fruity**
iso-Amyl (g)	131.1	88.148	0.533 kPa	Banana
Water	100	18.02	3.17 kPa	-

Table 1: List of Boiling Temperatures (Restek), Molecular Weight, Vapor Pressure, and Flavor/Smell Components. Bolded are Desirable

The fusel oils listed in Table 1 are present in the wine at E&J Gallo in different percentages. According to previous Gallo research, the fusel oils in a specific sample are present in the percentages noted in Table 2. These percentages are in weight percent, and the percent in the light phase is the percentage of each fusel oil coming off in the distillate stream, while the percentage in the heavy phase is the percent of each fusel oil in the bottoms stream. It is important to note that the composition breakdown varies from sample to sample, so this breakdown will not be the same for every sample under analysis.

Component	**% in Feed**	**% in Light Phase**	**% in Heavy Phase**
Active Amyl (g) (2-Methyl-1-Butanol)	6%	7%	5%
Methanol (g)	1%	0%	2%
n-Propanol (g)	43%	36%	47%
n-Butanol (g)	1%	2%	1%
iso-Butanol (g)	16%	18%	15%
sec-Butanol(g)	18%	18%	18%
iso-Amyl (g)	15%	19%	12%

Table 2: Breakdown of Fusel Oil Components

Using the separation information from Table 1 and Table 2, a distillation schematic was developed for the separation of the smoky and hot fusel oils from the more fruity fusel oils. The schematic was used as a potential means of ingredient development that could then contribute to flavor development of wines.

Distillation

Distillation in Winemaking

Distillation is a process of separation that can generally occur in either a batch process or a continuous process. Batch distillation tends to have a product with a lower alcohol content than with continuous distillation. With the production of alcoholic beverages, the distillation process separates alcohol and water. Heat is used to vaporize one of the components and isolate the alcohol and congeners within the feed (Total Wine & More, 2016 and How Distilling Works, n.d.). The first part of the alcohol mixture, known as the wash, is the heads. The heads contains the materials that have lower boiling points, such as methanol. The second part of the wash to vaporize is the hearts. The hearts have the highest concentration of the desirable alcohols, such as the esters, which contribute fruity flavors. Finally, the last part of the wash to vaporize is the tails. The tails predominantly contains water and fusel oils. Like in non-alcohol based distillation, each stream will have different concentrations of each component than originally found in the feed (Total Wine & More, 2016 and How Distilling Works, n.d.).

The distillation process starts with a base containing sugars. The sugars are converted in the fermentation process into alcohol, which can then be distilled. After distillation, flavoring can be adjusted to change the style and flavor template. In the wine process, the grape juice is fermented, and the product can then be distilled into brandy (Total Wine & More, 2016 and How Distillation Works, n.d.). Higher alcohol content in wine or wine products such as brandy require distillation because fermentation is not enough to achieve the high alcohol content, as alcohol levels around 14-18% are toxic to the yeast in the fermentation process. As a result, another method must be used to obtain a more concentrated beverage (How Distillation Works, n.d.).

Steam Stripping

Steam stripping is a type of distillation that makes use of steam at the bottom of the column instead of using a reboiler. In steam stripping, water is the heavy component from which the other components, generally volatile organics, are separated (Steam Stripping, n.d.). There are several typical applications for which steam stripping can be used, including alcohol removal from water. The process will usually take place at temperatures close to 100^{o}C, the boiling point of water. While steam stripping requires lower operating temperatures than air stripping, another separation technique, steam stripping is more capital intensive (Steam Stripping, n.d.).

In steam stripping, steam is injected into the bottom of a tower as a means of heating the system and beginning vapor flow. The heat provided from the steam then brings the organic material, in this case, alcohol, into the vapor phase, where it can be carried out the top of the column. The stream is fed into the top of the column, and vaporization occurs as the feed falls (Steam Stripping, n.d.). The flow rate and pressure of the steam varies with the operating pressure, the material being separated, and the desired percentage of separation. The separation thermodynamics cannot be based on Henry's law because of the temperatures, interactions between materials, and varying concentrations, so the non-random two liquid (NRTL) activity coefficient model is used. It is generally recommended that laboratory tests be completed to determine the varying parameters, but usually vapor pressure data proves to be adequate (Steam Stripping, n.d.). This information was important while completing Aspen simulations.

Multicomponent and Azeotropic Batch Distillation

Batch distillation is a unique style of distillation in which a still is charged, the contents are heated, and the vapors are passed through a column for separation. Batch stills are typically used when the components fed to the still can be separated over a range of properties, such as temperature, when infrequent pilot-scale separation is needed, when only a small volume of product is needed, or when the desired product contains impurities in the light or heavy keys (Kister, 1992). In batch distillation, the entire column is the enriching section, and part of the liquid that condenses on the top of the column is returned to the system as reflux. Additionally, as distillation progresses, the most volatile component decreases, and mass, temperature, and concentration vary (Batch Distillation, n.d.). This type of distillation can occur in two ways. The first is by using a constant reflux ratio and varying the product composition, and the second is by using a variable reflux ratio which can allow the product to have a constant composition (Kim & Ju, 2003).

Distillation columns and stills vary in size. The smallest still is bench scale, then pilot, then scale-up. Because these columns and stills vary in size, modeling and predicting their behavior can be dynamic. Modelling a batch distillation system mathematically is complex due to the use of differential algebraic equations used to model the system's behavior (García et al., 2014). However, mathematical modelers such as Aspen Technology can be used to help predict the behavior of a batch distillation system, but in practice, the results may differ from the simulations. Typically, it is easy to predict the degree of separation for multicomponent systems based on the volatility of the components. The most volatile component is the light key, the least volatile component is the heavy key, and all other components are considered as intermediate keys (Kister, 1992). The light key is more concentrated in the distillate while the heavy key is more concentrated in the residual (contents of still pot after distillation). Intermediate keys are split between the top and bottom products (Kister, 1992). Other factors need to be considered when batch distilling multicomponent mixtures. One important factor is the presence of azeotropes. Inverted batch distillation can be used when there are minimum-boiling azeotropes present in the system. Inverted batch distillation has the feed charged and entering at the top of the column, instead of being charged in the still (Batch Distillation, n.d.).

When there is an azeotrope present, it is possible to use inverted batch distillation. An azeotrope is when the vapor and liquid phases have the same composition, and a heteroazeotrope is when two more liquid phases are in equilibrium with the vapor phase (Tolsma, 1999). When a heteroazeotrope occurs, a special type of inverted batch distillation can be used and is shown in Figure 1. Figure 2 shows a continuous heteroazeotropic separation system.

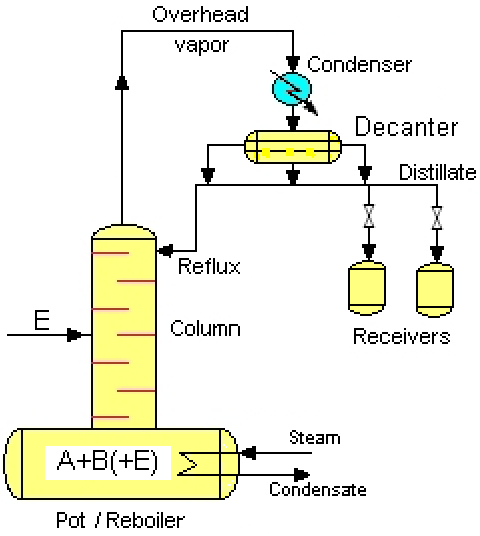

Figure 1: Heteroazeotropic Batch Distillation Schematic

https://upload.wikimedia.org/wikipedia/commons/a/a7/Bhad_column.png

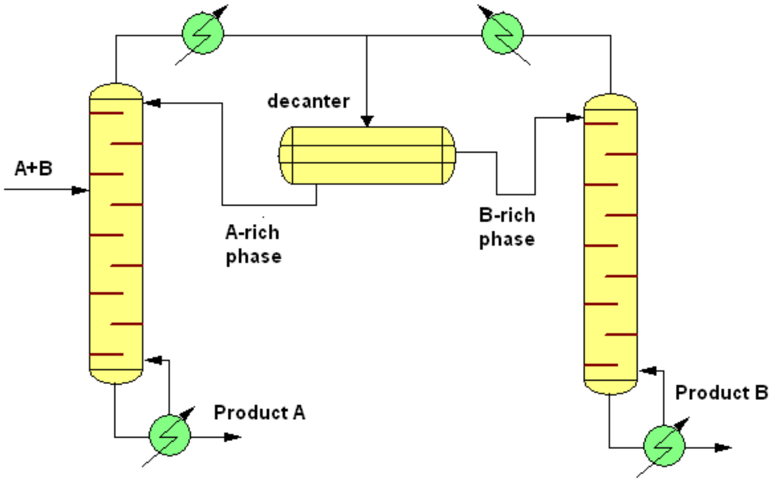

Figure 2: Heteroazeotropic Continuous Distillation Schematic

https://upload.wikimedia.org/wikipedia/en/f/f8/Conti_hetero_1.png

In heteroazeotropic batch distillation (Figure 1), an entrainer is added that allows for the separation of the immiscible components. Distillation then continues as in normal operation, until the condensate reaches a decanter, which separates the immiscible components. In the continuous method, two columns are used in combination with a decanter to separate the two immiscible components. Oftentimes, heteroazeotropic distillation is used to separate water and n-butanol, and has gained more recognition in recent years (Tolsma, 1999). These two methods will allow for the separation of immiscible fusel oils that distillation can bring about.

Purpose

The main goal of this project was to determine a way to separate fusel oils, potentially focusing on the separation of desired fusel oils (sweet and fruity) and undesired fusel oils (hot and spicy) using a combination of steam stripping and batch distillation techniques. The creation of this separation methodology may aid E&J Gallo in flavor development in the future. Additionally, the methodology may also aid the company in better utilizing the fusel oil components for their potential use in experimental procedures or physical sale. In order to complete this project, an understanding of the principles of continuous and batch distillation as well as steam stripping were imperative. Without this knowledge, it would have been impossible to complete the separation. Upon completion, E&J Gallo was presented with a detailed methodology to complete some fusel oil separation. Additionally, various Aspen runs simulating the process were included with the benchtop experiment data as a way to show the logistics behind the procedure.

Materials

Steam Stripping

A bench scale steam stripper was used. For the steam stripping of smoak components a 10 to 15 sieve tray column with a condenser was used. A round bottom flask was used as the steam pot (reboiler) and a beaker was used to collect the bottoms product. A similar, but smaller round bottom flask was used to collect the distillate. A separate beaker was filled with CT-04 oak product, VDR was added and the mixture was used as the feed. The feed was constantly heated and stirred by a hot plate and a stir bar. The feed was pumped from the beaker to the column using a peristaltic pump. Thermometers were placed in the reboiler, on the last sieve tray at the bottom, and in the overhead. An additional thermometer was placed in the beaker with the feed. Lastly, tubing was used to pump the feed into the column and retrieve the bottoms product from the column. To supply heat to the stripping column, a heater and PowerStat were used.

A similar setup was used for steam stripping fusel oils. For steam stripping fusel oils a three valve tray column was used. Wet Fusel Oils (from the rectifiers of a brandy stills) were used for the feed, however, VDR was not added.

Batch Distillation

A bench scale batch distillation column was used. A one inch diameter column packed with Pro-Pack© packing was used. A condenser was also attached to the top of the column. A round bottom flask was used as the still pot. The still pot was charged with Dry Fusel Oils (water has been professionally removed by a lab), and Lab Dried Fusel Oils (water has been removed using molecular sieve beads). Additionally, the bottoms product of the steam stripper was charged to the still pot, and Potassium Hydroxide and Sulfuric Acid were sometimes used to pH adjust the Dry and Lab Dried fusels being charged to the still. A thermometers were placed in the overhead. The residual was collected from the still pot at the end of each trial. A small round bottom flask was used to collect the distillate.

Finally, 95% Ethanol solution was used to clean each column after each trial.

Methodology

Typically at E&J Gallo, fusel oils are retrieved from the rectifier columns used in the brandy making process. The fusel oils are the effluent products of anaerobic digesters. Currently, the fusel oils are further processed and used as fuel in Gallo's power plant. However, there is a greater potential for fusel oils, and the key lies within its components. The fusel oils are composed of various alcohols that have useful sensory characteristics of taste and smell, and undesired characteristics that are better used as fuel. Figure 3 shows a breakdown of the components of the fusel oil.

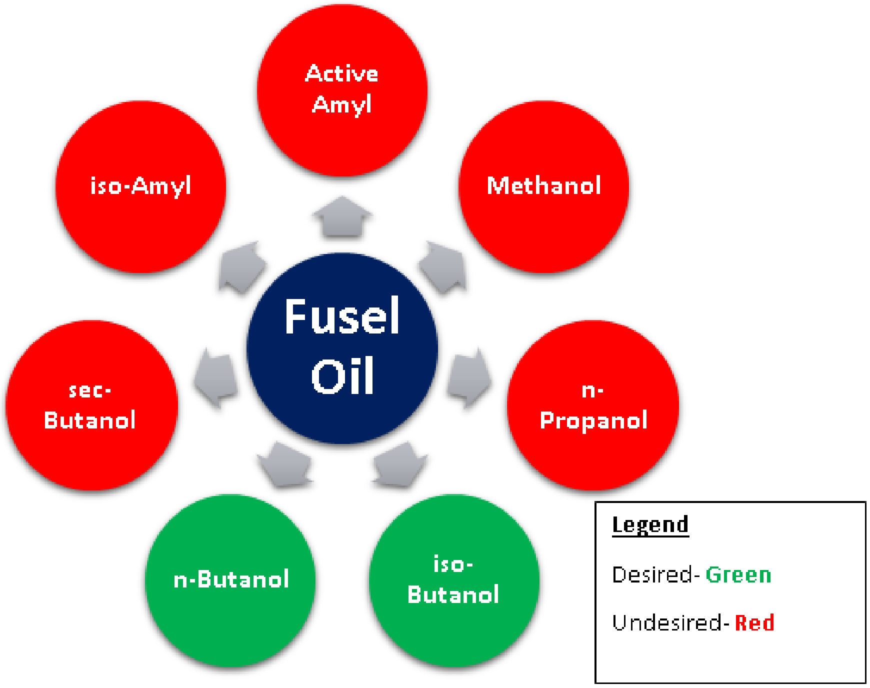

Figure 3: Desired and Undesired Components of Fusel Oils

The components of fusel oils in the right concentration can be useful to Gallo. The n-Butanol and iso-Butanol components can be used for ingredient development in the food industry if separated out appropriately. On the other, if their concentrations lie outside of the food grade range, then they can be sold for profit to other industries, such as the fragrance industry. The other undesired components can continue on the path of use for fuel for the powerhouse. Because separation is instrumental in seeing the fusel oils' true potential, distillation methodology was utilized.

During experimentation, there were three different types of fusel oil samples available: wet fusel oils, dry fusel oils, and lab dried fusel oils. Wet fusel oils were taken directly from the rectifier, as they were, still containing excess water and contaminates. The dry fusel oils were dried specifically for use at the Cummins laboratory, and had excess water and contaminates removed. However, the samples provided for experimental use were older, and may have reabsorbed some water from the atmosphere. Finally, lab dried fusel oils were created as an intermediate to the wet and dry fusel oils, using molecular sieves to remove approximately 5% by volume water from 3 liters of wet fusel oils.

The team was tasked with determining a steam stripping and batch distillation design to separate the desired and undesired components of the fusel oils on hand. Steam stripping and batch distillation were the chosen methods of separation because both the lab and the winery already have access to these tools, making them economical options. A bench scale steam stripper and batch distillation column were set up in the Process Technology area of Cummins Lab to complete experimentation. Initially, the plan was to use batch distillation and then steam stripping, however, after careful analysis of the types of fusel oils being used and the types of equipment available, the experimentation method was adjusted appropriately.

Initial Proposed Methodology

The process initially designed required a distillation step that would separate Active Amyl, methanol, and n-propanol from n-Butanol, iso-Butanol, sec-Butanol, iso-Amyl, and water. These two groups each contain both desirable, fruity or sweet, and undesirable, hot or spicy, components. Due to differences in boiling point, the unwanted components could be separated from the desirable components in a second step--steam stripping. If necessary, a decanter could be used for further separation. The theoretical separation process is shown in Figure 4.

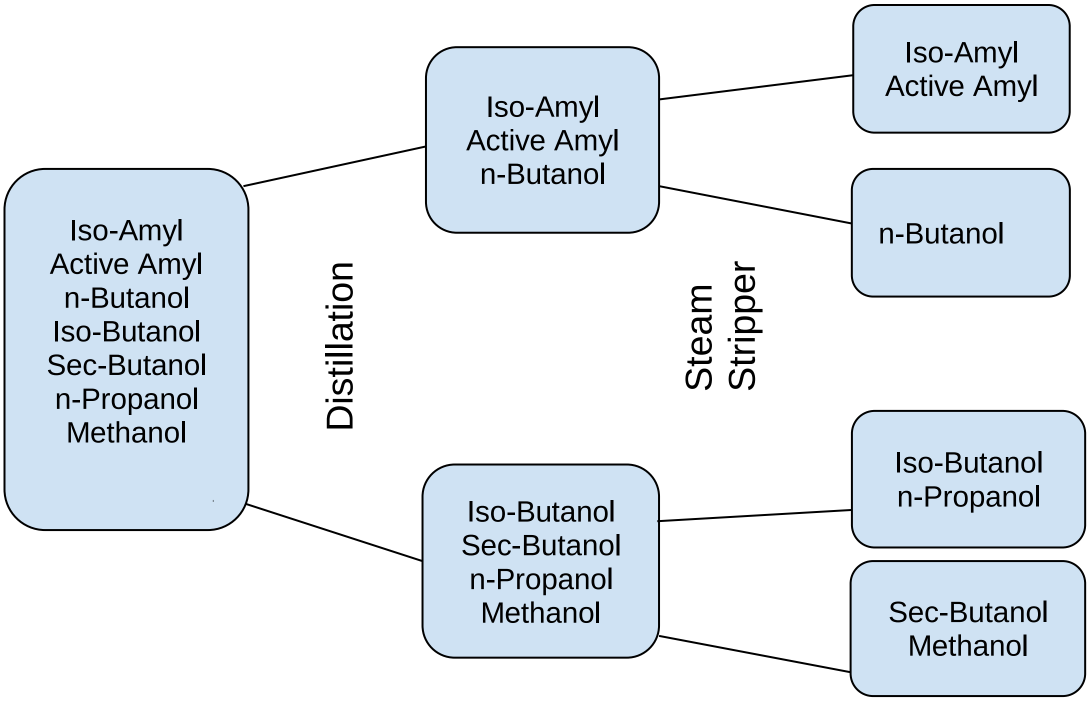

Figure 4: Theoretical Separation Process

However, after arriving at the lab and setting up the available equipment, it was quickly determined that the steam stripper and distillation tower would not provide enough heat to complete the desired separation. As a result, multiple batch distillation and steam stripping trials were completed to get a feel for how the limitations would affect separation, and a new methodology was established that better suited the hardware limitations.

New Methodology: Steam Stripping

The first benchtop experiments completed while on-site required building a bench-scale steam stripper from laboratory materials and then running the column. The instructions on how to set up and run the steam stripper are available in Appendix A.

When running the steam stripper, 500mL of liquid were fed into the column, ensuring that the overhead temperature did not drop below approximately 80^{o}C, as temperatures below this point would be less likely to provide adequate stripping capabilities. To combat decreases in overhead temperature, the feed was heated to approximately 55^{o}C-60^{o}C. The trial was allowed to run until the entire 500mL was fed, and the distillate and bottoms were then collected and their volume, mass, and pH were recorded.

Smoak Components

A sieve tray continuous distillation column was set-up to help with understanding how steam stripping would work with the lab equipment provided. The column was fitted with 10-15 stage sieve trays with a feed tube passing through a peristaltic pump system. The Smoak components were fed to the steam stripper as steam rose and engaged in an equilibrium exchange on the sieve trays. The stripped liquid components were directed to the bottom of the column where it was collected. The stripped vapor components were directed to the top of the column where the vapors were passed through a condenser and turned to liquid. Some of this liquid was fed back to the column as reflux and some was collected as distillate. Figure 5 shows the setup of the steam stripper used for the Smoak components.

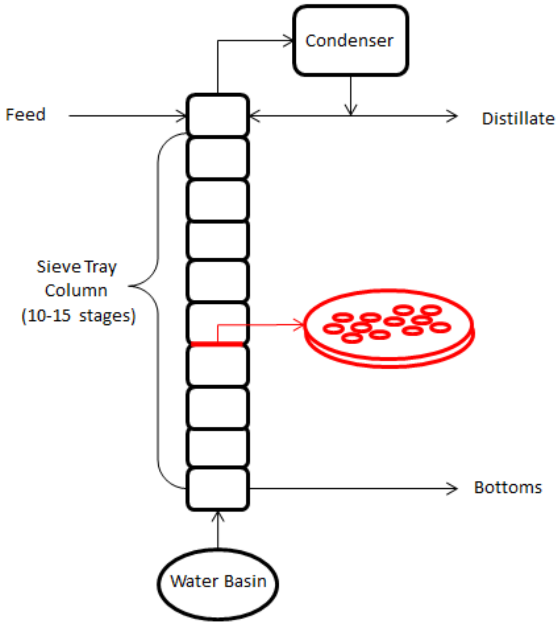

Figure 5: Experimental Setup of Smoak Component Steam Stripper

The steam was adjusted using a heater mechanism that was controlled by a voltmeter, which was called a PowerStat, shown in Figure 6. Voltages used for the heater ranged from 65 - 140 volts. The pump used to control the feed was kept within the range of 6-15 rpms (revolutions per minute).

Figure 6: Power Stat Used for Controlling the Heating of the Still

The steam stripper was initially run using CLT04, an unprocessed waste stream containing smoak components. This was done to get an understanding of how the column worked as well as provide valuable results for the Smoak Separation project. The smoak feed stream was initially transparent, so Valuable Dark Red (VDR), a grape component, was used to color the feed to a dark shade of pink. VDR is used in winemaking as a coloring agent, so it was expected to have negligible impact on the separation results and still comply with the component stipulations of wine. However, it was discovered that the VDR left solids in the CLT04 stream, and the impact of these solids was unknown. It was initially believed that the solids were oak particles, but after comparing the solid found in the bottoms and oak solids under a microscope, it was clear that this was not the case. Images of both materials can be seen in Appendix B.

Several trials were completed using the smoak component as the feed. Variations were made in the feed flow rate, which ranged from 6 rpm to 10 rpm, while all other parameters were kept constant. Samples from both the distillate and bottoms were collected and sent out to be analyzed. The results of the analyzation are shown in Appendix C, and Figure 7 shows the setup of the steam stripper used for the smoak components.

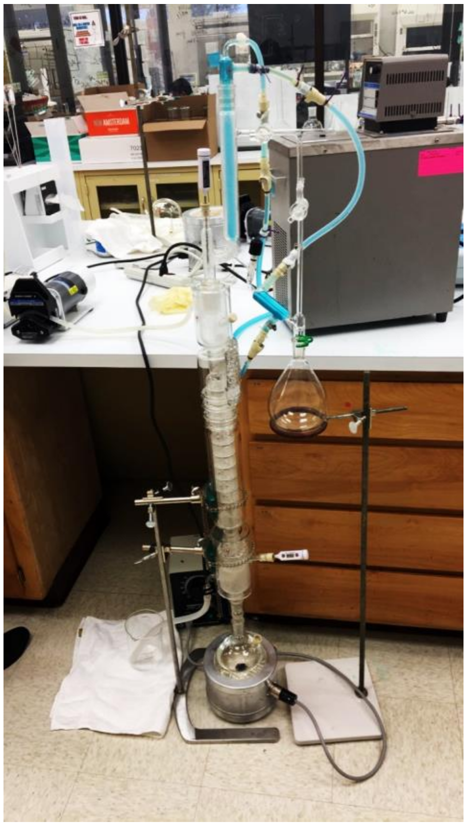

Figure 7: Steam Stripper Used for CT04 By-product Lab

Smell tests were done on both the bottoms and distillate samples to complete a sensory analysis. The samples taken from the distillate had a stronger alcohol smell, as was expected, because alcohol is more volatile than water, meaning it was more likely to come off the top of the column. This was corroborated by the lab results, which showed that most of the distillate samples contained predominantly furfural and furfural alcohol. The distillate was also clear, as the color components in the VDR were too heavy to transform into the vapor phase. Additionally, the samples collected from the bottoms had a significantly weaker smell than the distillate samples for the same amount of volume. However, the smell among each distillate sample and among each bottoms sample were very similar. The smells were reminiscent of oak, which was supported by the fact that the smoak material gets its scent from oak tannins.

After completing several trials of steam stripping, the initial feed was fortified, taking the ethanol content from about 7% to about 10% by volume. These variations with the feed were intended to see how the different levels of ethanol affected the overall separation. The results and calculations completed for these trials are also shown in Appendix C.

Fusel Components

A similar method was used for steam stripping the fusel oils, however, a different column was used. A three stage valve tray was used in place of the sieve trays. Figure 8 shows the setup of the steam stripper used for the fusel oil components.

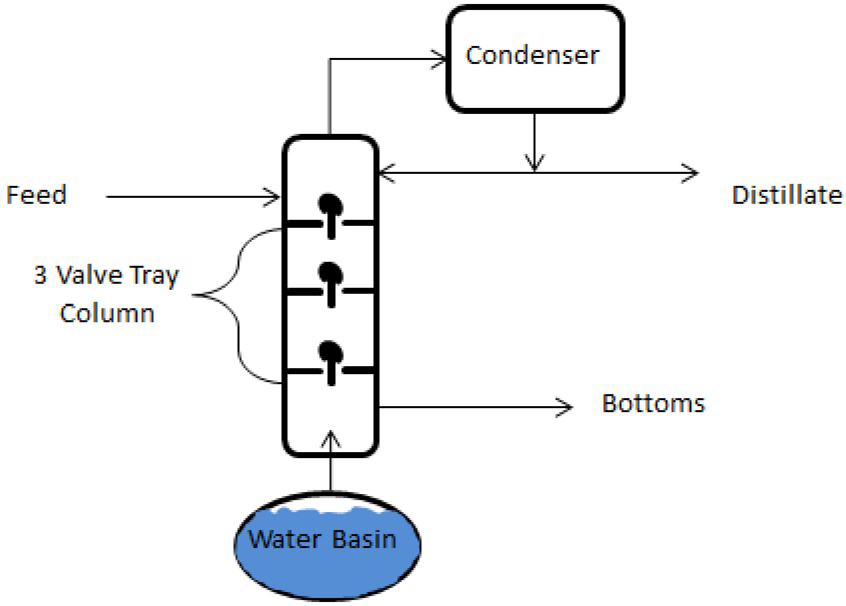

Figure 8: Experimental Setup of Fusel Oil Component Steam Stripper

New Methodology: Batch Distillation

After the fusel oil components were steam stripped, the bottoms was charged to a batch distillation still. The distillation column had a packed column filled with Pro-Pak© packing. Pro-Pak© packing is a high efficiency packing that offers increased contact between the fusel vapors rising and the condensed liquids going down the column. Some of the condensed liquid was collected as distillate, and the liquid in the still pot after operations was collected as the residual. Figure 9 shows the setup of the batch still used for the six components, and Figure 10 shows the type of packing used.

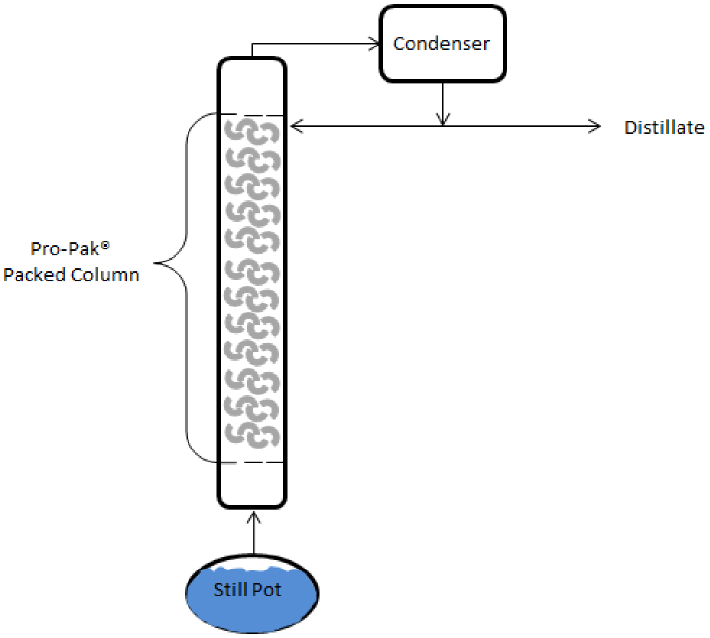

Figure 9: Experimental Setup of Batch Still used for Steam Stripped Fusel Oil components

Figure 10: Pro-Pak© Packing used in Batch Still

In order to determine the actual compositions of the output streams of trials completed, the samples were sent to Gallo’s analytical lab for testing. Tests searching for smoak (smoky-aroma) were utilized on the smoak samples, and tests searching for the alcohol content, refractive index, moisture content, and periodically the fusel oil breakdown were completed for the fusel oil samples.

Following the steam stripper trials, a batch distiller was set up. The body of the distiller was equipped with Pro-Pak© packing that made the tower and its approximately 17 theoretical stages very efficient. The theoretical number of stages for the batch distillation column was found using the diameter of the batch distillation column. The column had a diameter of one inch and was given by the manufacturer. The packing height of the Pro-Pack Packing was determined using a measuring tape to get an approximate packing height. The number of theoretical stages (N) of the column was calculated to help determine an approximate efficiency of the column, which can be used later on to determine if scale-up procedures will yield similar results to those collected during these trials. The HETP method was utilized, and stage calculations can be found in Appendix D. The batch distillation trials distilled 500-750 mL of fusel oils in the still for about 45-90 minutes, while varying the voltage control, which effectively varied the reboiler duty. This volume was chosen because it would create a large enough final sample that, if desired, further separation could be completed in addition to sending a sample to the lab for analysis. The varying reboiler duties were chosen to generate data to help find the optimum distillation conditions. The distillation column used is shown in Figure 11.

Figure 11: Packed Column Batch Distillation Tower Used in Lab

There were trials completed using “wet” fusel oils, which still contained water and contaminant; dry fusel oils, which had excess water removed; and fusel oils that were dried from the wet fusel oil supply using molecular sieves. The wet fusel oils were dried to get an idea of how much water was in the supply, and approximately 100 mL of water was removed from 3 liters of the wet fusel oils. Between running each type of sample, the column was cleaned by boiling 200 mL to 300 mL of ethanol with 500 mL of water through the column. This ensured that there were little to no contaminates within the column between the trials. A voltage range of 70-90V on the PowerStat, proved sufficient for boiling the liquid in the still. The PowerStat controlled the heat sent to the heating unit, and thus the reboiler duty. Lower temperatures were unable to create the steam necessary to move up the column, while higher temperatures proved too volatile for the diameter of column available, resulting in flooding, which is liquid hold-up on top of the packing in a packed column that can then bubble into the condensate (Kister, 1992). If the diameter of the column was wider, it might be possible to provide more heat to the still and evaporate some of the heavier components in the fusel oil base faster than with the narrower column.

Aspen Simulations

Aspen Plus and Aspen Batch Simulation software were used to initially understand the separation that could possible occur. Aspen Plus was used to understand how continuous separation would work for steam stripping, and the Aspen Batch Simulation would more closely model how the batch distillation column worked. To adequately model any system in Aspen, and get useful data, the physical conditions of the column such as temperature and pressure need to be known. These values were assumed to be 25 C and 15 psi for the feed and 5 psi for the top tray when simulating the steam stripper. Only the feed temperature could be used in the simulation with any certainty. For the Aspen Batch simulation, parameters such as the type of packing were not inputted and as such any results obtained would be uncertain.

Simulations are a useful tool to understand the expected results of distillation, however, to adequately simulate certain parameters are needed. The recommendations section of this paper highlights some of the ways parameters can be measured, that may help to accurately run Aspen simulations for both the steam stripping and batch distillation.

Results and Discussion

Batch Distillation

Samples of the distillate and residual from each trial were sent to the lab for analysis. Full lab results can be seen in Appendix E. While completing the trials, it was noticed that the dry fusel oils produced a more consistent overhead temperature than that produced by the wet fusel oils. This might have been caused by the water in the wet fusel oils. The increased amount of water meant that there was less room for the lighter keys, so as the more volatile components vaporized, more water was able to vaporize as well, increasing the temperature of the vapor going to the head of the column. It was also noticed with the wet fusel oils that by the end of a trial, the color in the still changed from a pale green to a dark yellow. It is highly possible that some of the contaminants causing the green color were vaporized, thus changing the color in the still. The results for each type of fusel oil are described in more detail in their accompanying sections.

Wet Fusel Oils Results

As a whole, the wet fusel oils had a significantly lower percentage of n-propanol than that found in the dry fusel oils, the composition of which was shown in Figure 2. There were 3 wet fusel oil trials completed, all of which ran for 45 minutes each, varying the voltage to the Power Stat. There was also a fourth batch distillation trial that was allowed to run for 134 minutes. These trials were completed to see how the variation in reboiler duty and time for distillation would affect the separation potential. Due to a miscommunication, only one set of samples from the first three wet fusel oil trials were submitted for fusel oil testing. However, based on an understanding of the how the reboiler duty affects separation, the composition breakdowns for the first three trials were expected to be approximately the same. Submitting samples from the other two trials may provide valuable results and should be considered The composition of the residual for the trial completed at 90V is shown in Figure 12.

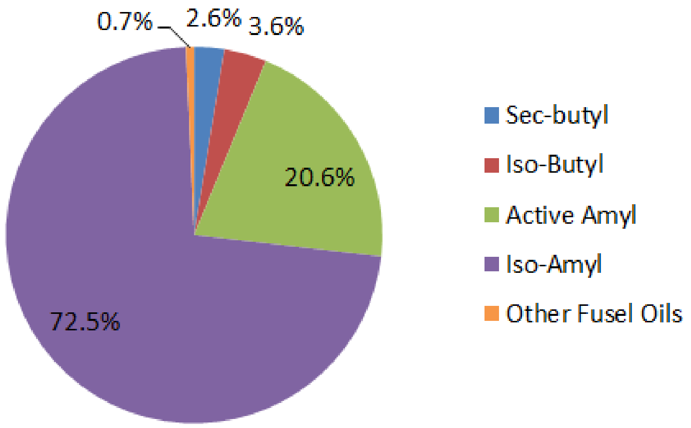

Figure 12: Residual of Wet Fusel Oils Distilled at 90V for 45 Minutes

The residual product contained approximately 72.5% Iso-Amyl and 20.6% Active Amyl. The remainder of the residual was about 7% sec-butanol, iso-butanol, and other fusel oils, which were those components that were not given a definitive value to their composition. The minimal amount of lighter fusel oils in the residual is a sign of relatively good separation. However, better separation would have all but isolated the active and iso-amyl, which were the heavier components.

While the separation present in the residual was decent, the separation shown in the distillate was less than satisfactory. As shown in Figure 13, about half of the distillate composition was active and iso-amyl.

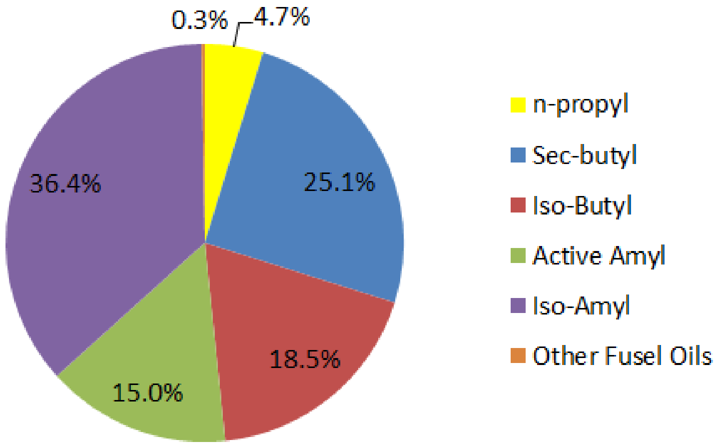

Figure 13: Distillate of Wet Fusel Oils Distilled at 90V for 45 Minutes

The relatively high concentration of n-propanol, sec-butanol, and iso-butanol is favorable, but the high concentration of active amyl and iso-amyl is both unfavorable and surprising. Based on the compositions found in the residual, it was expected that there would be little to no active amyl or iso-amyl in the distillate. It was noticed that there were light components present in the residual at the same time that there were heavy components in the distillate, which was unexpected. In order to see if better separation could have occurred in each sample type, future experiments adjusting the time allowed for distillation would be valuable. Suggested times include 15 minutes and 30 minutes to see what time frame would leave minimal active and iso-amyl in the distillate.

The other trial completed using the wet fusel oils was the extended trial, which ran for 134 minutes. The separation obtained in this trial was almost as mediocre as the separation for the previous wet fusel oil trials. However, the residual had an even lower concentration of sec-butanol, iso-butanol, and other fusel oils than the previous trials, meaning that the further separation of active and iso-amyl would be less contaminated. The composition breakdown for the residual is shown in Figure 14.

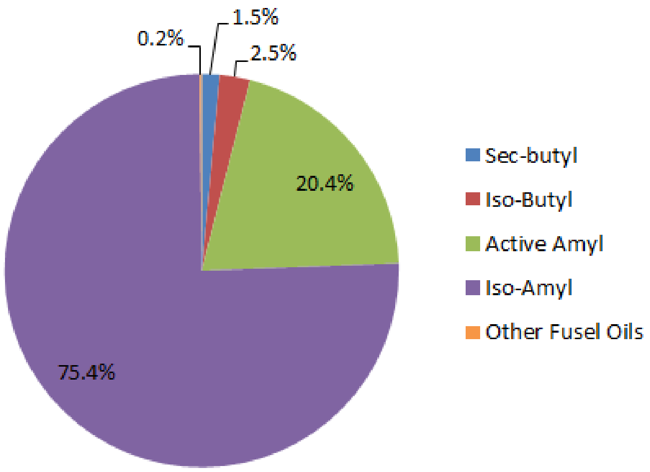

Figure 14: Residual of Wet Fusel Oils Distilled for 134 Minutes

Over the duration of the trial, there were three distillate samples collected, and each sample was 100 mL in volume. The first distillate sample had the least amount of active and iso-amyl, for a combined 34.7% total. The combined percentage of active and iso-amyl in the distillate increased as each sample was taken, rising to 52.1% in the second distillate sample and 61.8% in the third distillate sample. As a result, the first sample exhibited the best separation of the light and heavy keys, and supported the notion that a shorter time frame would be better to separate active and iso-amyl from the other fusel oil components. More detailed composition breakdowns for the distillate samples are shown in Figures 15-17.

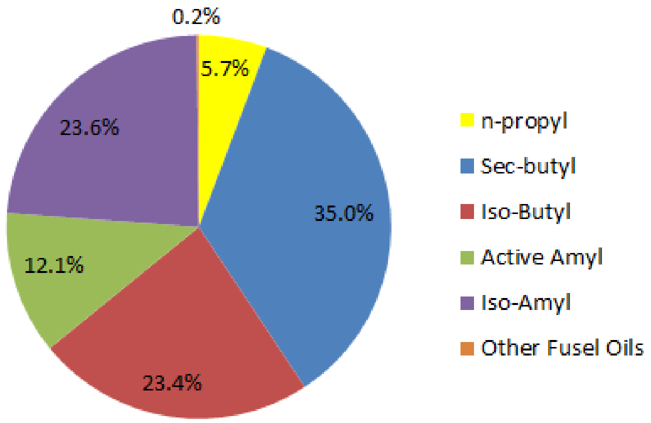

Figure 15: Distillate 1 of Wet Fusel Oils Distilled for 134 Minutes

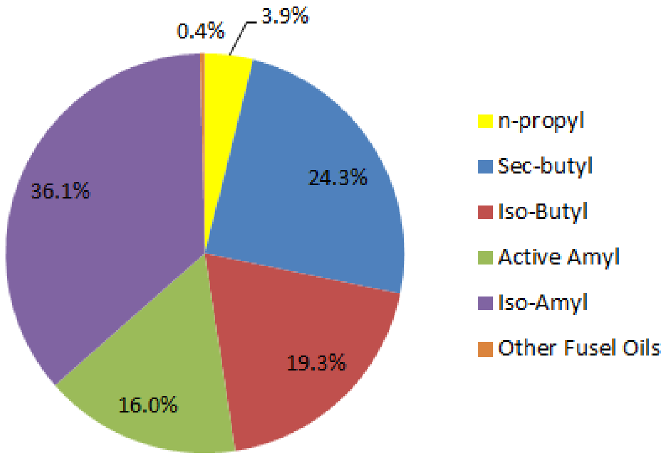

Figure 16: Distillate 2 of Wet Fusel Oils Distilled for 134 Minutes

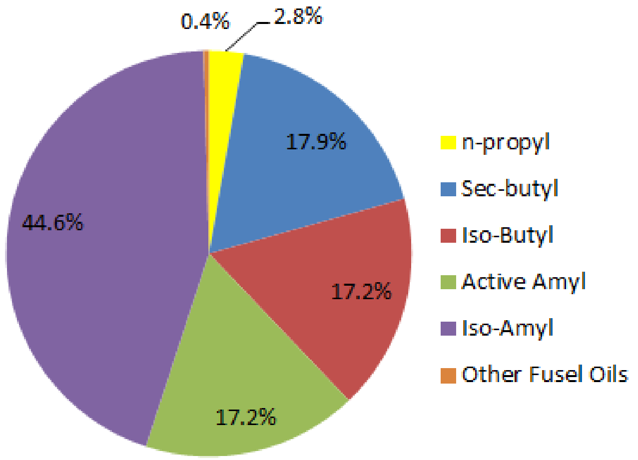

Figure 17: Distillate 3 of Wet Fusel Oils Distilled for 134 Minutes

Comparing the results from the first set of wet fusel oil trials and the extended trial, it is clear that at least one trial should have been completed for a shorter time span. Unfortunately, due to the amount of time it took to complete the fusel oil analysis on this idea was not formulated in time to be put into action.

Dry Fusel Oils Results

The dry fusel oil trials were run for 45 minutes each, varying the voltage to the Power Stat from 80V to 95V. Unfortunately, due to the same miscommunication mention under the We Fusel Oils Results section, only the 95V sample set was submitted for fuel oil testing. Looking at the results, it appears that batch distilling the dry fusel oils appeared to do a decent job separating n-propanol, iso-butanol, and sec-butanol from the other fusel oil components. The bottoms separation for the 95V sample set is shown in Figure 18.

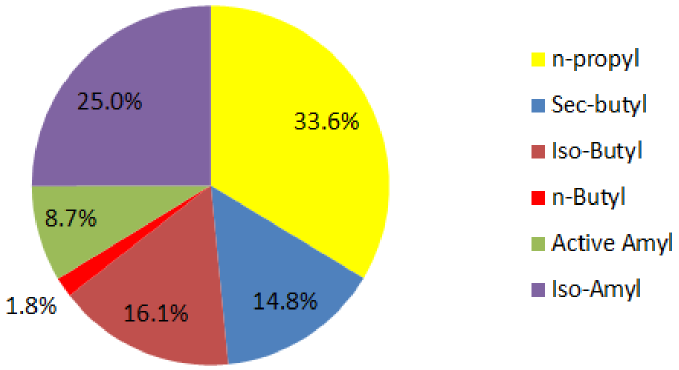

Figure 18: Residual of Dry Fusel Oils Distilled at 95V for 45 Minutes

There is still a significant amount of n-propanol, iso-butanol, and sec-butanol in the residual, but it is likely that if the trial had been allowed to run for a longer period of time, more of these lighter keys would have separated into the distillate. This would have left n-butanol, active amyl, and iso-amyl in the bottoms, meaning the separation would have looked more like that shown in the initially proposed methodology. The current composition of the distillate is shown in Figure 19.

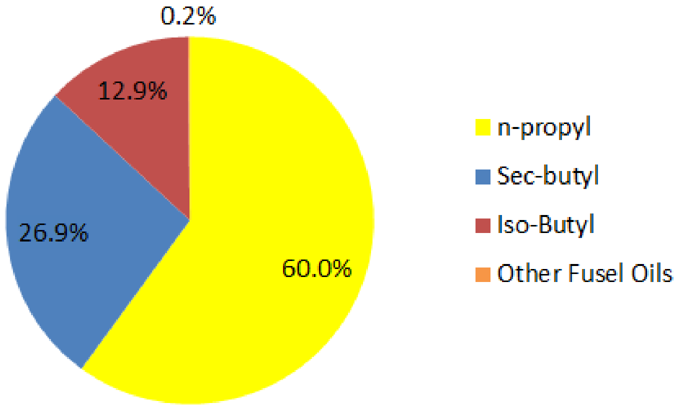

Figure 19: Distillate of Dry Fusel Oils Distilled at 95V for 45 Minutes

The boiling points of n-propanol and sec-butanol are very close, at approximately 98^{o}C, while the boiling point of iso-butanol is approximately 108^{o}C. As a result, it should be possible to further separate these components, perhaps through the use of a rotary evaporator. Because the dry fusel oils were processed to specifically remove water, it would be counter-intuitive to steam strip the residual or distillate to isolate n-butanol and iso-butanol, but completing a second round of distillation might provide the desired separation.

Lab Dried Fusel Oils Results

The lab dried fusel oils were produced by removing approximately 5% by volume of water from the wet fusel oils using molecular sieves. It is highly possible, however, that there was still water remaining in the final product, as the molecular sieves are only able to remove so much water. Regardless, trials involving the lab dried fusel oils showed that a heteroazeotrope occurred at approximately 90^{o}C. As a result, samples collected when the overhead temperature was higher than 90^{o}C had two liquid layers. Samples of these layers were sent for analysis, and the different layers were found to have a mostly conclusive concentration breakdown in both layers, which was unexpected based on previous results. The compositions for both distillate samples were very similar to the breakdown shown in Figure 13. Additionally, the residual composition was almost identical to that shown in Figure 12. For comparison purposes, the composition breakdowns for the lab dried fusel oil test samples are shown in Figures 20-22.

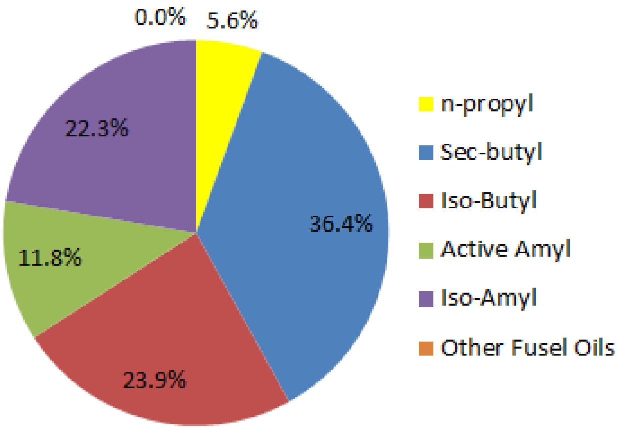

Figure 20: Residual of Lab Dried Fusel Oils Distilled at 80V for 90 Minutes

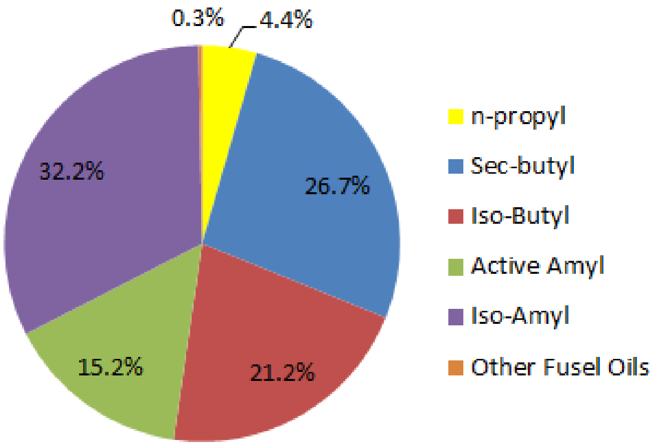

Figure 21: Distillate 1 of Lab Dried Fusel Oils Distilled at 80V for 90 Minutes

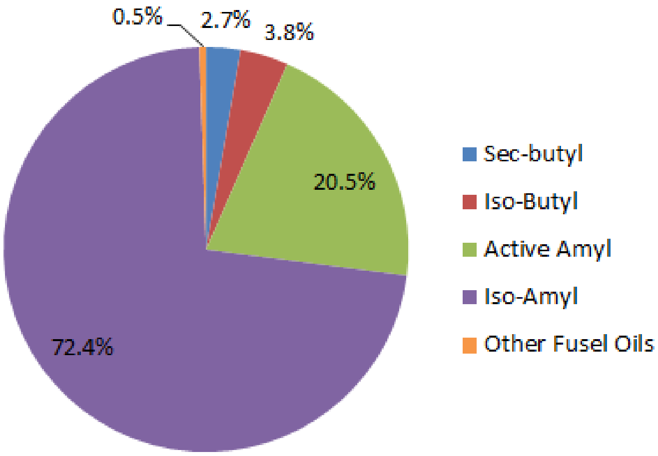

Figure 22: Distillate 2 of Lab Dried Fusel Oils Distilled at 80V for 90 Minutes

In addition to the varying reboiler duty trials, the lab dried fusel oils were used in a second long trial, where they were distilled for 271 minutes. The goal of this trial was to continue collecting distillate until after the overhead temperature reached the 100°C mark. There were three distillate samples collected; the first two samples were 100 mL and the third sample was 75 mL. The third distillate sample collected exhibited a heteroazeotrope and had two layers that were separated in the separatory funnel. The two layers were submitted for wine headspace aroma testing, but the results have yet to come in as of the submittal date of this report. The samples from this trial appear to have obtained the most desirable separation of all trials completed, with the bottoms containing a combined active and iso-amyl composition of 99.4% and 0.6% being other fusel oils. This composition breakdown is shown in Figure 23.

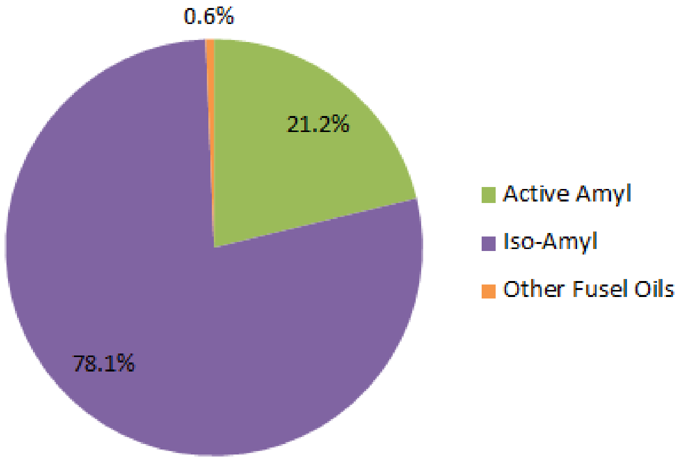

Figure 23: Residual of Lab Dried Fusel Oils Distilled at 80V for 271 Minutes

The two distillate samples also had relatively good separation, with the first distillate sample, shown in Figure 24, having only 21.7% active and iso-amyl and the second distillate sample, shown in Figure 25, having 33.9% active and iso-amyl.

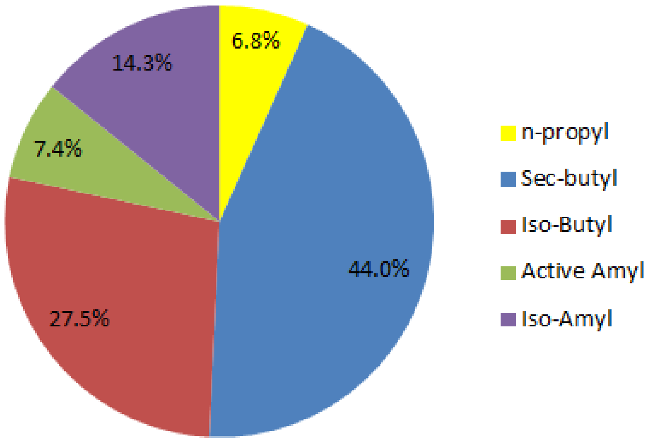

Figure 24: Distillate 1 of Lab Dried Fusel Oils Distilled at 80V for 271 Minutes

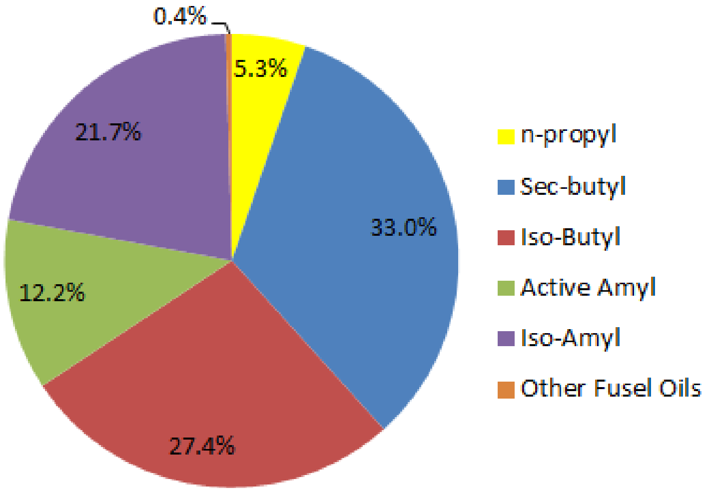

Figure 25: Distillate 2 of Lab Dried Fusel Oils Distilled at 80V for 271 Minutes

As expected from the shorter distillation times of 45 or 90 minutes, the first distillate sample had lower percentages of the heavier keys. However, the longer distillation time of 271 minutes can be looked at as a trade-off to get better separation in the residual. In larger quantities, this process may prove to be worthwhile and produce a significant amount of usable active and iso-amyl.

Adjusted pH Fusel Oils Results

After completing several batch distillation trials, it was noticed that the pH of each distillate sample would be relatively neutral and close to the feed pH, which was approximately six or seven. However, the residual pH would generally be lower, usually around five. Because of these trends, pH adjusted trials were completed. The pH of some samples was reduced to 2.15 using sulfuric acid while the pH of the other samples was increased to 12.34 and 13.12 using potassium hydroxide. The trials completed were allowed to run for 90 minutes, however, the second decreased pH trial was only allowed to run for 68 minutes due to the escape of vapors from the bottom of the still.

The purpose of these tests were to see if adjusting the pH would affect the volume of distillate or residual collected, how the change in pH would affect the final distillate and residual pH, and if it would aid separation. After analyzing the volume, mass, and pH of the collected samples, it was clear that adjusting the pH had a minimal effect on how much distillate was collected. Figure 26 compares the volumes and pH values for each pH adjusted trial compared to an unadjusted trial.

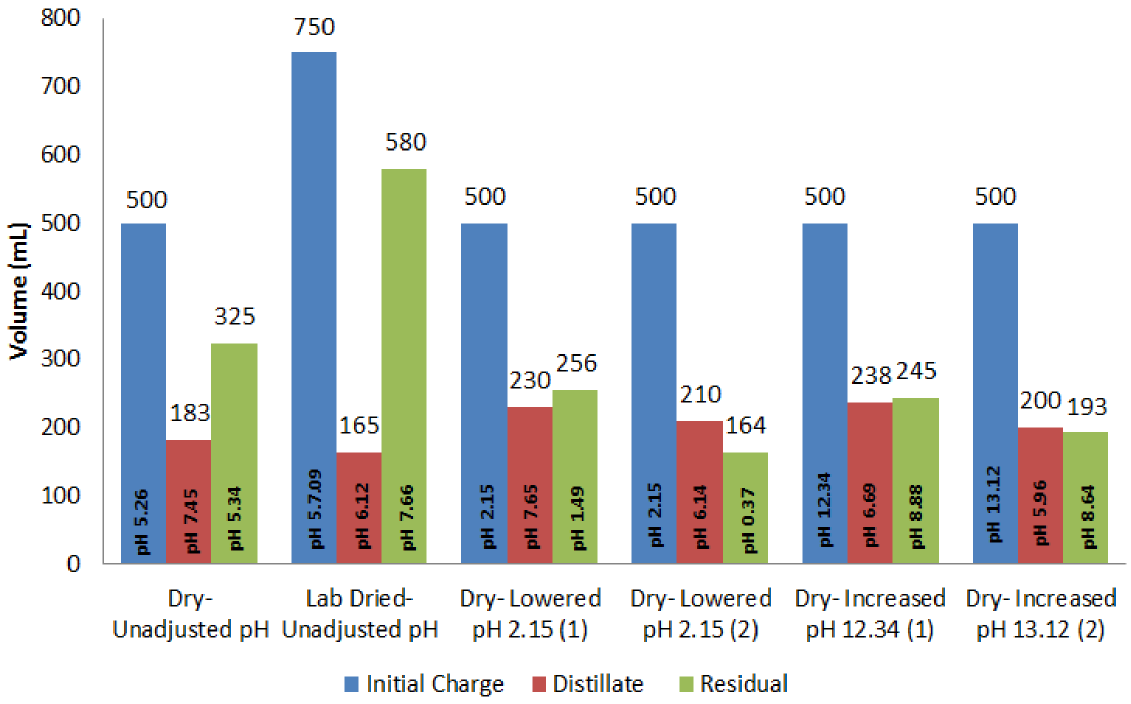

Figure 26: pH Adjusted Trials Compared to Non-Adjusted Trials

For each set of samples shown, all trials were run for 90 minutes, with the exception of Dry-Unadjusted pH and Dry-Lowered pH 2.15 (2), which were run for 45 and 68 minutes respectively. The Dry-Unadjusted sample was added to Figure 25 to show how the trials occurred under regular circumstances. The Lab Dried-Unadjusted sample was shown to give a time span comparison. With that information, the data suggests that pH adjusting increases the amount of distillate collected. However, over the span of 45 minutes, the dry-unadjusted sample was able to collect 183 mL of distillate while the pH adjusted samples collected 200-238 mL of distillate, which is not a proportional increase in volume.

In addition to the slight distillate volume change, it was noted that the pH of the residual was greatly impacted by the pH adjustment. Similar to the non-pH adjusted trials, the final pH of the distillate was close to neutral, ranging from approximately 6-7.6. The pH of the residual tended to vary more greatly, unlike that of the distillate. For example, in the Dry-Increased pH 13.12 (2) trial, the pH of the initial charge was 13.12, and the pH of the residual dropped to 8.61, a 4.5 drop in pH. This change in pH may prove to have an impact on separation, potentially also causing reactions that will change the flavor components in the fusel oil sample.

While the pH adjustment did not have a major impact on the volume of distillate collected, the impact on the separation was noticeable. For example, the pH adjusted trials were the only trials in which n-butanol showed up with a definitive concentration value in the results. In both the low pH and high pH residual samples, the composition was approximately 2% n-butanol, 10% active amyl, and 30% iso-amyl. The composition breakdowns are shown in Figures 27 and 28.

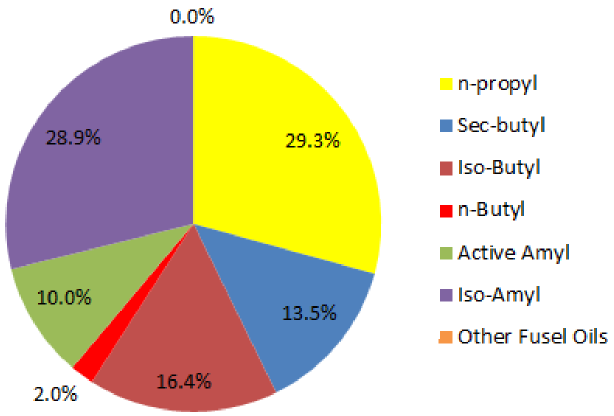

Figure 27: Residual of Low pH Dry Fusel Oils Distilled at 85V for 90 Minutes

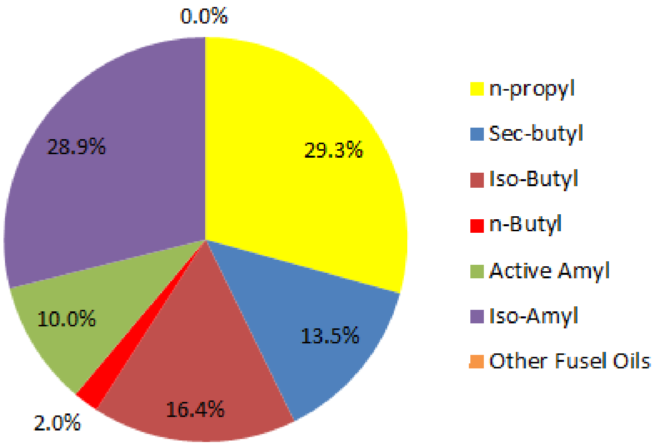

Figure 28: Residual of High pH Dry Fusel Oils Distilled at 85V for 90 Minutes

While it was a new development to see the n-butanol in the residual, the high concentration of the light keys suggests that the samples could have been distilled for a longer period of time. On a positive note, the amount of time allowed for distillation prevented any active or iso-amyl from going into the distillate, which is promising for future separation. The composition breakdown of the low pH distillate sample is shown in Figure 29.

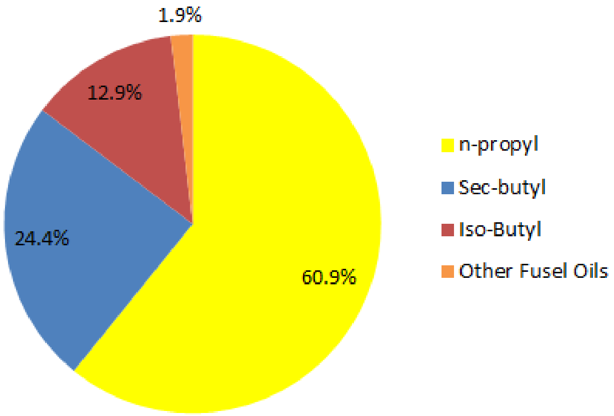

Figure 29: Distillate of Low pH Dry Fusel Oils Distilled at 85V for 90 Minutes

Unfortunately, the results for the high pH distillate sample were not returned in time for the submittal of this report, but based on the similarity between the low and high pH residual samples, it was expected that the low and high pH distillate samples would have similar compositions. However, it would be interesting to see how if the pH differences had an effect on the flavor qualities in the samples.

Relationship of Type of Fusel Oil With Average Overhead Temperature

There was a relationship between the type of fusel oil and the average overhead temperature that was noticed during experimentation, and it was something that the team wanted to better understand. Looking at trials that ran for 45 minutes, with the PowerStat maintained between 80-90 V, it was noticed that the wet fusel oils achieved the highest average overhead temperature of 90°C, while the dry fusels achieved the lowest of 84°C. The lab dried fusels fell in the middle range with an average overhead temperature of 86°C. Each fusel oil type contained a different percentage by volume of water. The wet fusels contained the most water and the dried fusels contained the least. The dried fusels had about 5% by volume of its water removed. The relationship between the type of fusel oil and the average overhead temperature can be observed in Figure 30.

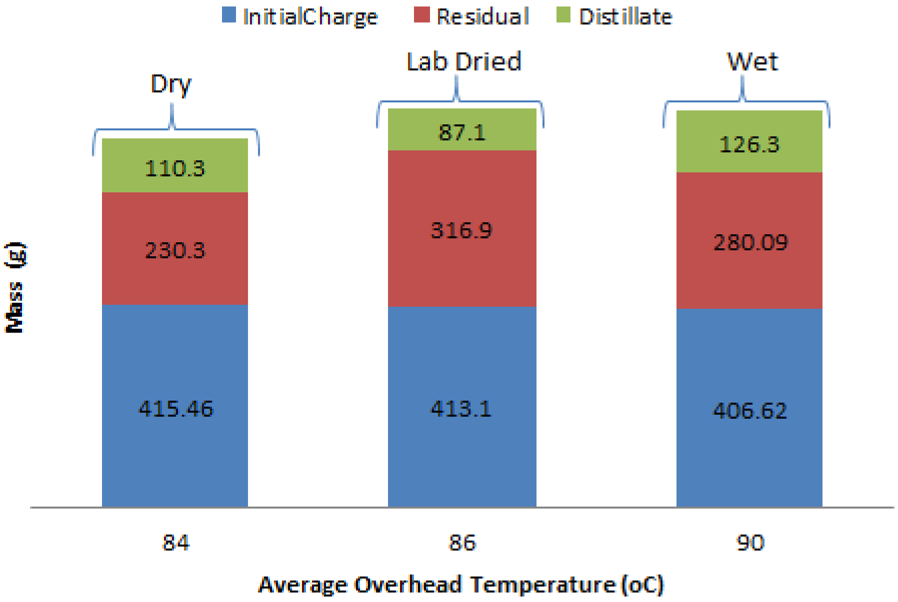

Figure 30: Mass of Distillate and Bottoms Produced From Varying Overhead Temperatures in 45min Batch Trials

The more water fusel oils contain, the less space that exists for the lighter components. These lighter components are more volatile and will vaporize at lower temperatures. Therefore, if there are less lighter components, there should be more heavier components. In the case of the dry fusel oils, there was less water and the lighter components were able to vaporize first, meaning that within a 45 minute time frame, the overhead temperature was only able to reach 84°C. On the other hand, the wet fusel oils had the most water, meaning the lighter components vaporized more quickly, which allowed the heavier components to vaporize faster. As a result, the overhead temperature for the wet fusel oils was able to reach 90^{o}C.

The mass of distillate and residual products were also of importance. The lab dried fusel oils produced the heaviest residual, but the lightest distillate. The wet fusel oils produced more residual than the dry fusel oils, but less distillate. These results show that it is worthwhile to look further at how the percent volume of water present in the fusel oils affects the amount of product produced.

Sequential Distillation: Steam Stripping and Batch Distillation

The final tests completed had two steps. First, 500 mL of either wet or lab dried fusel oils were steam stripped. Various physical traits were measured, including pH, volume, and mass. During the steam stripping process, it was noticed that there were two stages in both the bottoms product and the distillate, caused by a heteroazeotrope. However, only one layer of the bottoms had enough material to batch distill. For each batch distilling trial, this volume was taken and allowed to undergo distillation until it was noticed that there was vapor escaping from the connection between the column and the still. The first (wet fusel oils) and second (lab dried fusel oils) distillation trials were allowed to run for 47 minutes and 38 minutes respectively. The full results for these trials can be seen in Appendix F.

Steam Stripping

Wet fusel oils were steam stripped according to the parameters previously described using the column shown in Figure 31. It was found that when the overhead temperature stayed at approximately 90.9^{o}C, both the bottoms and distillate had two distinct liquid layers. These layers were separated using a separatory funnel, and the larger of the two bottoms samples was later batch distilled. The samples collected were sent to the analytical lab for fusel oil analysis.

Figure 31: Valve-Tray Steam Stripper Used for Fusel Oil Steam Stripping

The lab results for the bottoms of both the steam stripped wet and lab dried fusel oils were nearly identical, as was expected based on how little water was removed from the wet fusel oils during the creation of the lab dried fusel oils. Both samples were approximately 71% iso-amyl and 20% active amyl, so if this separation process is good at anything in particular, it is concentrating these undesired components. The composition breakdowns of these steam stripped samples can be seen in Figure 32.

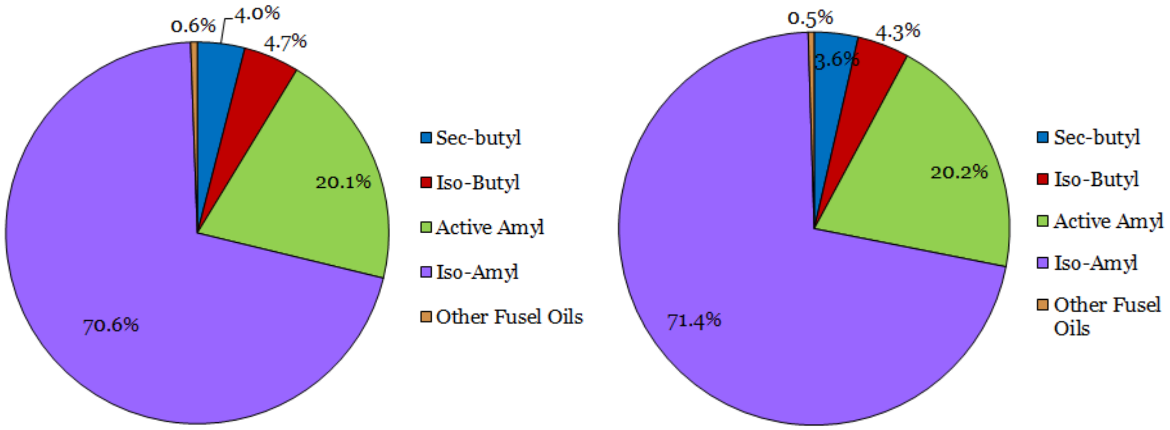

Figure 32: Steam Stripped Bottoms for Wet (left) and Lab Dried (Right) Fusel Oils

The data showed that there were small amounts of the more volatile components left in the bottoms, which was expected as a result of the heating capabilities of the still as well as the number of stages in the column. Had the steam stripper been able to provide more steam or more liquid vapor contact time, it is likely that there would have been a smaller concentration of iso- and sec-butyl in the bottoms, and a higher concentration in the distillate. In addition to the bottoms composition shown in Figure 32, there was a second bottoms layer collected. However, the data from both the wet and lab dried samples was not conclusive, giving no definitive value on any component.

While the concentration in the bottoms product contained a combination of about 75% iso- and active amyl, the distillate contained about 66%, which, while still high, is still some separation. In small concentrations, iso-amyl can give a banana flavor, so it is still possible that this composition would be acceptable for ingredient development in the future. The breakdown of the distillate for both steam stripped wet and lab dried fusel oils can be seen in Figure 33.

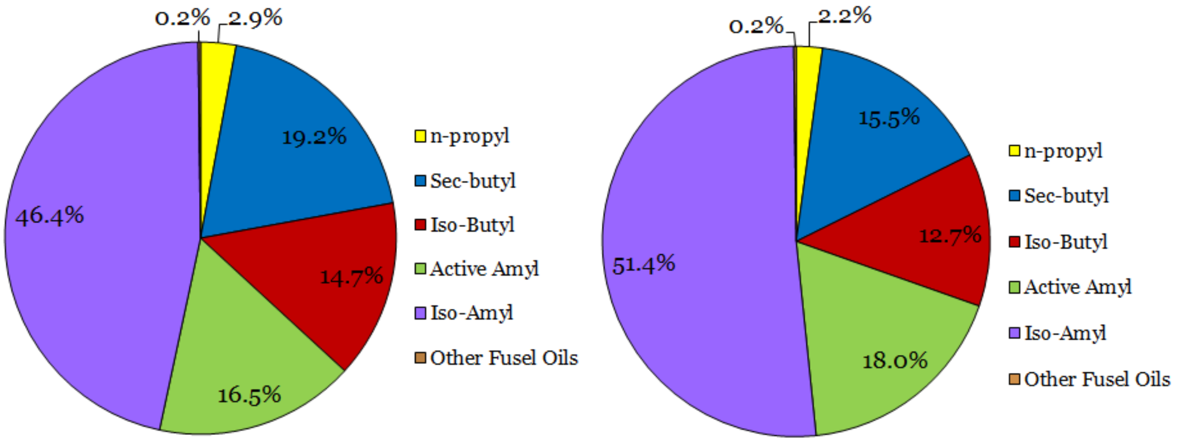

Figure 33: Steam Stripped Distillate for Wet (left) and Lab Dried (Right) Fusel Oils

In addition to the distillate shown in Figure 33, there was a second distillate layer collected. However, the data from both the wet and lab dried samples was significantly less conclusive, containing about approximately 31% sec-butyl, 17% iso-butyl, 36% iso-amyl, and 17% other fusel oils.

Batch Distilling

After completing the two steam stripping trials, one with wet fusel oils and the other with lab dried fusel oils, the viable bottoms samples were saved and batch distilled. Unfortunately, the results obtained from batch distilling the steam stripped products were only available for the wet fuel oils at the time of the report submittal. However, based on the similarities shown in the steam stripped results, it is expected that the batch distillation results for both the wet and lab dried samples will also be similar. The results for the residual can be seen in Figure 34.

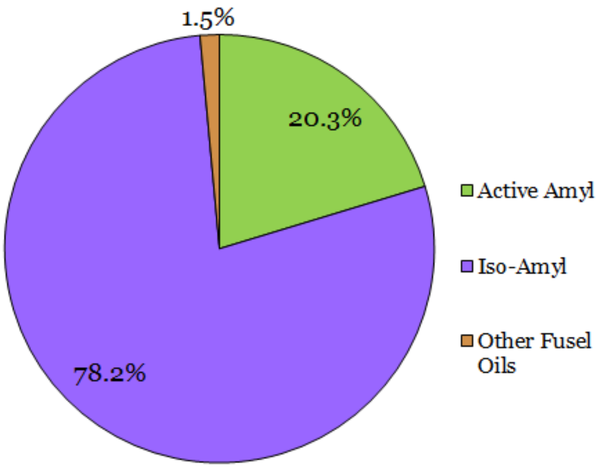

Figure 34: Batch Distilled Bottoms for Wet Fusel Oils

The residual was shown to be very concentrated in both active and iso-amyl, which suggests that batch distillation is a decent method for separating these two components from the lighter keys in fusel oils. The 1.5% other fusel oils are present in a small enough amount that they should have little impact on further separation of this product, should it be desired. However, if deemed necessary, putting the sample through a rotary evaporator should be sufficient in removing the remaining lighter keys.

Because the residual showed almost only active and iso-amyl, it was expected that the distillate would show almost only the sec- and iso-butanol along with n-propanol. Unfortunately, the distillate had a combined 56.2% concentration of active and iso-amyl. The distillate concentration breakdown is shown in Figure 35.

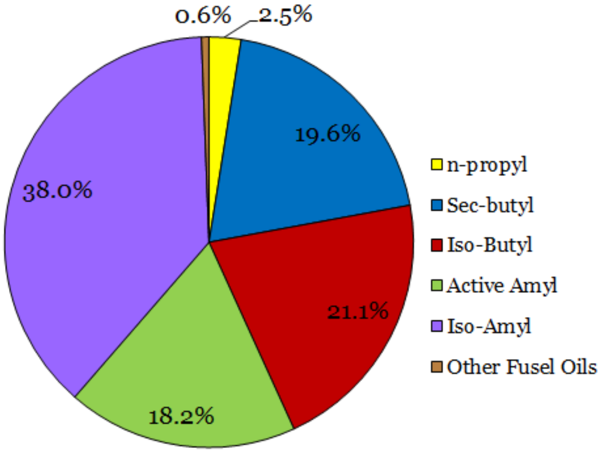

Figure 35: Batch Distilled Distillate for Wet Fusel Oils

Based on the results provided, the separation of the different components of fusel oils was mediocre, at best. However, it is important to note that as distillation continues, the concentration of heavier keys in the distillate increases. As such, it is likely that the sample was allowed to distill for too long, resulting in both active and iso-amyl making it into the distillate. If the temperature of the still had been able to be monitored, it would have been possible to ensure that the temperature did not rise above 110^{o}C, the highest boiling temperature of any fusel oil component before active and iso-amyl.

Aspen Simulations

Both the steam stripper and batch distillation column were modeled using Aspen software. However, it was not possible to exactly model the steam stripper a result of the limitations of Aspen and the overall design and setup of the steam stripper. As such, features were either added or removed to sufficiently model the column.

Continuous Process Aspen Simulations

There were several trial simulations of the fusel oil separation using both continuous and batch methods. For continuous simulations, UNIFAC calculations were utilized, and the effect of different reflux ratios and feed stages were analyzed. A summary of the compositions in the bottoms, distillate, and feed can be seen in Table 3. For all simulations completed, the feed temperature is 25^{o}C, the feed pressure is 1 atm, the distillate flow is 50 kmol/h, the pressure at the top of the column is 0.5 atm, and it is assumed that there are 40 stages in the column. The percent of component column indicates the amount of each component from the original feed amount in either the bottoms or distillate feed. Additional data from the continuous process simulations can be found in Appendix G.

Component	**x_B**	**% of component in bottoms**	**x_D**	**% of component in distillate**	**z_F**
Active Amyl	12%	**98%**	0%	2%	6%
Methanol	0%	0%	2%	**100%**	1%
n-Propanol	74%	26%	64%	**74%**	43%
n-Butanol	6%	**86%**	0%	14%	1%
iso-Butanol	70%	66%	11%	**34%**	16%
sec-Butanol	45%	37%	23%	**63%**	18%
iso-Amyl	30%	**99%**	0%	1%	15%

Table 3: Compositions for Continuous Simulation with L/D = 0.5 and Feed Stage = 20

Upon analyzing Table 3, it has been determined that a reflux ratio (L/D) of 0.5 with the feed entering at stage 20 provides simulation results most similar to the group's expected results. As such, these parameters would be a good starting point during benchtop testing to separate the different components of the fusel oils. Because n-butanol and sec-butanol are being considered as desirable for their fruity taste, further separation after the initial distillation step will need to occur in order to isolate these components.

In addition to the potential continuation in separation, it is to be noted that all of the isoamyl is removed in the distillate stream. As isoamyl is considered one of the most undesirable components of fusel oils, possible flavor experimentation may be completed on the distillate stream, upon removal of excess methanol. Methanol's high volatility makes separation relatively easy, making the additional separation more feasible. One could also continue experimenting with the bottoms stream for potential ingredient development in the future. A potential plan might involve mixing the resulting streams after the separation of iso-amyl and methanol, and adjusting the amount of the liquid added to wine to understand the effect on flavor. It would also be possible to simply use one of the resulting bottoms or distillate streams as a fuel source.

Challenges and Drawbacks

Over the course of our time at Gallo, there were some drawbacks that prevented extensive data analysis. The biggest issue corresponded with the fusel oil analysis testing and the corresponding time restraints brought on by a seven week term. Fusel oil testing is done on the gas chromatograph (GC), and the tests take 30 minutes to run, and must be completed 2-3 times to obtain viable results. The fusel oil testing que was already backed up, due to the time intensive nature of the testing, meaning that without a priority on our samples, it would have been impossible to get any results back while at Gallo. Without the fusel oil test, there would be virtually no indication of whether the separation completed was reliable or adequate. After speaking with Ravi, the head of process technology, it was possible to get a priority status on a handful of samples, but it was impossible to prioritize them all. As a result, there are still eight samples still awaiting results as of the time of the report submittal.

Additionally, the limitations on the bench scale equipment also hindered efforts to change parameters for separation. There were several limitations on the equipment: lack of ability to adjust pressure, lack of ability to adjust or completely control temperature, lack of ability to fully control reflux ratio on the distillation column, trouble getting steam to rise in the steam stripper, heating capability of the stills, and steam production. All of these limitations made it incredibly difficult to vary the separation parameters and find the best option available to separate the fusel oils. Should these limitations be addressed, then more thorough research and separation trials may be completed.

Conclusions and Recommendations

Overall, there were several key points and recommendations to be made. The most noteworthy conclusion was that the dry fusel oils showed the best potential for separation of the individual fusel oil components. The dry fusel oils had the most definitive composition value for n-butanol, which was a desirable component. It would be beneficial to have fresh dry fusel oils, to minimize the chances of moisture reabsorption. Drying the fusel oils would require more preparation in the future, but if better products can be obtained, the extra work would be beneficial. Unfortunately, with a few exceptions, it was common to find a combination of active and iso-amyl that comprised approximately 30-50% of the total distillate composition. These numbers are relatively unsatisfactory, as they show that the separation obtained was mediocre, at best. However, there is still potential for the other components to be utilized and make what little separation occurred worthwhile.

It was also found that separation times of 45-90 minutes or higher resulted in heavy components making their way into the distillate despite there still being light components in the residual. This was unexpected, and it is difficult to explain why this happened, however, it is our belief that with more experimentation this occurrence could be further analyzed. One possible explanation could be that the heavy components present in the distillate had been vaporized with the water that was contained in the fusel oils.

In addition to the potential benefits, there are also several recommendations to be made on behalf of this project. One recommendation is to ensure proper cleaning of all separation columns. Both the steam stripper and the batch distillation column required thorough cleaning to ensure that no material would be left behind to cause fouling. Especially in the steam stripper, it was noted in the lab results from the cleaned bottoms and distillate streams that, even after running 500 mL of water through the column, the resulting stream still contained various components that were present in the fusel oils. The batch distillation column also held some material, as noted by the strong smell of fusel oils coming from the column, even after evaporating 400 mL of ethanol through the still.

Another recommendation would be to continue completing both batch distillation and steam stripping trials while testing different components and scales. This will provide a better understanding of the changes that may occur when scaling up the process to production scale, should the process be taken that far. Additionally, different tools may also be considered. It was discovered with the wet fusel oils that flooding is a problem when the temperature gets too high (a voltage of 90V on the temperature control led to flooding). To combat this, it is recommended that pressure gauges are utilized along the column (Wankat, 333), as this will alert the operator of any pressure buildup in the column.. Should this process be taken to production scale, an automatic heat shut-off may also be beneficial to drop the heat quickly. Steam traps would also prove useful during steam stripping, because the current column requires as much steam as possible to obtain the best separation, and a significant amount of steam was lost to the atmosphere during testing.

One of the final recommendations is to look more into azeotropic distillation. From azeotropic distillation, the two liquid layers obtained during distillation from what we saw could result in more superior separation. than what is currently being achieved. However, this type of separation process is more involved, and may require additional tools.

Upon completion of this project, E&J Gallo was left with a methodology that allowed for the separation of the different components of fusel oils. The desired components have the potential to be utilized in flavor development, and the undesired components can be further developed and used as fuel. As an alternative, the fusel oil components also have the potential to be used in other experiments, thus saving on the costs of purchasing some chemicals. The creation of new sensory components for wine or other spirits produced by E&J Gallo will open doors for new production processes and products, and therefore new markets for profit. Additionally, the processes designed for this project utilize the equipment already available to E&J Gallo and as such, will not require new equipment, making it more feasible to begin new operations. Even though the separation results obtained were less than satisfactory, they provided a learning opportunity and a basis for further experimentation that E&J Gallo can use to continue testing separation techniques involving fusel oils.

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Appendices

Appendix A: Steam Stripper Set-Up and Running Instructions (With Pictures)

Procedure for laboratory steam stripper

Note: Carefully record the volumes of starting material, distillate collected, and bottoms collected. This will be useful for calculating the amount of steam used for the stripping process.

1. Obtain:
    a. One heating mantle with controller
    b. One hot plate/stirrer with stir bar
    c. One one-liter double-necked round-bottom flask with plug
    d. Two beakers or Erlenmeyer flasks for hold unstripped and stripped liquid
    e. Any number trays worth of oldershaw columns
    f. One distillation column middle-stage liquid collector
    g. One distillation column middle-stage liquid injector
    h. One distillation reflux/condenser head
    i. Two 24/40 to 29/42 GGJ adapters
    j. Boiling stones
    k. Ring stands for securing glassware
    l. Flask for collecting distillate
    m. One digital readout peristaltic pump with 24-gauge masterflex tubing
    n. One glass elbow with ball-in-socket GGJ for collecting stripped bottoms
    o. High-temperature tubing for collecting stripped bottoms

2. Fill three-quarters of one round bottom flask with a saturated salt solution (note: salt is optional but will create hotter steam temperatures) and drop in a few boiling stones. Keep more pure water reserved for refilling.

3. Put water-filled flask in heating mantle and turn on the heat to 80-100.

4. Stack the glassware in the following order. Please apply a small amount of grease on all GGJ’s:
    a. Liquid collector (must be adapted from 24/40 to 29/42)
        i. Attach glass elbow to ball-in-socket GGJ with clip
        ii. Attach high-temp hose to glass elbow
        iii. Put end of hose in clean beaker to collect water during heat-up
        iv. Plug open port with stopper or thermometer
    b. Oldershaw column
    c. Liquid injector
        i. Attach masterflex tubing to injection port
        ii. Plug open port with stopper
    d. Condenser/reflux head (must be adapted from 29/42 to 24/40)
    e. Attach collection flask to reflux head using keck clip
    f. Insulate areas of single-walled glass using aluminum foil or padded insulation.

5. Put the liquid to be stripped on the hot plate/stirrer. Heat and stir, but monitor the temperature closely. Do not allow this liquid to boil or evaporate significantly unless a reflux is set up.
    a. Note: pre-heating the liquid will improve the efficiency of the stripper, but over-heating the liquid with cause the masterflex hose to break down as it is not rated for high temperatures. Significant evaporation of this liquid will cause fractionation before the stripper and this will skew results.

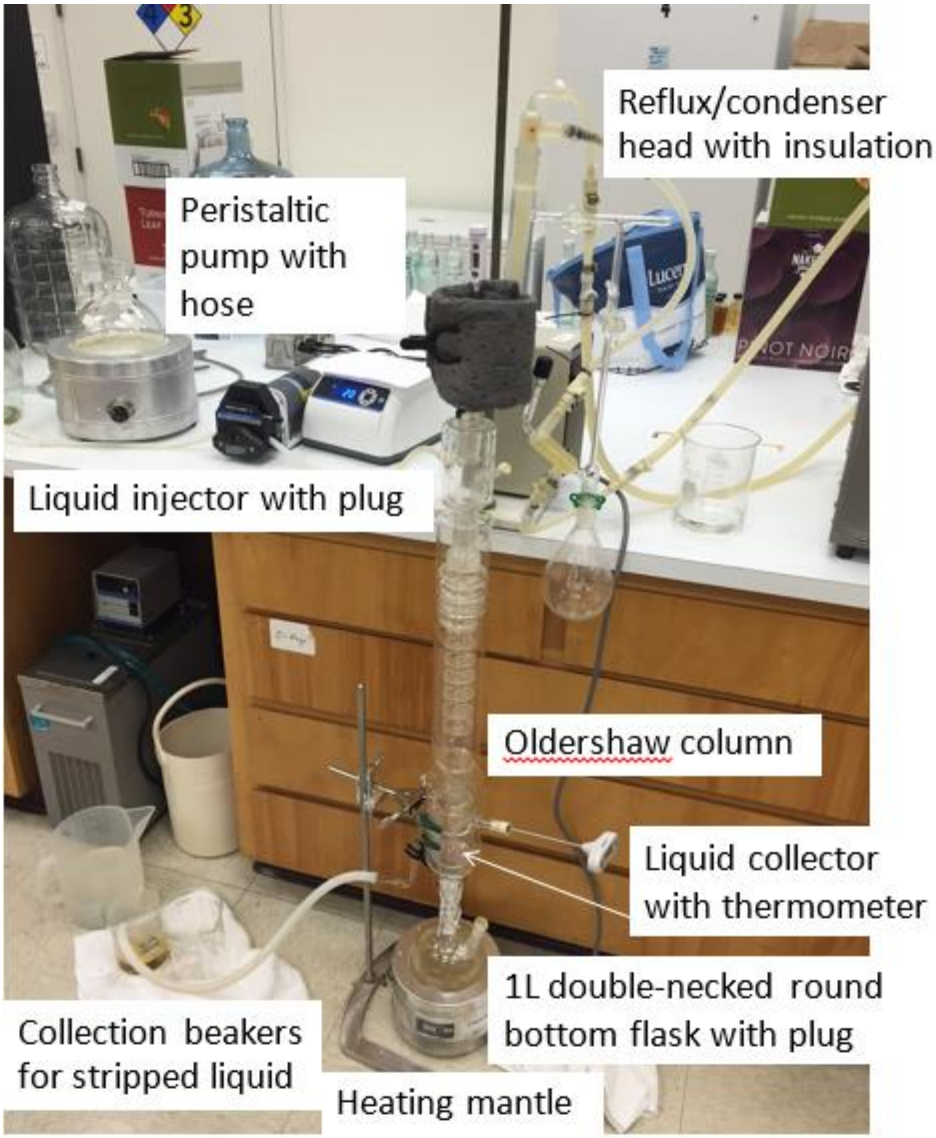
6. Allow the glass to heat up. Watch the distillate collection for condensate dripping and watch for the thermometer on the top of the reflux head to reach over 98 C. Once this happens, turn the heat up to max. This might take quite a while, an hour or more. Collect the condensed water in the collection flask, but remember to switch this flask out before collecting product

7. Slowly introduce the liquid to be stripped to the top of the column by turning on the peristaltic pump.

  a. Start with a low setting, around 10, and ramp up slowly. Monitor the vapor temperature at the top of the column and make sure it is stable. Make sure there is vapor reaching the condenser. Ideally the liquid would be loaded as quickly as possible without
  b. Monitor the color of the stripped bottoms and when the bottoms begin to change color, begin collecting in an empty, clean beaker or flask.
  c. If the top stages of the column cool down too much and vapor fails to reach the condenser, pause the pump and close the distillate collection valve to allow vapor to reflux back into the top of the column. Then restart the column following steps 7a and 7b.
  d. Monitor the level of the water at the base of the column. If the level drops below the top of the mantle, pause the column following step 7c and refill the flask with more pure water, preheated would be best.

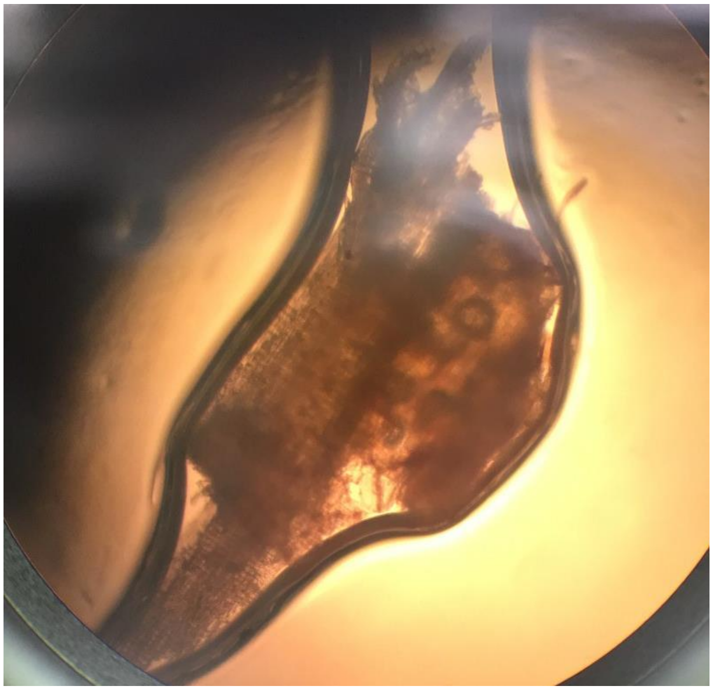
8. Once the stripping liquid is gone and the bottoms turns back to water, pause the column following step 7c. Empty the distillate collection flask and decide whether or not to do another pass on the stripped material.
  a. If so, restart the stripping process with the collected bottoms.
  b. If not, restart the process with pure water instead. Allow this to run for some time to rinse out the system and then turn off the heat and the pump. Allow the column to cool down while the chiller still runs.
  c. Once water at the base of the column ceases to boil and vapor is no longer seen at the top of the column, turn off the chiller.
  d. Disassemble and clean glassware once cool

Steam Stripper Diagram

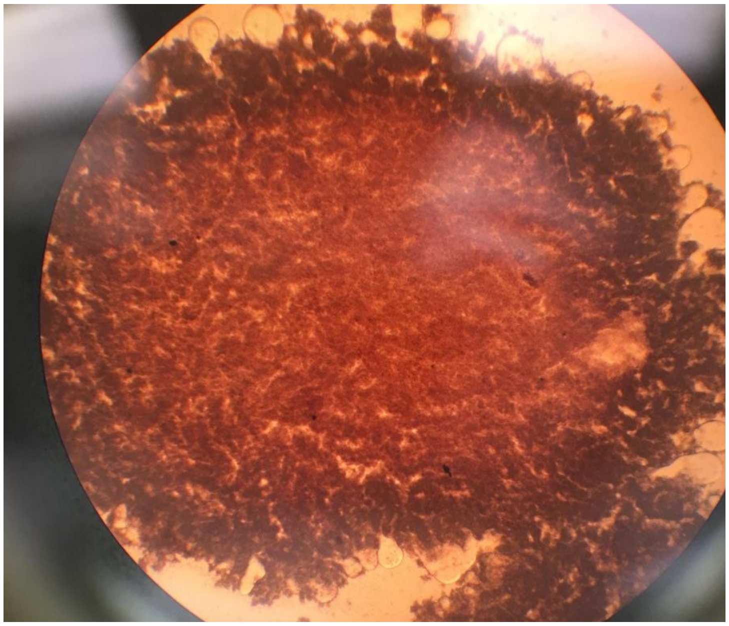


Appendix B: Microscope Images of Solid Oak and Solids Found in CLT04 Stream

Oak Microscope Image

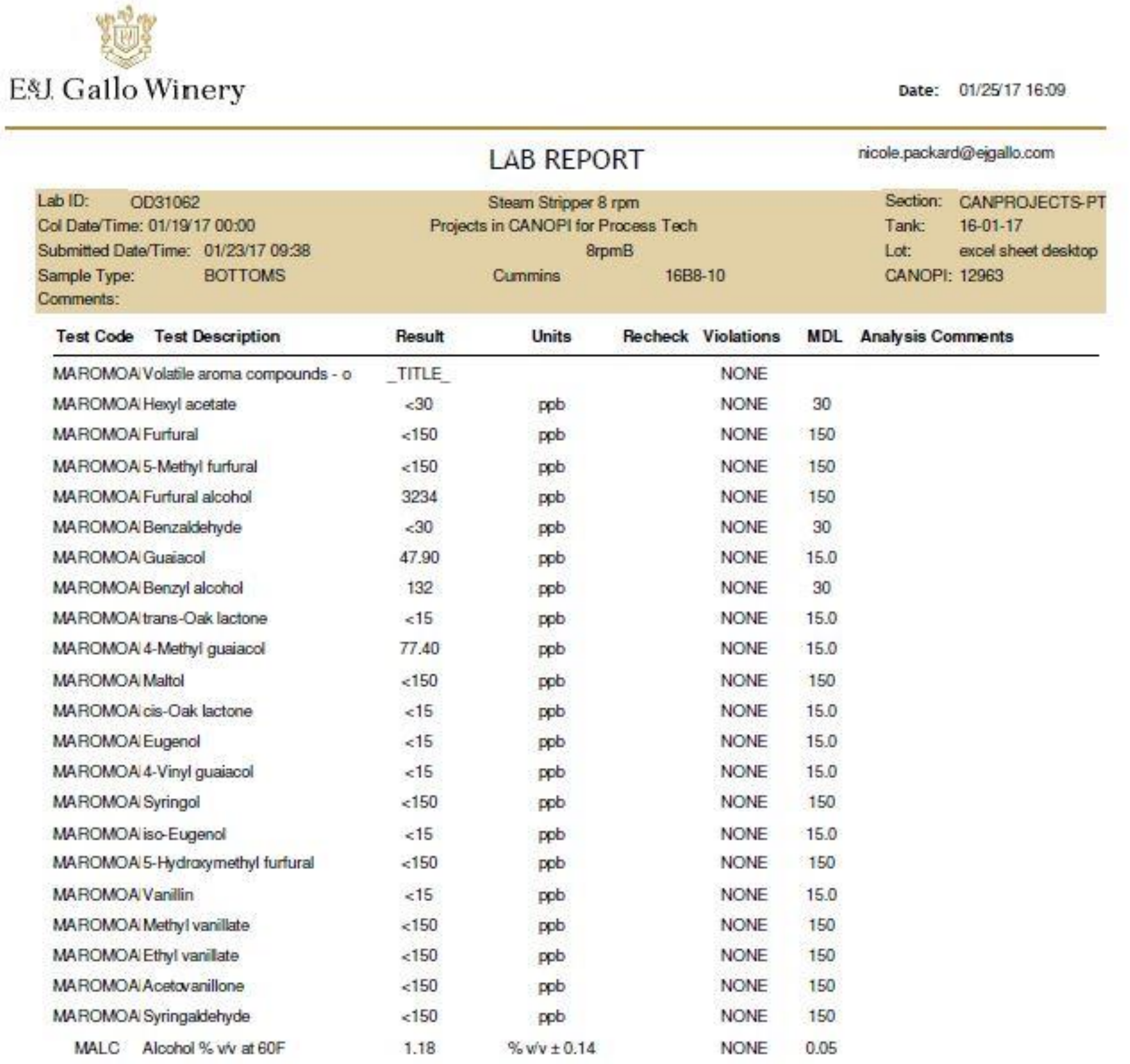


VDR Solid Microscope Image



Appendix C: Lab Results and Calculations for Smoak Steam Stripping

1-16-2017 Bottoms, 6rpm, 10 stages



E&J. Gallo Winery

Date: 01/25/17 16:09

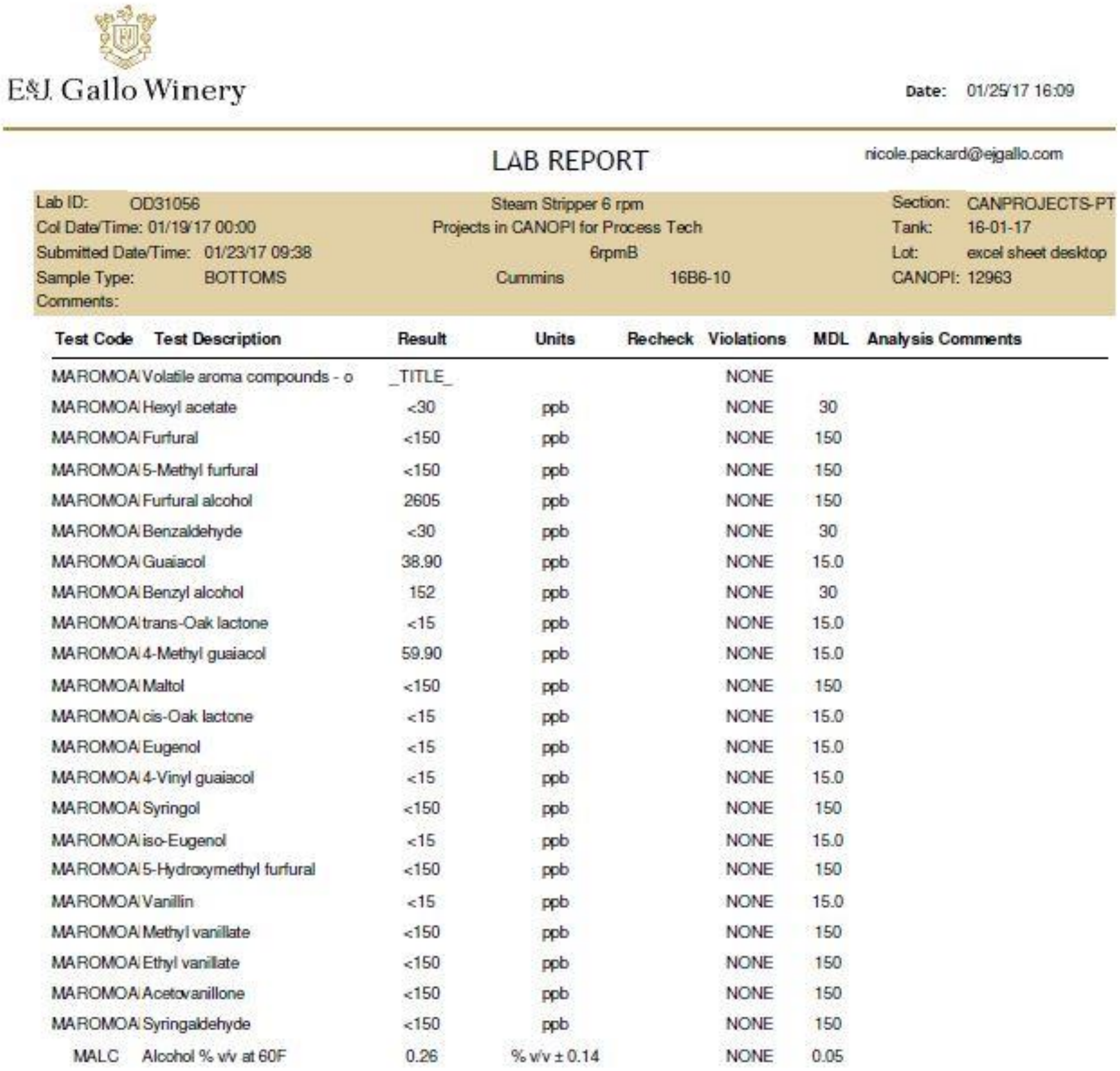
LAB REPORT

nicole.packard@ejgallo.com

Lab ID: OD31062	Steam Stripper 8 rpm		Section: CANPROJECTS-PT
Col Date/Time: 01/19/17 00:00	Projects in CANOPI for Process Tech		Tank: 16-01-17
Submitted Date/Time: 01/23/17 09:38	8rpmB		Lot: excel sheet desktop
Sample Type: BOTTOMS	Cummins	16B8-10	CANOPI: 12963
Comments:			

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	3234	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	47.90	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	132	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	77.40	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	1.18	% v/v ± 0.14		NONE	0.05	

1-16-2017 Bottoms 8 rpm 10 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

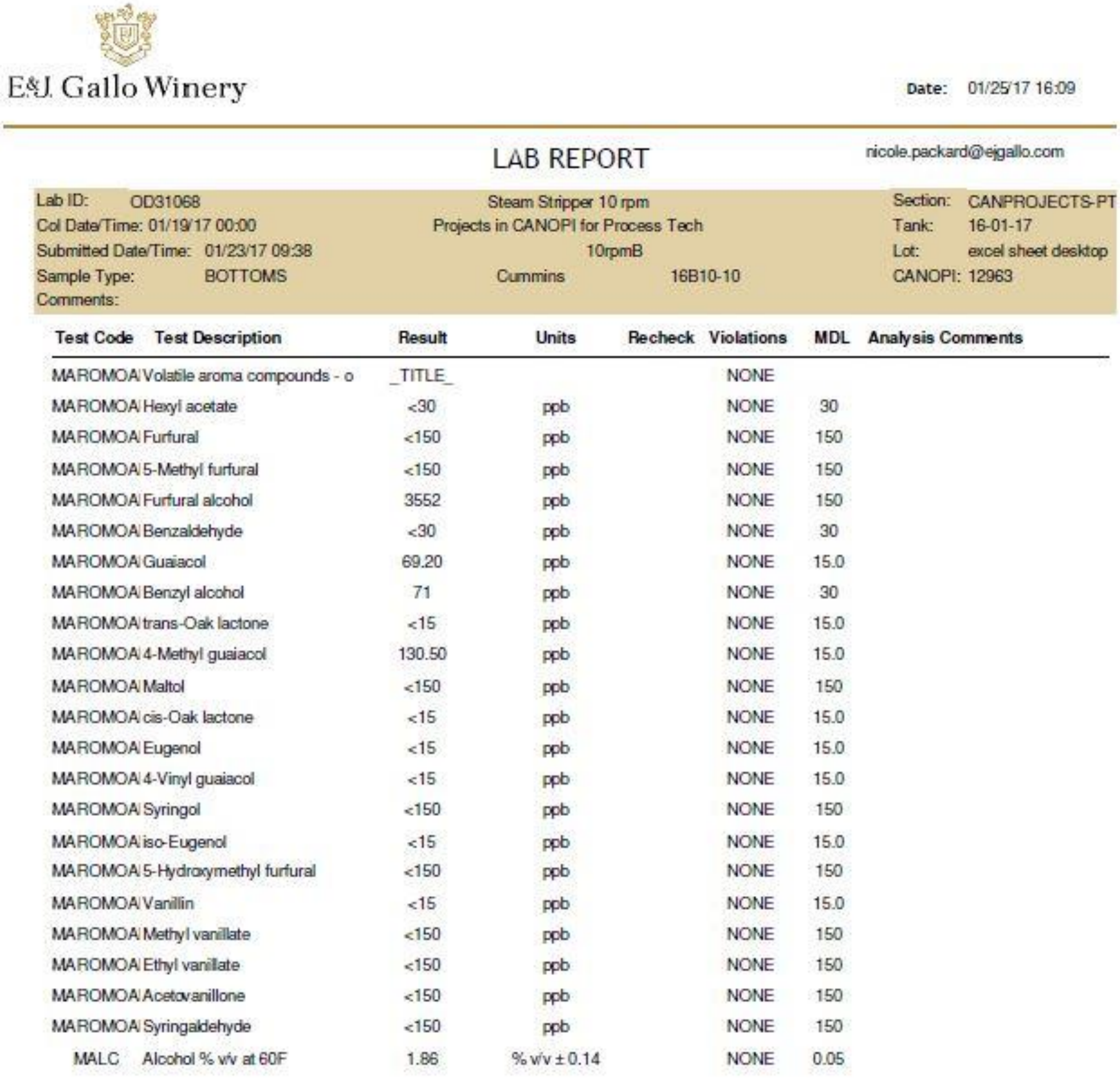
Lab ID: OD31056
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: BOTTOMS
Comments:

Steam Stripper 6 rpm
Projects in CANOPI for Process Tech
6rpmB
Cummins 16B6-10

Section: CANPROJECTS-PT
Tank: 16-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	2605	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	38.90	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	152	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	59.90	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	0.26	% v/v ± 0.14		NONE	0.05	

1-16-2017 Bottoms 10rpm 10 stages



E&J Gallo Winery

Date: 01/25/17 16:09

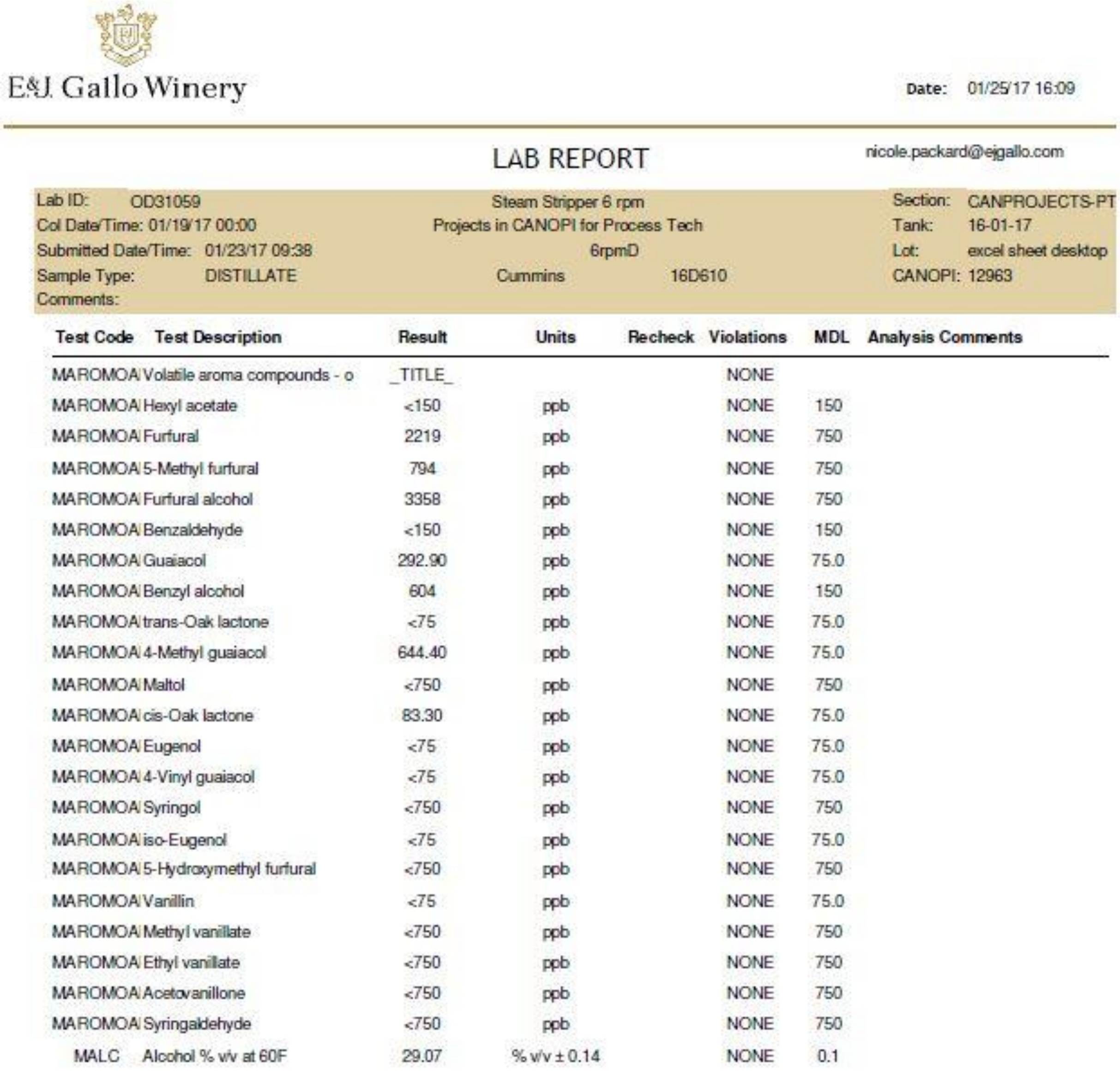
LAB REPORT

nicole.packard@ejgallo.com

Lab ID: OD31068	Steam Stripper 10 rpm		Section: CANPROJECTS-PT
Col Date/Time: 01/19/17 00:00	Projects in CANOPI for Process Tech		Tank: 16-01-17
Submitted Date/Time: 01/23/17 09:38	10rpmB		Lot: excel sheet desktop
Sample Type: BOTTOMS	Cummins	16B10-10	CANOPI: 12963
Comments:			

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	3552	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	69.20	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	71	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	130.50	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	1.86	% v/v ± 0.14		NONE	0.05	

1-16-2017 Distillate 6 rpm 10 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

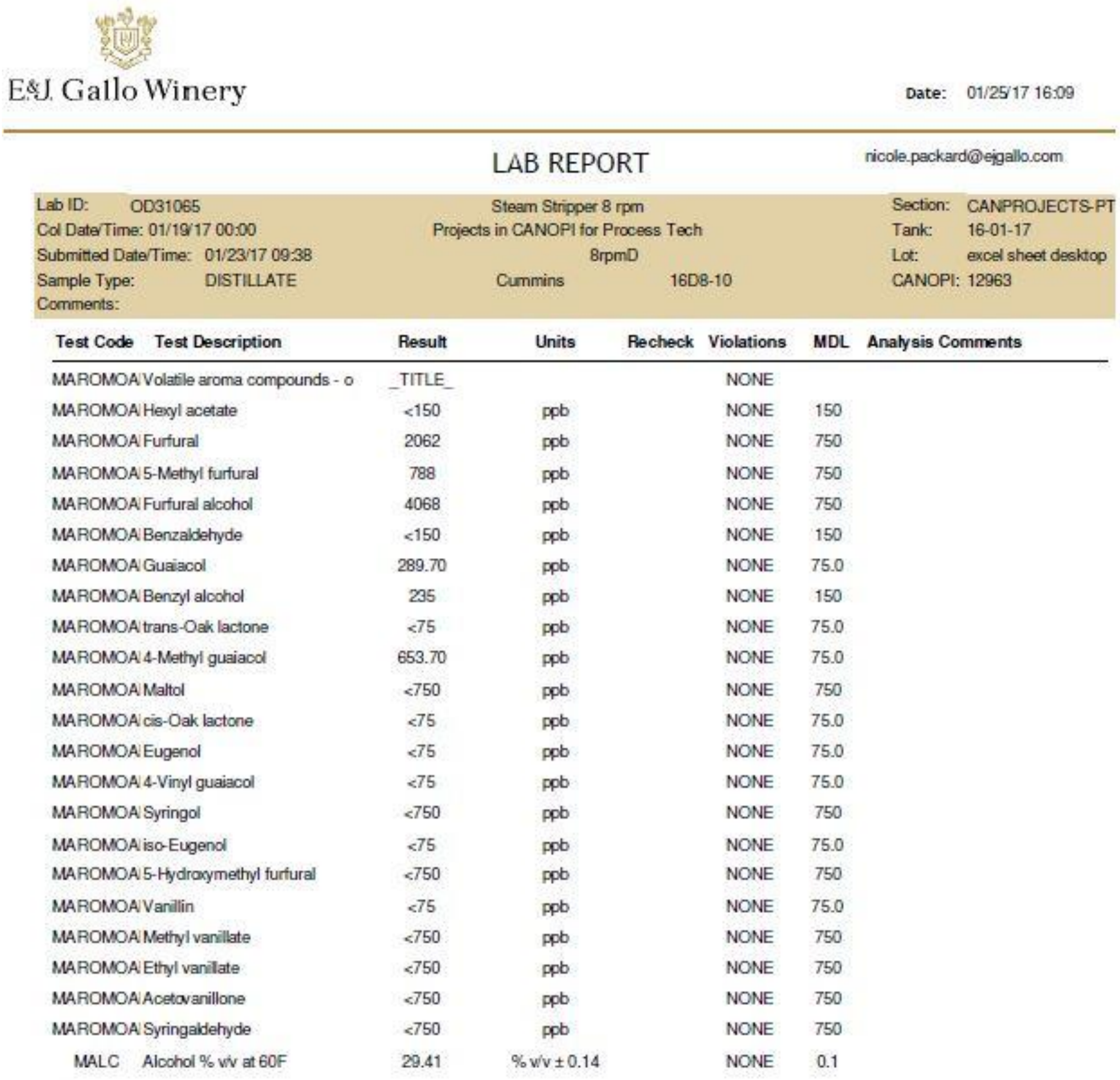
Lab ID: OD31059
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: DISTILLATE
Comments:

Steam Stripper 6 rpm
Projects in CANOPI for Process Tech
6rpmD
Cummins 16D610

Section: CANPROJECTS-PT
Tank: 16-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<150	ppb		NONE	150	
MAROMOA	Furfural	2219	ppb		NONE	750	
MAROMOA	5-Methyl furfural	794	ppb		NONE	750	
MAROMOA	Furfural alcohol	3358	ppb		NONE	750	
MAROMOA	Benzaldehyde	<150	ppb		NONE	150	
MAROMOA	Guaiacol	292.90	ppb		NONE	75.0	
MAROMOA	Benzyl alcohol	604	ppb		NONE	150	
MAROMOA	trans-Oak lactone	<75	ppb		NONE	75.0	
MAROMOA	4-Methyl guaiacol	644.40	ppb		NONE	75.0	
MAROMOA	Maltol	<750	ppb		NONE	750	
MAROMOA	cis-Oak lactone	83.30	ppb		NONE	75.0	
MAROMOA	Eugenol	<75	ppb		NONE	75.0	
MAROMOA	4-Vinyl guaiacol	<75	ppb		NONE	75.0	
MAROMOA	Syringol	<750	ppb		NONE	750	
MAROMOA	iso-Eugenol	<75	ppb		NONE	75.0	
MAROMOA	5-Hydroxymethyl furfural	<750	ppb		NONE	750	
MAROMOA	Vanillin	<75	ppb		NONE	75.0	
MAROMOA	Methyl vanillate	<750	ppb		NONE	750	
MAROMOA	Ethyl vanillate	<750	ppb		NONE	750	
MAROMOA	Acetovanillone	<750	ppb		NONE	750	
MAROMOA	Syringaldehyde	<750	ppb		NONE	750	
MALC	Alcohol % v/v at 60F	29.07	% v/v ± 0.14		NONE	0.1	

1-16-2017 Distillate 8 rpm 10 stages



E&J. Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

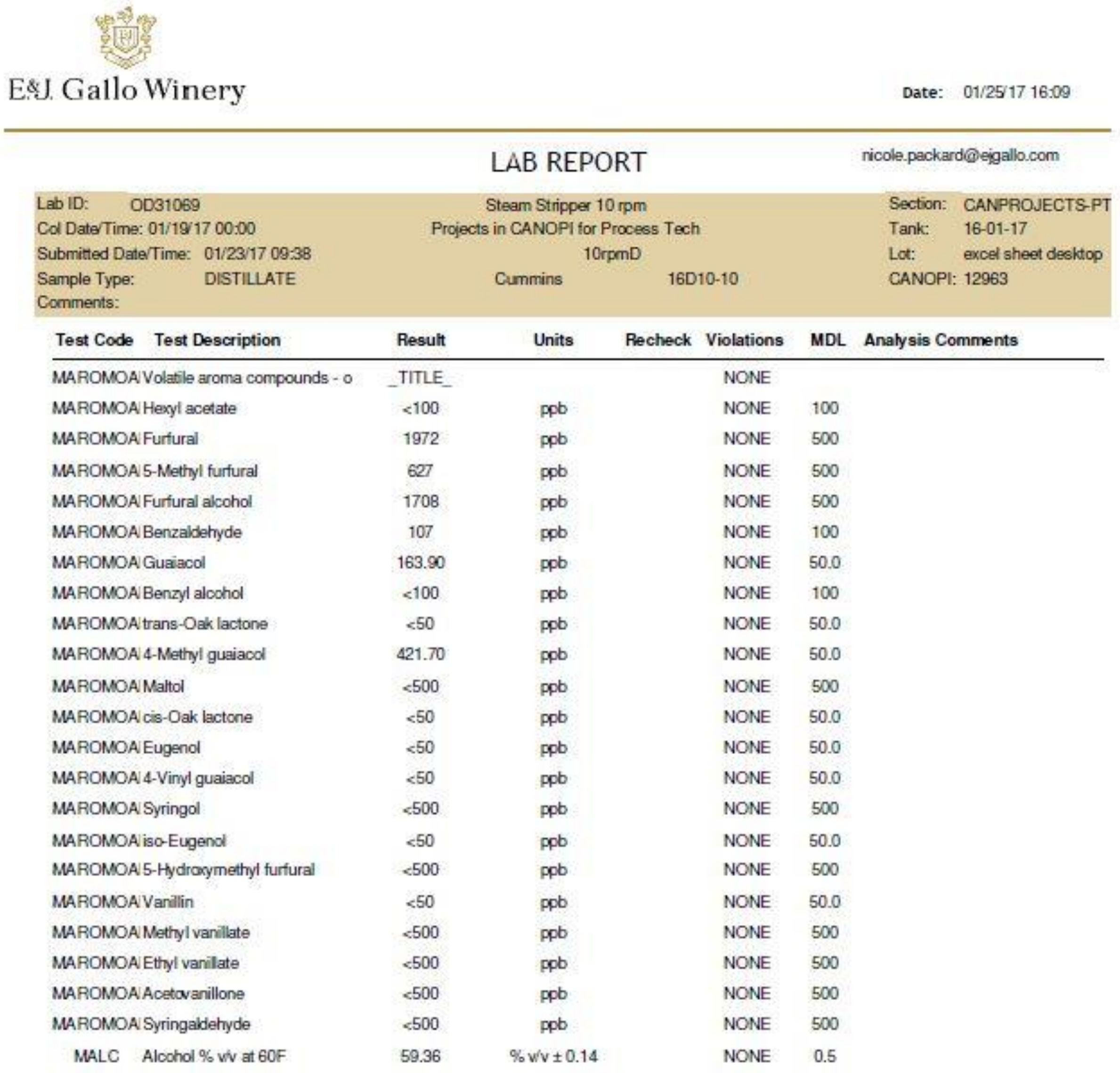
Lab ID: OD31065
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: DISTILLATE
Comments:

Steam Stripper 8 rpm
Projects in CANOPI for Process Tech
8rpmD
Cummins 16D8-10

Section: CANPROJECTS-PT
Tank: 16-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<150	ppb		NONE	150	
MAROMOA	Furfural	2062	ppb		NONE	750	
MAROMOA	5-Methyl furfural	788	ppb		NONE	750	
MAROMOA	Furfural alcohol	4068	ppb		NONE	750	
MAROMOA	Benzaldehyde	<150	ppb		NONE	150	
MAROMOA	Guaiacol	289.70	ppb		NONE	75.0	
MAROMOA	Benzyl alcohol	235	ppb		NONE	150	
MAROMOA	trans-Oak lactone	<75	ppb		NONE	75.0	
MAROMOA	4-Methyl guaiacol	653.70	ppb		NONE	75.0	
MAROMOA	Maltol	<750	ppb		NONE	750	
MAROMOA	cis-Oak lactone	<75	ppb		NONE	75.0	
MAROMOA	Eugenol	<75	ppb		NONE	75.0	
MAROMOA	4-Vinyl guaiacol	<75	ppb		NONE	75.0	
MAROMOA	Syringol	<750	ppb		NONE	750	
MAROMOA	iso-Eugenol	<75	ppb		NONE	75.0	
MAROMOA	5-Hydroxymethyl furfural	<750	ppb		NONE	750	
MAROMOA	Vanillin	<75	ppb		NONE	75.0	
MAROMOA	Methyl vanillate	<750	ppb		NONE	750	
MAROMOA	Ethyl vanillate	<750	ppb		NONE	750	
MAROMOA	Acetovanillone	<750	ppb		NONE	750	
MAROMOA	Syringaldehyde	<750	ppb		NONE	750	
MALC	Alcohol % v/v at 60F	29.41	% v/v ± 0.14		NONE	0.1	

1-16-2017 Distillate 10rpm 10 stages



E&J. Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

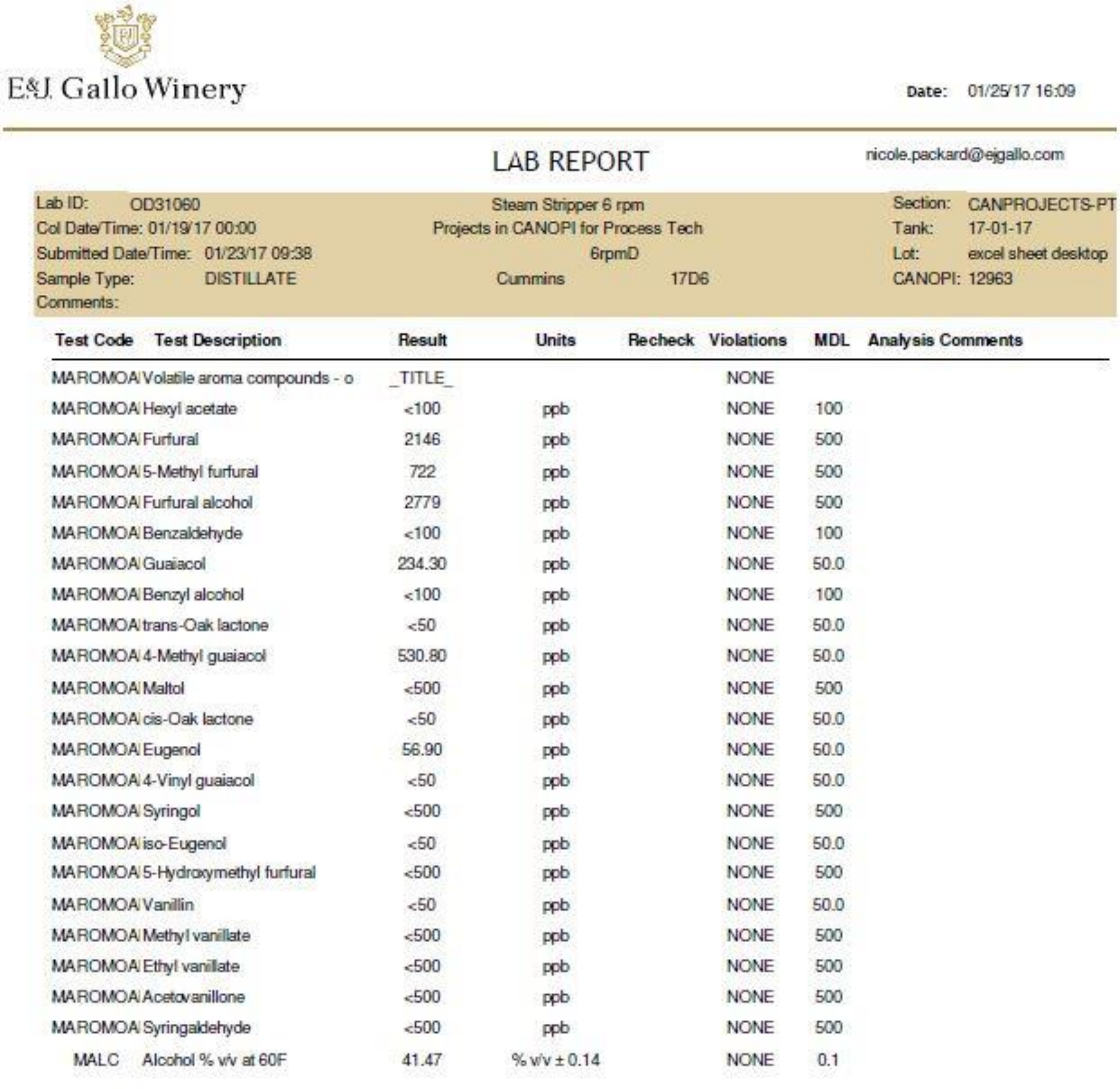
Lab ID: OD31069
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: DISTILLATE
Comments:

Steam Stripper 10 rpm
Projects in CANOPI for Process Tech
10rpmD
Cummins 16D10-10

Section: CANPROJECTS-PT
Tank: 16-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<100	ppb		NONE	100	
MAROMOA	Furfural	1972	ppb		NONE	500	
MAROMOA	5-Methyl furfural	627	ppb		NONE	500	
MAROMOA	Furfural alcohol	1708	ppb		NONE	500	
MAROMOA	Benzaldehyde	107	ppb		NONE	100	
MAROMOA	Guaiacol	163.90	ppb		NONE	50.0	
MAROMOA	Benzyl alcohol	<100	ppb		NONE	100	
MAROMOA	trans-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	4-Methyl guaiacol	421.70	ppb		NONE	50.0	
MAROMOA	Maltol	<500	ppb		NONE	500	
MAROMOA	cis-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	Eugenol	<50	ppb		NONE	50.0	
MAROMOA	4-Vinyl guaiacol	<50	ppb		NONE	50.0	
MAROMOA	Syringol	<500	ppb		NONE	500	
MAROMOA	iso-Eugenol	<50	ppb		NONE	50.0	
MAROMOA	5-Hydroxymethyl furfural	<500	ppb		NONE	500	
MAROMOA	Vanillin	<50	ppb		NONE	50.0	
MAROMOA	Methyl vanillate	<500	ppb		NONE	500	
MAROMOA	Ethyl vanillate	<500	ppb		NONE	500	
MAROMOA	Acetovanillone	<500	ppb		NONE	500	
MAROMOA	Syringaldehyde	<500	ppb		NONE	500	
MALC	Alcohol % v/v at 60F	59.36	% v/v ± 0.14		NONE	0.5	

1-17-207 Distillate 6 rpm, 10 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

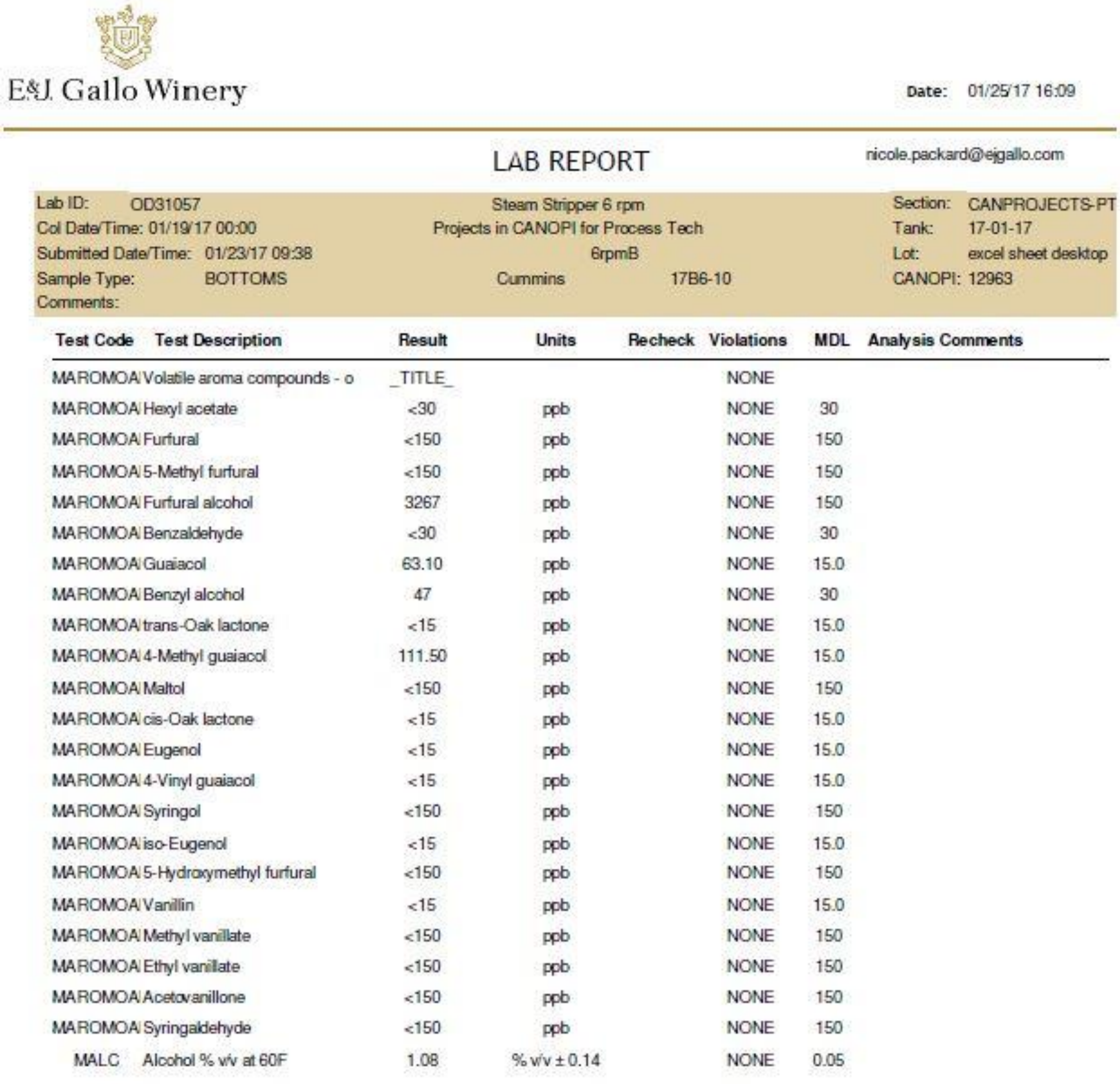
Lab ID: OD31060
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: DISTILLATE
Comments:

Steam Stripper 6 rpm
Projects in CANOPI for Process Tech
6rpmD
Cummins 17D6

Section: CANPROJECTS-PT
Tank: 17-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<100	ppb		NONE	100	
MAROMOA	Furfural	2146	ppb		NONE	500	
MAROMOA	5-Methyl furfural	722	ppb		NONE	500	
MAROMOA	Furfural alcohol	2779	ppb		NONE	500	
MAROMOA	Benzaldehyde	<100	ppb		NONE	100	
MAROMOA	Guaiacol	234.30	ppb		NONE	50.0	
MAROMOA	Benzyl alcohol	<100	ppb		NONE	100	
MAROMOA	trans-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	4-Methyl guaiacol	530.80	ppb		NONE	50.0	
MAROMOA	Maltol	<500	ppb		NONE	500	
MAROMOA	cis-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	Eugenol	56.90	ppb		NONE	50.0	
MAROMOA	4-Vinyl guaiacol	<50	ppb		NONE	50.0	
MAROMOA	Syringol	<500	ppb		NONE	500	
MAROMOA	iso-Eugenol	<50	ppb		NONE	50.0	
MAROMOA	5-Hydroxymethyl furfural	<500	ppb		NONE	500	
MAROMOA	Vanillin	<50	ppb		NONE	50.0	
MAROMOA	Methyl vanillate	<500	ppb		NONE	500	
MAROMOA	Ethyl vanillate	<500	ppb		NONE	500	
MAROMOA	Acetovanillone	<500	ppb		NONE	500	
MAROMOA	Syringaldehyde	<500	ppb		NONE	500	
MALC	Alcohol % v/v at 60F	41.47	% v/v ± 0.14		NONE	0.1	

1-17-2017 6rpm bottoms, 10 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

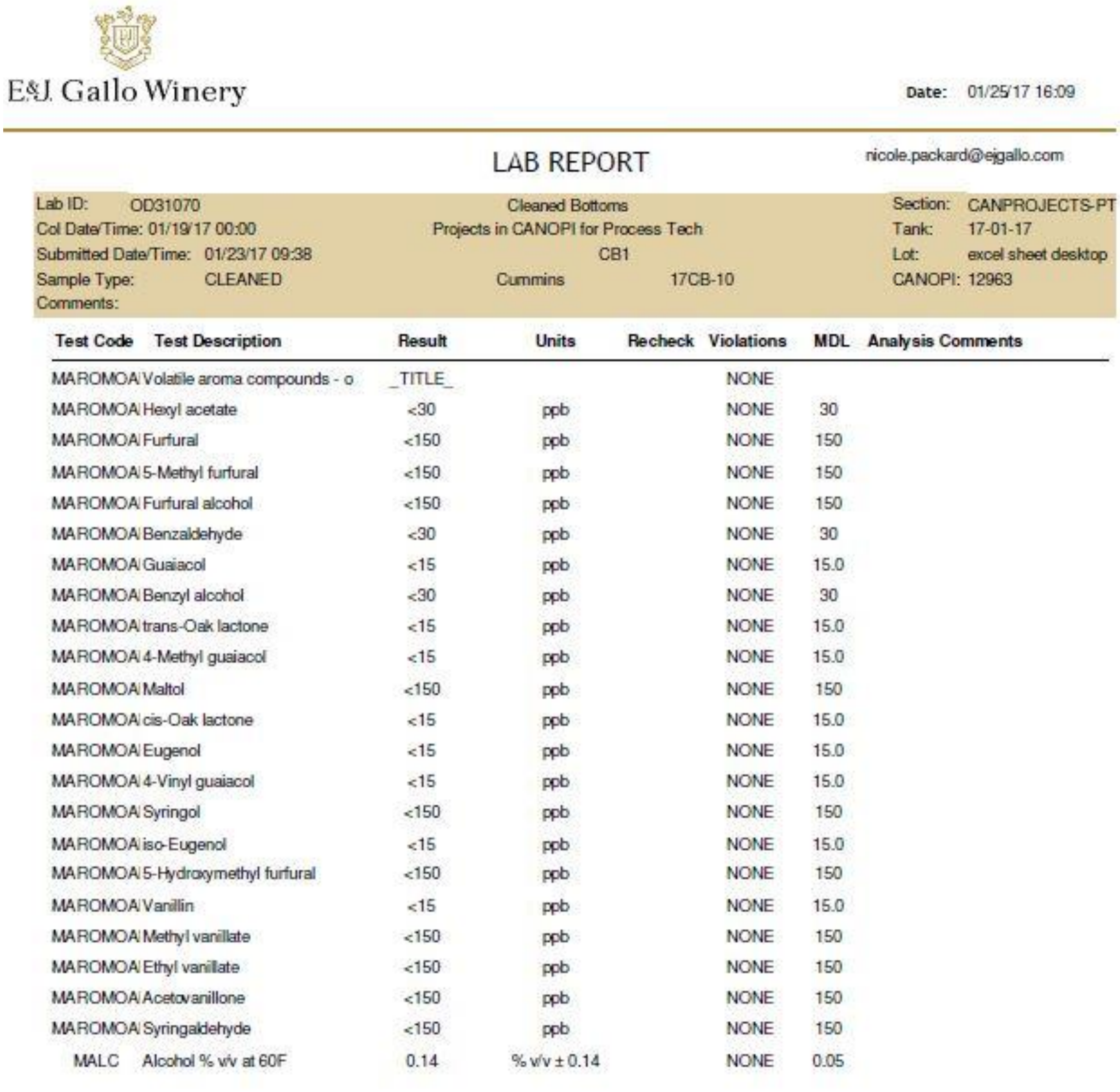
Lab ID: OD31057
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: BOTTOMS
Comments:

Steam Stripper 6 rpm
Projects in CANOPI for Process Tech
6rpmB
Cummins 17B6-10

Section: CANPROJECTS-PT
Tank: 17-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	3267	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	63.10	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	47	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	111.50	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	1.08	% v/v ± 0.14		NONE	0.05	

1-17-2017 Cleaned Bottoms 10 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

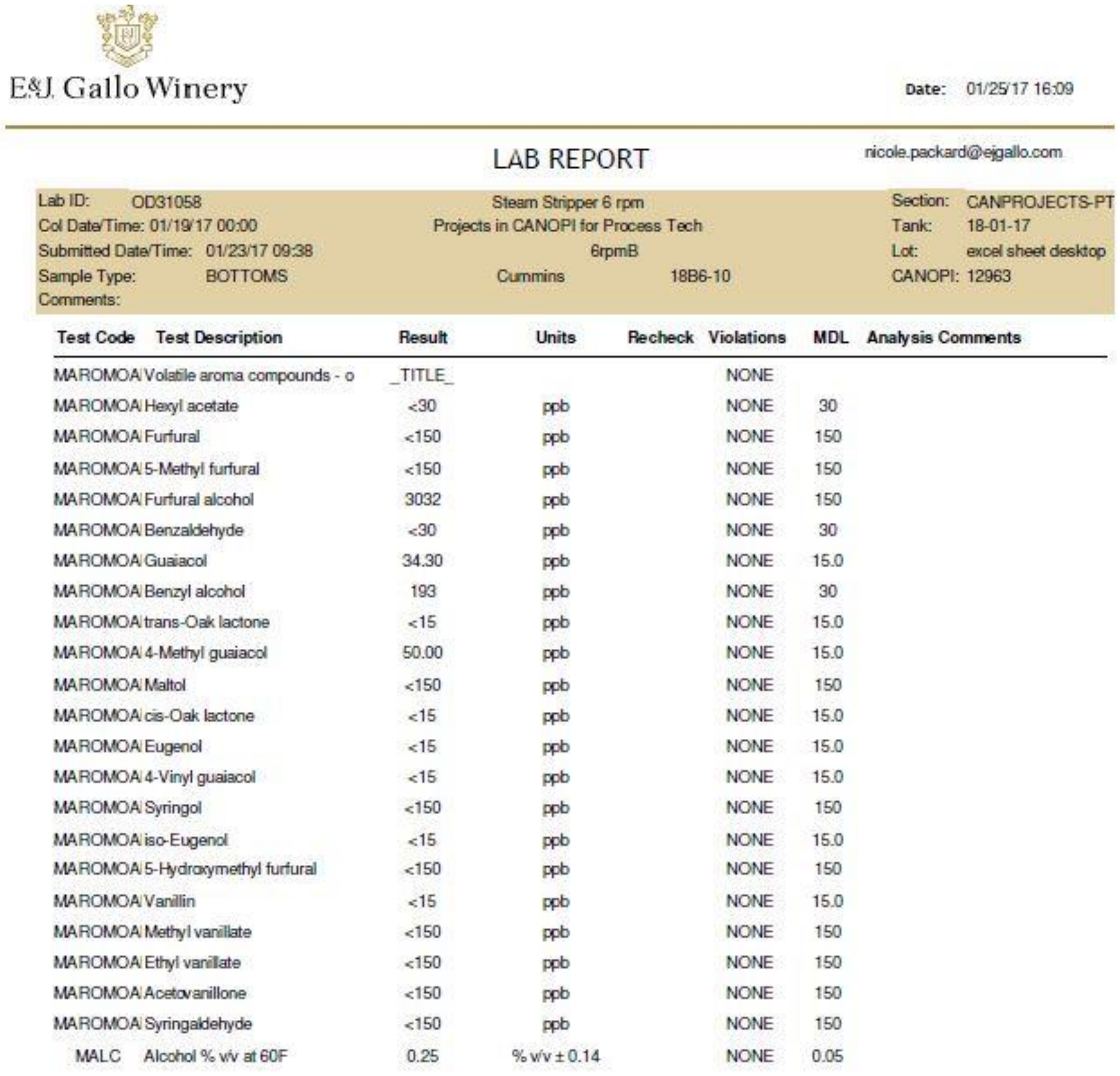
Lab ID: OD31070
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: CLEANED
Comments:

Cleaned Bottoms
Projects in CANOPI for Process Tech
CB1
Cummins 17CB-10

Section: CANPROJECTS-PT
Tank: 17-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	<150	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	<30	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	0.14	% v/v ± 0.14		NONE	0.05	

1-18-2017 bottoms 6rpm, 10 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

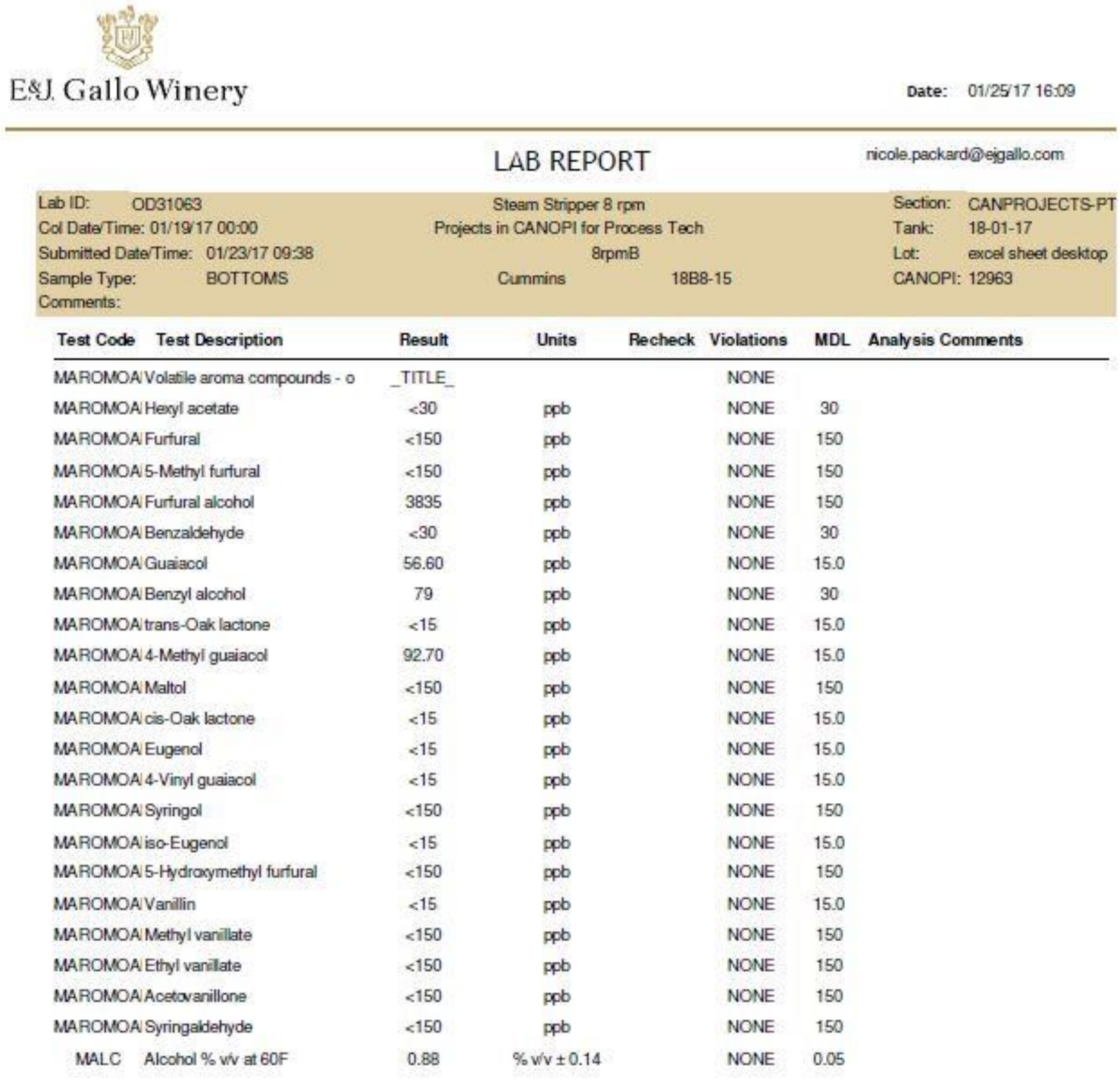
Lab ID: OD31058
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: BOTTOMS
Comments:

Steam Stripper 6 rpm
Projects in CANOPI for Process Tech
6rpmB
Cummins 18B6-10

Section: CANPROJECTS-PT
Tank: 18-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	3032	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	34.30	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	193	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	50.00	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	0.25	% v/v ± 0.14		NONE	0.05	

1-18-2017 Bottoms 8rpm 15 Stages



E&J. Gallo Winery

Date: 01/25/17 16:09

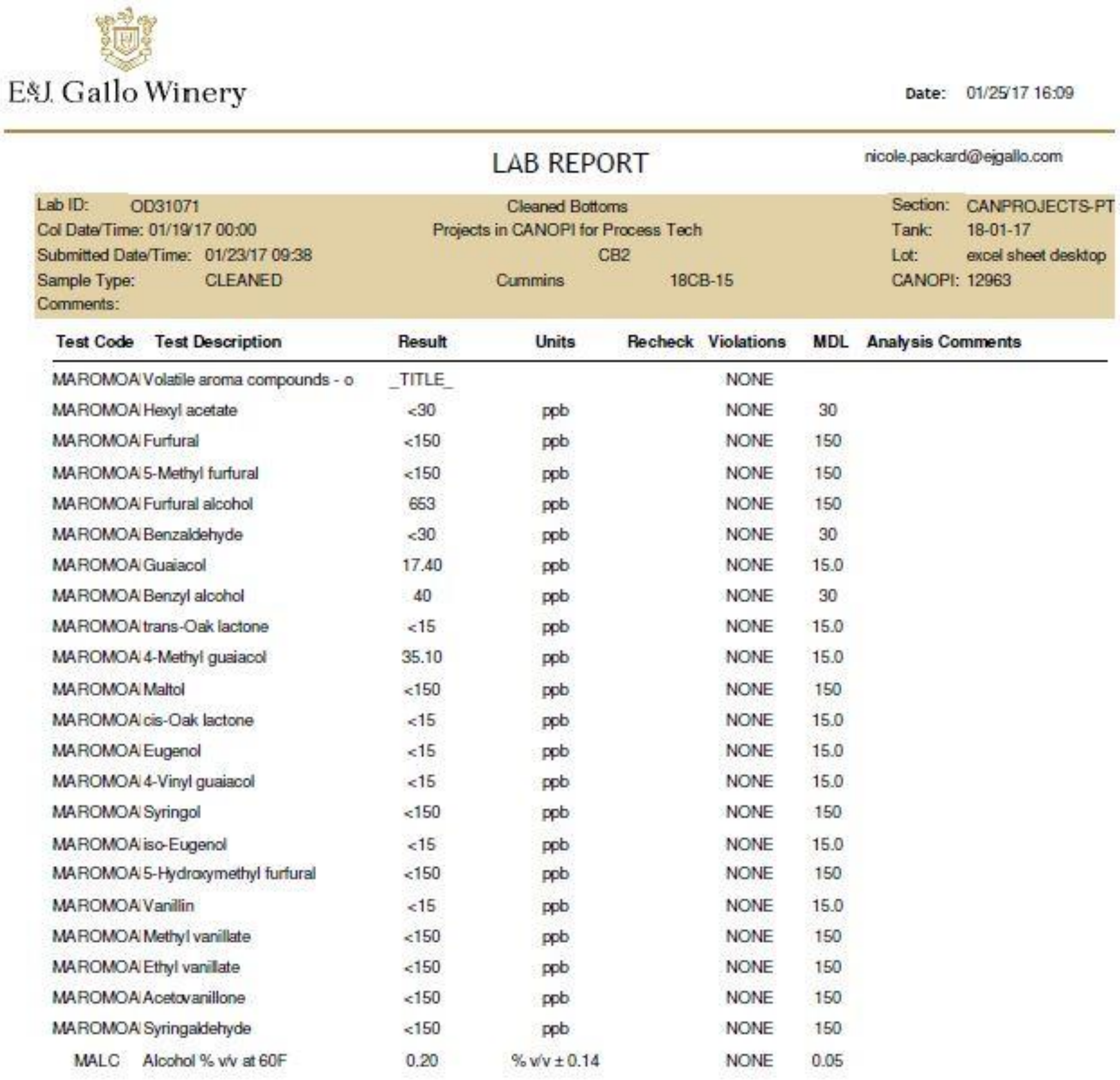
LAB REPORT

nicole.packard@ejgallo.com

Lab ID: OD31063	Steam Stripper 8 rpm	Section:	CANPROJECTS-PT
Col Date/Time: 01/19/17 00:00	Projects in CANOPI for Process Tech	Tank:	18-01-17
Submitted Date/Time: 01/23/17 09:38	8rpmB	Lot:	excel sheet desktop
Sample Type: BOTTOMS	Cummins 18B8-15	CANOPI:	12963
Comments:			

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	3835	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	56.60	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	79	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	92.70	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	0.88	% v/v ± 0.14		NONE	0.05	

1-18-2017 Cleaned Bottoms 15 Stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

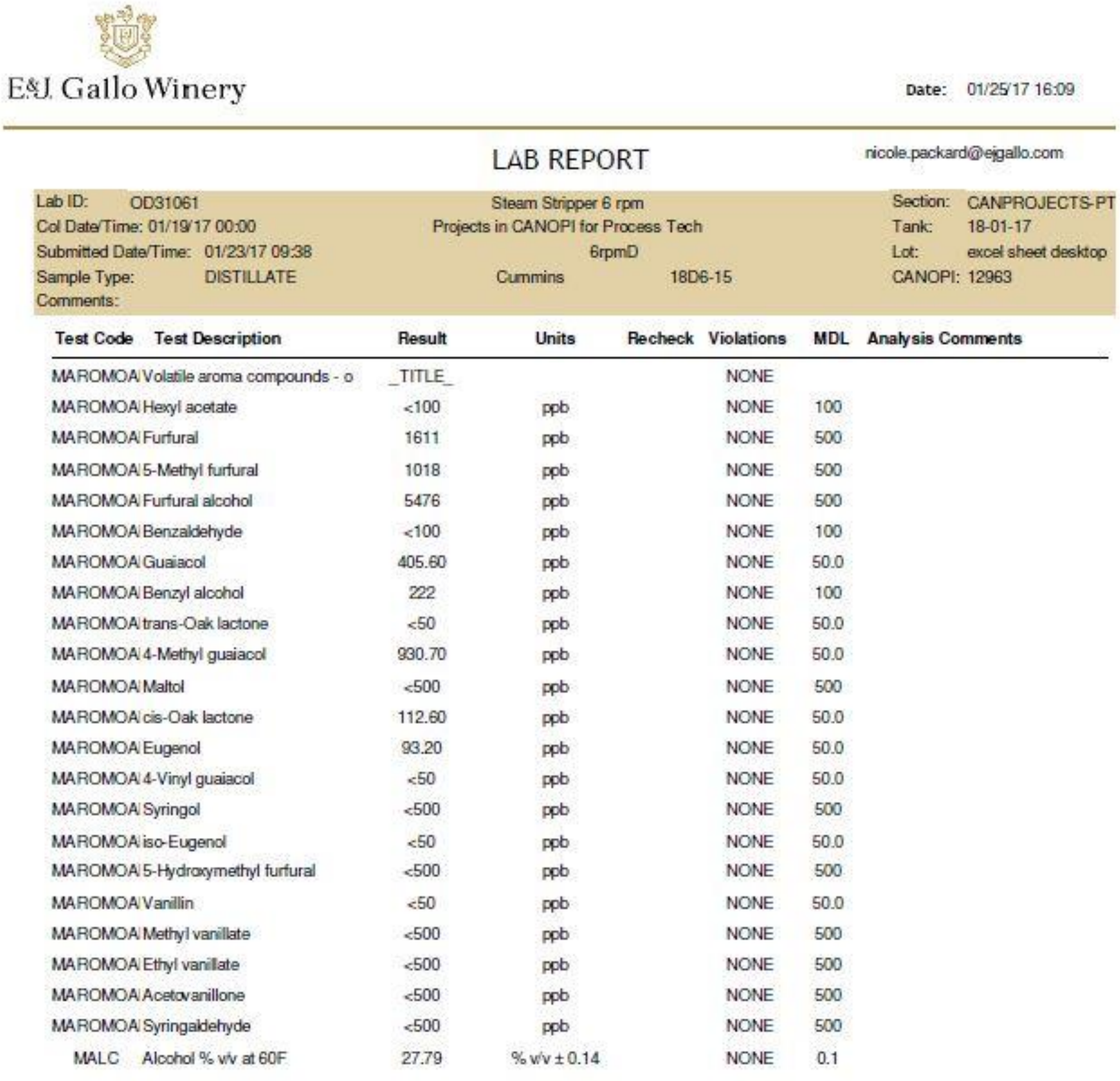
Lab ID: OD31071
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: CLEANED
Comments:

Cleaned Bottoms
Projects in CANOPI for Process Tech
CB2
Cummins 18CB-15

Section: CANPROJECTS-PT
Tank: 18-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<30	ppb		NONE	30	
MAROMOA	Furfural	<150	ppb		NONE	150	
MAROMOA	5-Methyl furfural	<150	ppb		NONE	150	
MAROMOA	Furfural alcohol	653	ppb		NONE	150	
MAROMOA	Benzaldehyde	<30	ppb		NONE	30	
MAROMOA	Guaiacol	17.40	ppb		NONE	15.0	
MAROMOA	Benzyl alcohol	40	ppb		NONE	30	
MAROMOA	trans-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	4-Methyl guaiacol	35.10	ppb		NONE	15.0	
MAROMOA	Maltol	<150	ppb		NONE	150	
MAROMOA	cis-Oak lactone	<15	ppb		NONE	15.0	
MAROMOA	Eugenol	<15	ppb		NONE	15.0	
MAROMOA	4-Vinyl guaiacol	<15	ppb		NONE	15.0	
MAROMOA	Syringol	<150	ppb		NONE	150	
MAROMOA	iso-Eugenol	<15	ppb		NONE	15.0	
MAROMOA	5-Hydroxymethyl furfural	<150	ppb		NONE	150	
MAROMOA	Vanillin	<15	ppb		NONE	15.0	
MAROMOA	Methyl vanillate	<150	ppb		NONE	150	
MAROMOA	Ethyl vanillate	<150	ppb		NONE	150	
MAROMOA	Acetovanillone	<150	ppb		NONE	150	
MAROMOA	Syringaldehyde	<150	ppb		NONE	150	
MALC	Alcohol % v/v at 60F	0.20	% v/v ± 0.14		NONE	0.05	

1-18-2017 Distillate 6 rpm 15 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

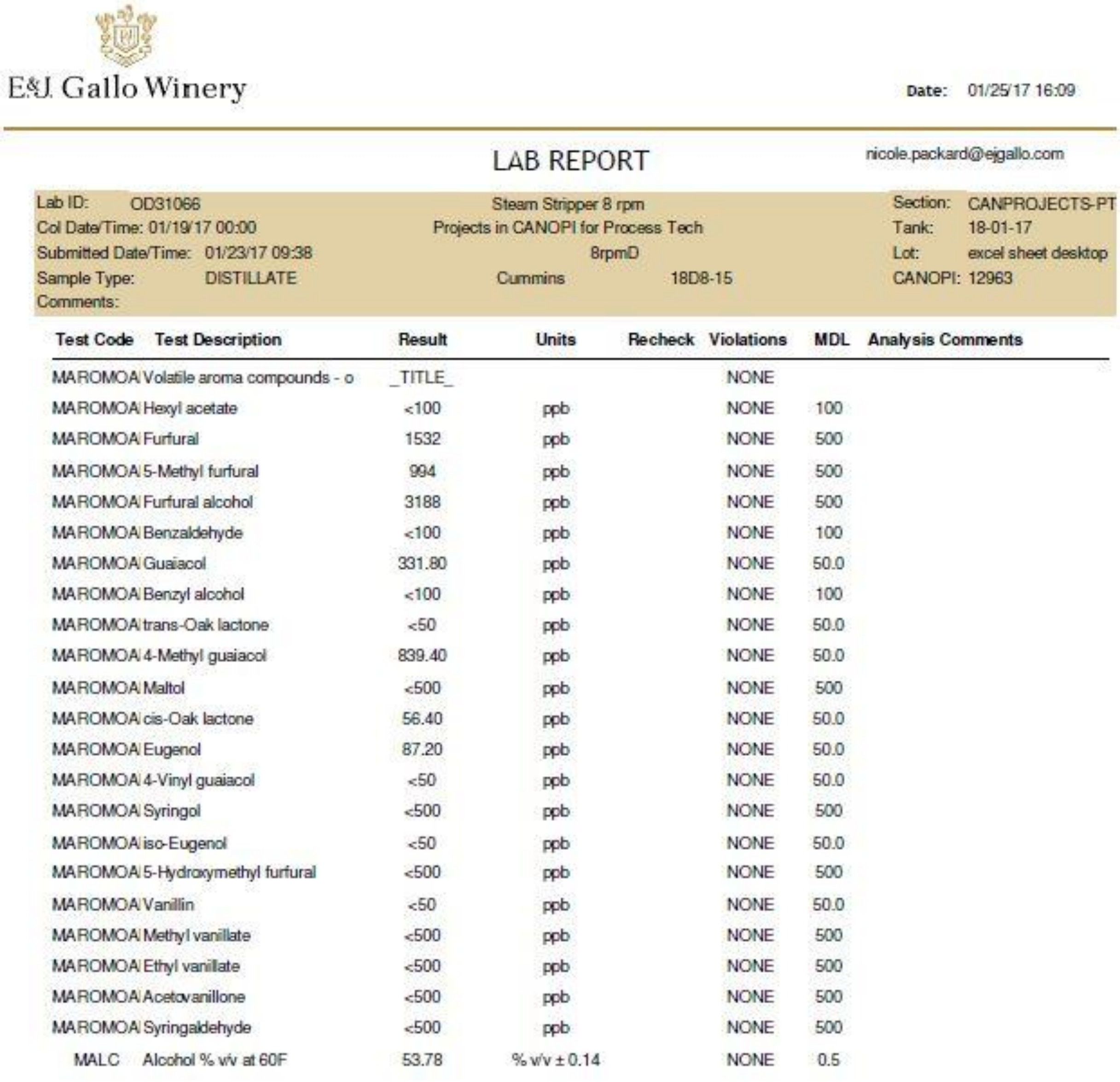
Lab ID: OD31061
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: DISTILLATE
Comments:

Steam Stripper 6 rpm
Projects in CANOPI for Process Tech
6rpmD
Cummins 18D6-15

Section: CANPROJECTS-PT
Tank: 18-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<100	ppb		NONE	100	
MAROMOA	Furfural	1611	ppb		NONE	500	
MAROMOA	5-Methyl furfural	1018	ppb		NONE	500	
MAROMOA	Furfural alcohol	5476	ppb		NONE	500	
MAROMOA	Benzaldehyde	<100	ppb		NONE	100	
MAROMOA	Guaiacol	405.60	ppb		NONE	50.0	
MAROMOA	Benzyl alcohol	222	ppb		NONE	100	
MAROMOA	trans-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	4-Methyl guaiacol	930.70	ppb		NONE	50.0	
MAROMOA	Maltol	<500	ppb		NONE	500	
MAROMOA	cis-Oak lactone	112.60	ppb		NONE	50.0	
MAROMOA	Eugenol	93.20	ppb		NONE	50.0	
MAROMOA	4-Vinyl guaiacol	<50	ppb		NONE	50.0	
MAROMOA	Syringol	<500	ppb		NONE	500	
MAROMOA	iso-Eugenol	<50	ppb		NONE	50.0	
MAROMOA	5-Hydroxymethyl furfural	<500	ppb		NONE	500	
MAROMOA	Vanillin	<50	ppb		NONE	50.0	
MAROMOA	Methyl vanillate	<500	ppb		NONE	500	
MAROMOA	Ethyl vanillate	<500	ppb		NONE	500	
MAROMOA	Acetovanillone	<500	ppb		NONE	500	
MAROMOA	Syringaldehyde	<500	ppb		NONE	500	
MALC	Alcohol % v/v at 60F	27.79	% v/v ± 0.14		NONE	0.1	

1-18-2017 Distillate 8rpm 15 stages



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

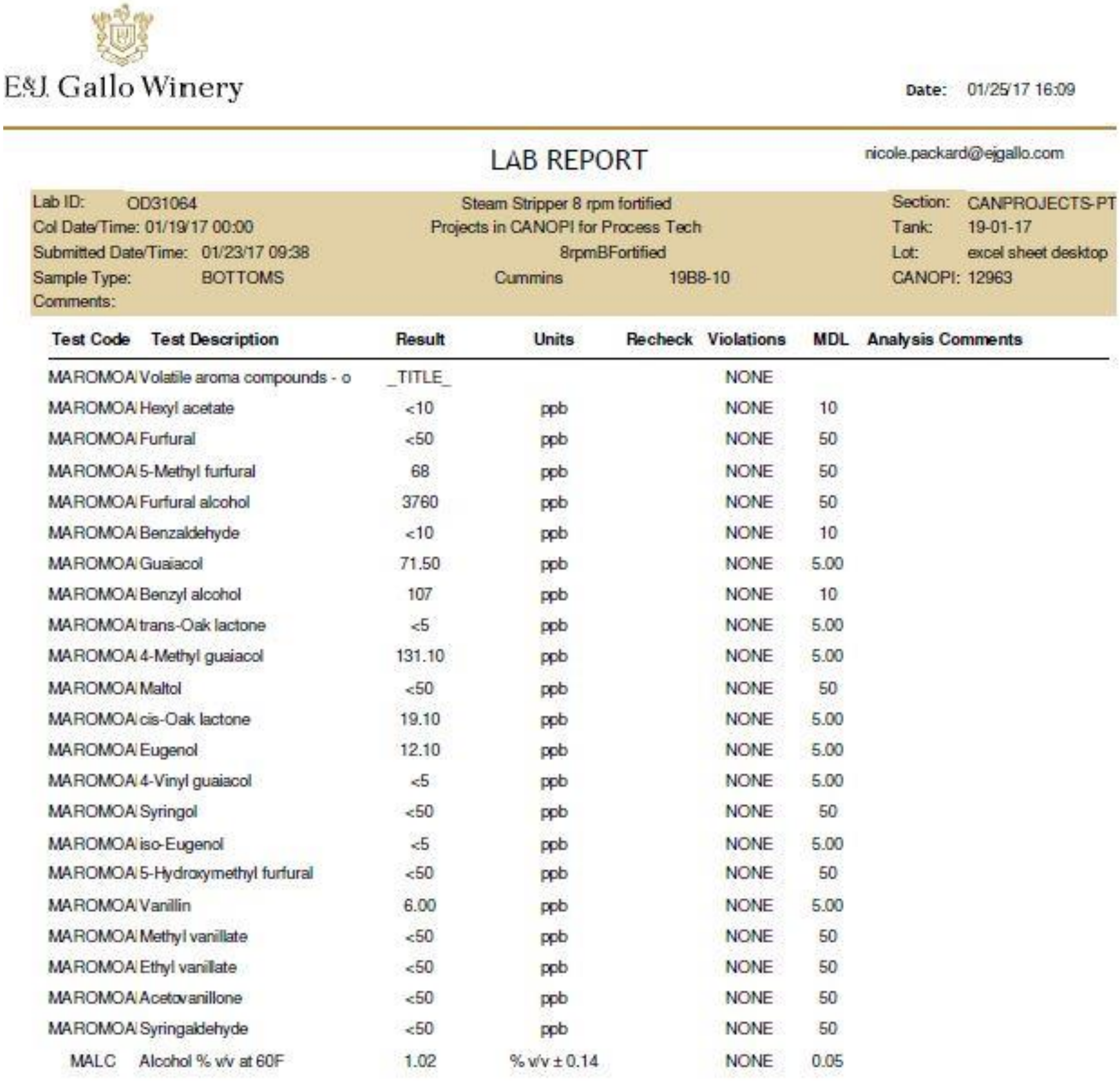
Lab ID: OD31066
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: DISTILLATE
Comments:

Steam Stripper 8 rpm
Projects in CANOPI for Process Tech
8rpmD
Cummins 18D8-15

Section: CANPROJECTS-PT
Tank: 18-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<100	ppb		NONE	100	
MAROMOA	Furfural	1532	ppb		NONE	500	
MAROMOA	5-Methyl furfural	994	ppb		NONE	500	
MAROMOA	Furfural alcohol	3188	ppb		NONE	500	
MAROMOA	Benzaldehyde	<100	ppb		NONE	100	
MAROMOA	Guaiacol	331.80	ppb		NONE	50.0	
MAROMOA	Benzyl alcohol	<100	ppb		NONE	100	
MAROMOA	trans-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	4-Methyl guaiacol	839.40	ppb		NONE	50.0	
MAROMOA	Maltol	<500	ppb		NONE	500	
MAROMOA	cis-Oak lactone	56.40	ppb		NONE	50.0	
MAROMOA	Eugenol	87.20	ppb		NONE	50.0	
MAROMOA	4-Vinyl guaiacol	<50	ppb		NONE	50.0	
MAROMOA	Syringol	<500	ppb		NONE	500	
MAROMOA	iso-Eugenol	<50	ppb		NONE	50.0	
MAROMOA	5-Hydroxymethyl furfural	<500	ppb		NONE	500	
MAROMOA	Vanillin	<50	ppb		NONE	50.0	
MAROMOA	Methyl vanillate	<500	ppb		NONE	500	
MAROMOA	Ethyl vanillate	<500	ppb		NONE	500	
MAROMOA	Acetovanillone	<500	ppb		NONE	500	
MAROMOA	Syringaldehyde	<500	ppb		NONE	500	
MALC	Alcohol % v/v at 60F	53.78	% v/v ± 0.14		NONE	0.5	

1-19-2017 Bottoms 8rpm 10 stages; Fortified



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

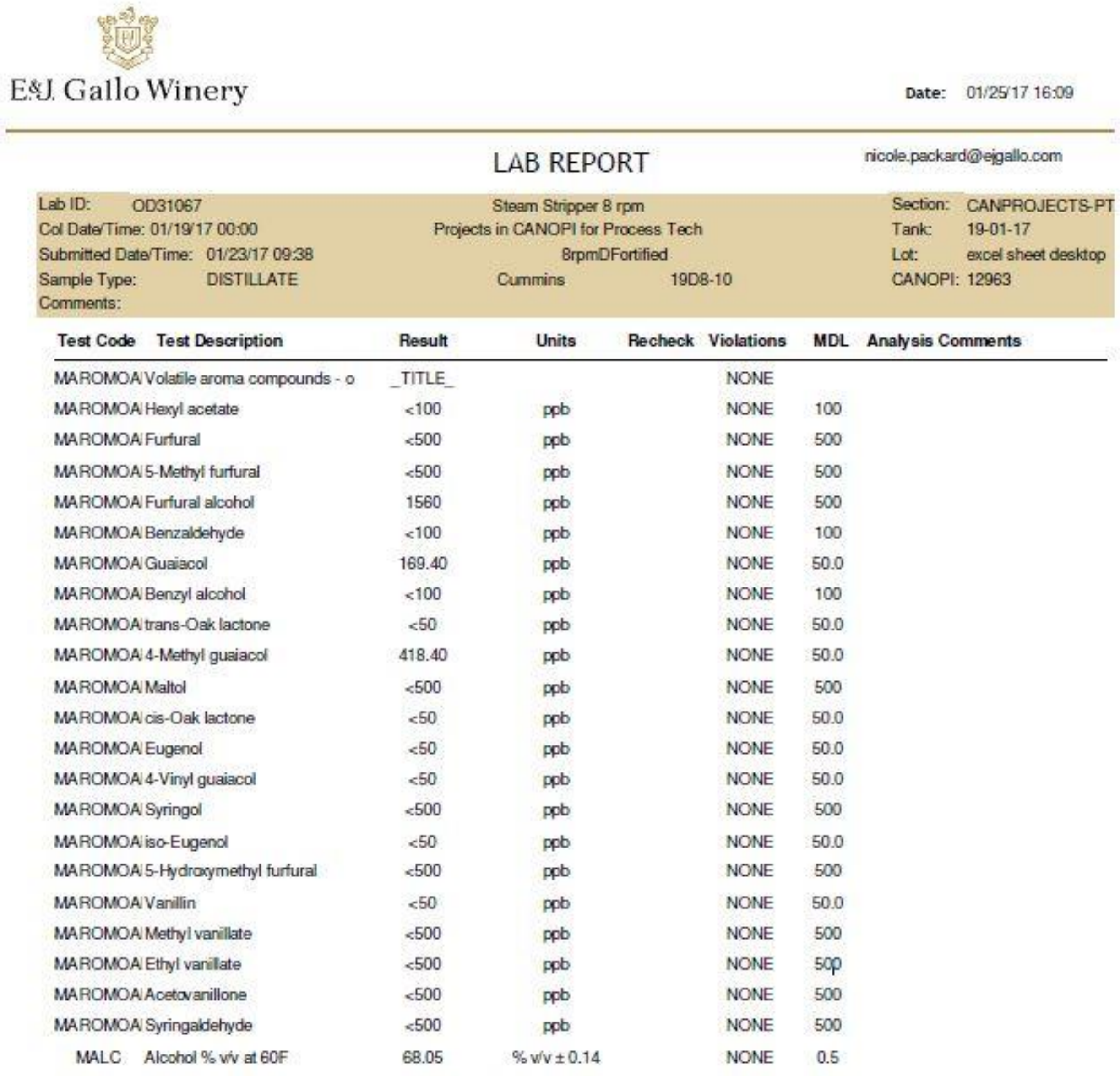
Lab ID: OD31064
Col Date/Time: 01/19/17 00:00
Submitted Date/Time: 01/23/17 09:38
Sample Type: BOTTOMS
Comments:

Steam Stripper 8 rpm fortified
Projects in CANOPI for Process Tech
8rpmBFortified
Cummins 19B8-10

Section: CANPROJECTS-PT
Tank: 19-01-17
Lot: excel sheet desktop
CANOPI: 12963

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<10	ppb		NONE	10	
MAROMOA	Furfural	<50	ppb		NONE	50	
MAROMOA	5-Methyl furfural	68	ppb		NONE	50	
MAROMOA	Furfural alcohol	3760	ppb		NONE	50	
MAROMOA	Benzaldehyde	<10	ppb		NONE	10	
MAROMOA	Guaiacol	71.50	ppb		NONE	5.00	
MAROMOA	Benzyl alcohol	107	ppb		NONE	10	
MAROMOA	trans-Oak lactone	<5	ppb		NONE	5.00	
MAROMOA	4-Methyl guaiacol	131.10	ppb		NONE	5.00	
MAROMOA	Maltol	<50	ppb		NONE	50	
MAROMOA	cis-Oak lactone	19.10	ppb		NONE	5.00	
MAROMOA	Eugenol	12.10	ppb		NONE	5.00	
MAROMOA	4-Vinyl guaiacol	<5	ppb		NONE	5.00	
MAROMOA	Syringol	<50	ppb		NONE	50	
MAROMOA	iso-Eugenol	<5	ppb		NONE	5.00	
MAROMOA	5-Hydroxymethyl furfural	<50	ppb		NONE	50	
MAROMOA	Vanillin	6.00	ppb		NONE	5.00	
MAROMOA	Methyl vanillate	<50	ppb		NONE	50	
MAROMOA	Ethyl vanillate	<50	ppb		NONE	50	
MAROMOA	Acetovanillone	<50	ppb		NONE	50	
MAROMOA	Syringaldehyde	<50	ppb		NONE	50	
MALC	Alcohol % v/v at 60F	1.02	% v/v ± 0.14		NONE	0.05	

1-19-2017 Distillate 8rpm 10 stages; Fortified



E&J Gallo Winery

Date: 01/25/17 16:09

LAB REPORT

nicole.packard@ejgallo.com

Lab ID: OD31067	Steam Stripper 8 rpm	Section:	CANPROJECTS-PT
Col Date/Time: 01/19/17 00:00	Projects in CANOPI for Process Tech	Tank:	19-01-17
Submitted Date/Time: 01/23/17 09:38	8rpmDFortified	Lot:	excel sheet desktop
Sample Type: DISTILLATE	Cummins 19D8-10	CANOPI:	12963
Comments:			

Test Code	Test Description	Result	Units	Recheck	Violations	MDL	Analysis Comments
MAROMOA	Volatile aroma compounds - o	_TITLE_			NONE		
MAROMOA	Hexyl acetate	<100	ppb		NONE	100	
MAROMOA	Furfural	<500	ppb		NONE	500	
MAROMOA	5-Methyl furfural	<500	ppb		NONE	500	
MAROMOA	Furfural alcohol	1560	ppb		NONE	500	
MAROMOA	Benzaldehyde	<100	ppb		NONE	100	
MAROMOA	Guaiacol	169.40	ppb		NONE	50.0	
MAROMOA	Benzyl alcohol	<100	ppb		NONE	100	
MAROMOA	trans-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	4-Methyl guaiacol	418.40	ppb		NONE	50.0	
MAROMOA	Maltol	<500	ppb		NONE	500	
MAROMOA	cis-Oak lactone	<50	ppb		NONE	50.0	
MAROMOA	Eugenol	<50	ppb		NONE	50.0	
MAROMOA	4-Vinyl guaiacol	<50	ppb		NONE	50.0	
MAROMOA	Syringol	<500	ppb		NONE	500	
MAROMOA	iso-Eugenol	<50	ppb		NONE	50.0	
MAROMOA	5-Hydroxymethyl furfural	<500	ppb		NONE	500	
MAROMOA	Vanillin	<50	ppb		NONE	50.0	
MAROMOA	Methyl vanillate	<500	ppb		NONE	500	
MAROMOA	Ethyl vanillate	<500	ppb		NONE	500	
MAROMOA	Acetovanillone	<500	ppb		NONE	500	
MAROMOA	Syringaldehyde	<500	ppb		NONE	500	
MALC	Alcohol % v/v at 60F	68.05	% v/v ± 0.14		NONE	0.5	

Fortified Calculations:

Want 500 mL of 10% ethanol by volume smoak by adding y mL of 95% ethanol solution

Original smoak mixture is 7% ethanol by volume

$x*(0.07) + y*(0.95) = 500*(0.10)$

$x + y = 500$

$x*(0.07) + (500 - x)*(0.95) = 50$

$0.07x + 475 - 0.95x = 50$

$x = 483$ mL smoak

$y = 17$ mL 95% Ethanol Solution

Appendix D: Theoretical Stages Calculations for Batch Distillation Tower

The theoretical number of stages for the batch distillation column was found using the diameter of the batch distillation column. The column had a diameter of 1inch that was given by the manufacturer. The packing height of the Pro-Pack Packing was determined using measuring tape to get an approximate packing height. The number of theoretical stages (N) of the column was calculated to help determine an approximate efficiency of the column.

Packing height (z) ~ 1 foot and 0.5 inch
Diameter (D) ~ 1 inch

The Pro-Pack Packing was made up of both 0.16 inch and 0.24 inch saddles

For a 1 inch diameter column, the manufacturer gave a height equivalent to a theoretical plate (HETP) for 0.16 inch and 0.24 inch saddles to be anywhere between 0.5inch to 1.4 inches.

HETP= 0.5 inch or 1.4 inches
z = 12.5 inch

$$N = \frac{z}{HETP}$$

When HETP= 0.5 inch, z = 12.5 inch

$$N = \frac{12.5}{0.5} = 25\ stages$$

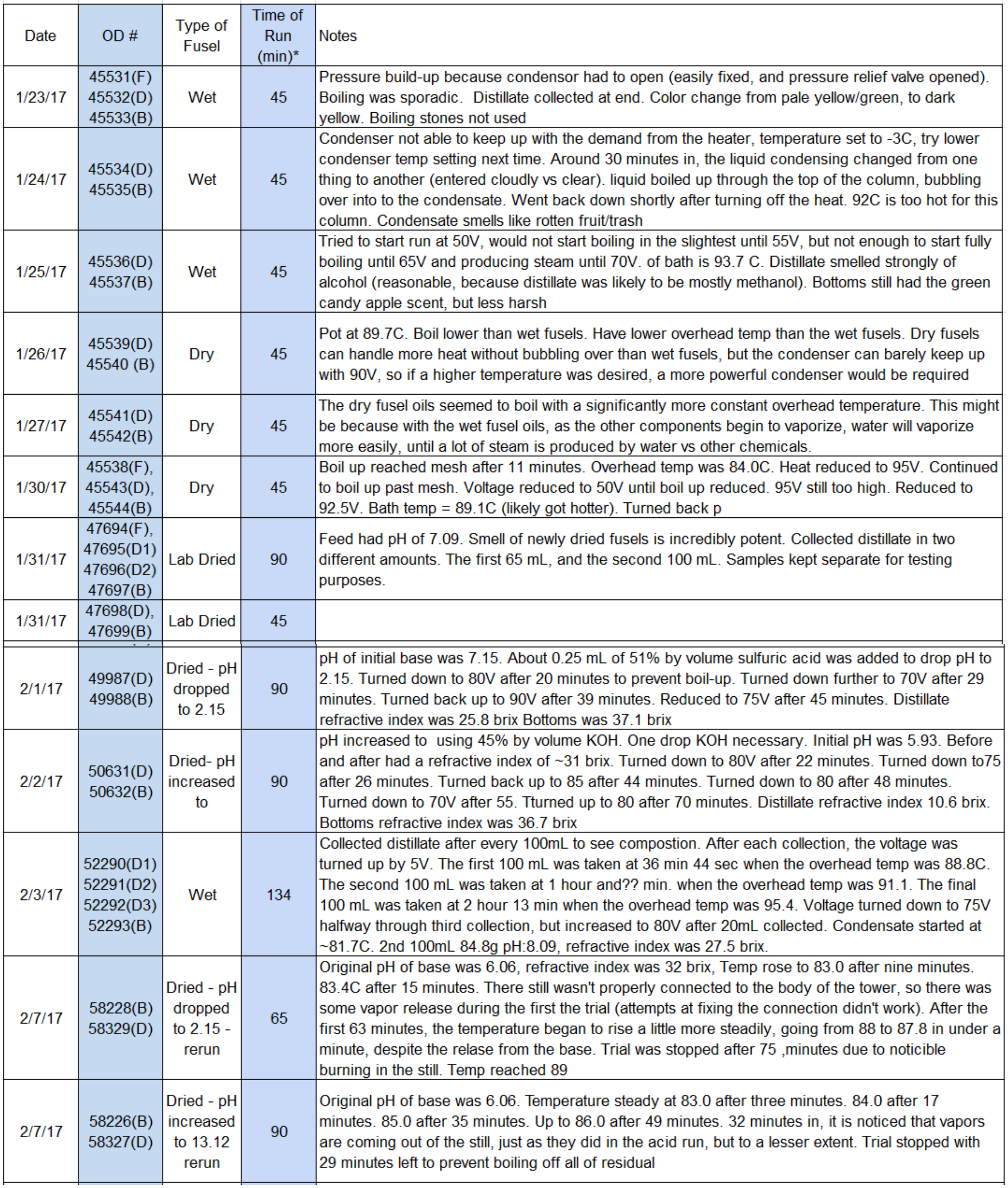
When HETP= 1.4 inches, z = 12.5 inch

$$N = N = \frac{12.5}{1.4} = 8.9 \approx 9 stages$$

Therefore, there are between 9 and 25 theoretical stages. Hence approximately 17 theoretical stages are present in the batch distillation column.

Appendix E: Raw Data and Lab Results for Fusel Oil Batch Distillation

Date	Type of Fusel	Time of Run (min)*	Volume Base (mL)	Mass Base (g)	Temp Set Voltage (V)	Average Temp at Heads (C)	Final Overhead Temp	Volume Distillate (mL)	% Volume of Total: Distillate	Mass Distillate (g)	Volume Bottoms (mL)	Mass Bottoms (g)	pH Distillate	pH Bottoms
1/23/17	Wet	45	500	402.14	80	88.5	90	134	26.80%	115.54	355	268.54	8.71	6.00
1/24/17	Wet	45	500	411.09	90	90	92	145	29.00%	126.3	365	280.09	6.55	4.93
1/25/17	Wet	45	500	not recorded	70	85	88	68	13.60%	58.2	455	356.3	6.3	4.82
1/26/17	Dry	45	500	415.8	90	84.4	85.4	190	38.00%	160.6	280	218.3	6.53	5.32
1/27/17	Dry	45	500	416.1	80	83.85	84.7	156	31.20%	110.3	380	230.3	6.84	5.73
1/30/17	Dry	45	500	414.5	100-->95	84.3	85.8	183	36.60%	155.2	325	256	7.45	5.34
1/31/17	Lab Dried	90	750	620.4	80	89.1	91.5	165	22.00%	164.3	580	451.3	6.12	7.66
1/31/17	Lab Dried	45	500	not recorded	80	86	89	102	20.40%	87.1	408	316.9	7.62	7.90
2/1/17	Dried - pH dropped to 2.15	90	500	413.1	90-->75	82.85	85.7	230	46.00%	189.7	256	196.9	7.65	1.49
2/2/17	Dried- pH increased to	90	500	414.0	90-->70	85.2	87.4	238	47.60%	201.4	245	184.1	6.96	8.88
2/3/17	Wet	134	750	600.6	80-->85-->90	89.2	95.4	300	40.00%	86.1, 84.8, 86.3 (Total = 257.2)	457	363.8	7.58, 8.09, 4.27	4.98
2/7/17	Dried - pH dropped to 2.15 - rerun	65	500	412.3	85	85	89	210	42.00%	177.4	164	125.1	6.14	0.37
2/7/17	Dried - pH increased to 13.12 rerun	90	500	415.5	85	84.85	86.7	200	40.00%	190.8	193	149.1	5.96	8.64
2/8/17	Lab Dried- Long Run	271	800	652.4	80	N/A	130.4	105, 100, 75 (Total = 280)	35.00%	87.1, 88.0, 64.6 (Total = 239.7)	520	339.6	5.25, 5.21, 5.48	6.64
2/15/17	wet, steam stripped from 2/14/17	47	325	266.8	80	92.1	94.5	21, 33 (Total = 54)	16.62%	20, 27.2 (Total = 47.2)	200	157.6	6.20,6.39	5.44
2/16	lab dried, steam stripped from 2/15/17	38	315	260.9	85	93.55	94.5	32, 12 (Total = 54)	17.14%	26.7, 16.5 (Total = 43.2)	190	147.1	6.04, 6.60	6.87



Date	OD #	Type of Fusel	Time of Run (min)*	Notes
1/23/17	45531(F) 45532(D) 45533(B)	Wet	45	Pressure build-up because condensor had to open (easily fixed, and pressure relief valve opened). Boiling was sporadic. Distillate collected at end. Color change from pale yellow/green, to dark yellow. Boiling stones not used
1/24/17	45534(D) 45535(B)	Wet	45	Condenser not able to keep up with the demand from the heater, temperature set to -3C, try lower condenser temp setting next time. Around 30 minutes in, the liquid condensing changed from one thing to another (entered cloudly vs clear). liquid boiled up through the top of the column, bubbling over into to the condensate. Went back down shortly after turning off the heat. 92C is too hot for this column. Condensate smells like rotten fruit/trash
1/25/17	45536(D) 45537(B)	Wet	45	Tried to start run at 50V, would not start boiling in the slightest until 55V, but not enough to start fully boiling until 65V and producing steam until 70V. of bath is 93.7 C. Distillate smelled strongly of alcohol (reasonable, because distillate was likely to be mostly methanol). Bottoms still had the green candy apple scent, but less harsh
1/26/17	45539(D) 45540 (B)	Dry	45	Pot at 89.7C. Boil lower than wet fusels. Have lower overhead temp than the wet fusels. Dry fusels can handle more heat without bubbling over than wet fusels, but the condenser can barely keep up with 90V, so if a higher temperature was desired, a more powerful condenser would be required
1/27/17	45541(D) 45542(B)	Dry	45	The dry fusel oils seemed to boil with a significantly more constant overhead temperature. This might be because with the wet fusel oils, as the other components begin to vaporize, water will vaporize more easily, until a lot of steam is produced by water vs other chemicals.
1/30/17	45538(F), 45543(D), 45544(B)	Dry	45	Boil up reached mesh after 11 minutes. Overhead temp was 84.0C. Heat reduced to 95V. Continued to boil up past mesh. Voltage reduced to 50V until boil up reduced. 95V still too high. Reduced to 92.5V. Bath temp = 89.1C (likely got hotter). Turned back p
1/31/17	47694(F), 47695(D1) 47696(D2) 47697(B)	Lab Dried	90	Feed had pH of 7.09. Smell of newly dried fusels is incredibly potent. Collected distillate in two different amounts. The first 65 mL, and the second 100 mL. Samples kept separate for testing purposes.
1/31/17	47698(D), 47699(B)	Lab Dried	45	
2/1/17	49987(D) 49988(B)	Dried - pH dropped to 2.15	90	pH of initial base was 7.15. About 0.25 mL of 51% by volume sulfuric acid was added to drop pH to 2.15. Turned down to 80V after 20 minutes to prevent boil-up. Turned down further to 70V after 29 minutes. Turned back up to 90V after 39 minutes. Reduced to 75V after 45 minutes. Distillate refractive index was 25.8 brix Bottoms was 37.1 brix
2/2/17	50631(D) 50632(B)	Dried- pH increased to	90	pH increased to using 45% by volume KOH. One drop KOH necessary. Initial pH was 5.93. Before and after had a refractive index of ~31 brix. Turned down to 80V after 22 minutes. Turned down to75 after 26 minutes. Turned back up to 85 after 44 minutes. Turned down to 80 after 48 minutes. Turned down to 70V after 55. Tturned up to 80 after 70 minutes. Distillate refractive index 10.6 brix. Bottoms refractive index was 36.7 brix
2/3/17	52290(D1) 52291(D2) 52292(D3) 52293(B)	Wet	134	Collected distillate after every 100mL to see compostion. After each collection, the voltage was turned up by 5V. The first 100 mL was taken at 36 min 44 sec when the overhead temp was 88.8C. The second 100 mL was taken at 1 hour and?? min. when the overhead temp was 91.1. The final 100 mL was taken at 2 hour 13 min when the overhead temp was 95.4. Voltage turned down to 75V halfway through third collection, but increased to 80V after 20mL collected. Condensate started at ~81.7C. 2nd 100mL 84.8g pH:8.09, refractive index was 27.5 brix.
2/7/17	58228(B) 58329(D)	Dried - pH dropped to 2.15 - rerun	65	Original pH of base was 6.06, refractive index was 32 brix, Temp rose to 83.0 after nine minutes. 83.4C after 15 minutes. There still wasn't properly connected to the body of the tower, so there was some vapor release during the first the trial (attempts at fixing the connection didn't work). After the first 63 minutes, the temperature began to rise a little more steadily, going from 88 to 87.8 in under a minute, despite the relase from the base. Trial was stopped after 75 ,minutes due to noticible burning in the still. Temp reached 89
2/7/17	58226(B) 58327(D)	Dried - pH increased to 13.12 rerun	90	Original pH of base was 6.06. Temperature steady at 83.0 after three minutes. 84.0 after 17 minutes. 85.0 after 35 minutes. Up to 86.0 after 49 minutes. 32 minutes in, it is noticed that vapors are coming out of the still, just as they did in the acid run, but to a lesser extent. Trial stopped with 29 minutes left to prevent boiling off all of residual

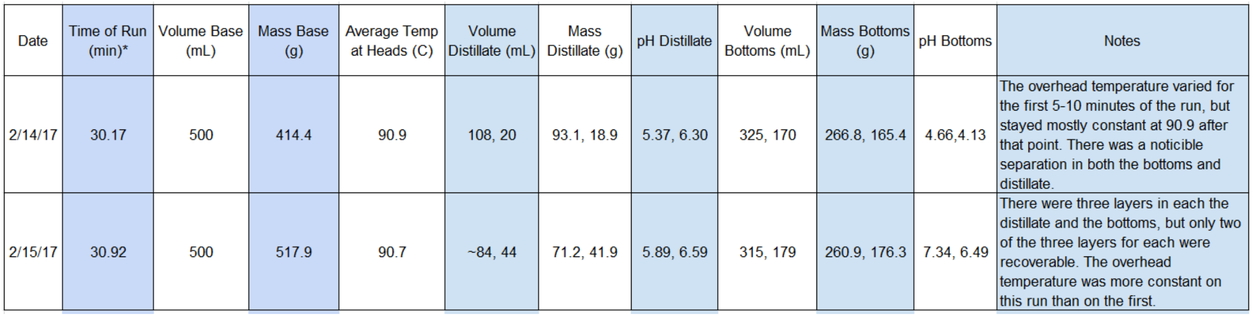
2/8/17	58330(B) 58331(D1) 58332(D2) 59881(3A) 59882(3B)	Lab Dried-Long Run	271	Trial allowed to run until overhead temperatures reached the 100s. Samples taken every 100mL. First trial completed with larger condensor. Seems to be affecting how much distillate is collected. Temp increased to 81.6C after 7 minutes. 83.1C after 13 minutes. Reached 84.6C after 26 minutes. Reached 87.2C when the first distillate was collected after approximately 52 minutes. After 1 hour, temp was at 88.4 C. reached 89.6C after 1 hour 27 minutes. up to 90.6C after 1 hour 47 minutes. Around this time, minor separation was noticed. D2 collected at 2 hours 7minutes with noticible separation, and the temp was 91.4C. 2 hours 37 minutes, flooding occured when overhead temp was 93.4 C, voltage down to 70V. 2 hours 44 min. flooding finished voltage increased to 80V. Temp was 93.7C. 2 hours 55 minutes in, overhead temp has dropped to 93C, and collection is going very slowly, condensate is very oily. Temp increased back to 93.7 after 2 hours 58 minutes, and is continuing to rise. At this time, it is noticed that flooding is beginning to occur. Voltage reduced to 70 V (temp at 94.2C) Voltage increased to 75V after 3 hours 7 minutes, temperature has dropped back to 93.7C. 3 hours 12 minutes, temp is down to 92.1C and apparently still dropping. Voltage increased to 80V after 3 hours 20 minutes. The increase in voltage is helping the temperature increase quickly, up to 94.0 after 3 hours 28 minutes. Temperature rising quickly. Up to 99C after 3 hours 31 minutes, rising quickly. 100C 5 seconds later. column rose approximately 25C in 3.5minutes, condensate is still collecting slowly. Voltage turned down to 75 to prevent flooding after 3 hours 5 minutes. Voltage reduced to 70V after 3 hours 40 minutes. Temperature had risen to 125, but dropped quickly to 120C after reducing the voltage. 3 hours 47 minutes, Voltage increased to 80V. 4 hours and 9 minutes, overhead temp at 16.6. Max temp of 130.0 seen at 4 hours 31 minutes at 80V distillate 3 was put into the separatory funnel to separate the two liquids
2/10/17	NOT SUBMITTED	Dry	157	pH of base was 5.83. Trying to keep overhead constant around 78.5-81.5C. Column kept in total reflux until temperature achieved, and then reflux adjusted. Flooding started after 23 minutes, so voltage was reduced to 70V. Valve first opened at 74.0C after 53 minutes. Temperature increased to 75.4 and slowly began to drop again. Valve opened again after 1 hour 7 min. Closed at1 hour 10 minutes when temperature was 75.7. After 1 hour 17 minutes, condensate was collected and temperature allowed to rise to 79C before being held between 79C-81.5C. Closed at 1 hour 42 minutes. Reopened at 1 hour 56 minutes when temp was 78.4. How far open the nozzle was was adjusted to attepmt to keep the temperature more steady. Nozzle closed at 2 hours 14 minutes when temp was 81.5C. Trial stopped after 2 hours 23 minutes. Approximately60 mL distillate collected. Trial was finished on 2/13/17. Timer was started when overhead temperature began to rise. overhead temperature reached 83.6 immediately, but slowly began to drop after the overhead valve was not open. the wrong plug was put into the still, so some vapor is escaping from the bottoms. Valve opened after 22 minutes when temperature was 80.0C, Closed at 25 minutes when temp was 81.4C. Valve reopened at 1 hour when temperature is 79.3C. Valve closed at 1 hour 4 minutes when tempe was 81.4C. Temperature only dropped 1.5C after 30 minutes (at the 1 hour 34 minute mark).Nozzle opened at 2 hours 34 minutes when the temp was 78.7C. Closed at 2 hours 37 minutes when temp was 81.4C. At this point, the run was ceased. Too much of the residual had evaporated through the plug and the temperature would not stay within the range.
2/15/17	68804(B) 68805(DT) 68806(DB)	wet, steam stripped from 2/14/17	47	This batch started with the top layer of the steam stripping bottoms. Batch distillation is being completed to see what further separation can be completed. The boiling process took longer than anticipated, and the liquid looked very thick. Overhead temperature started higher than normal, as to be expected, because there should have been little to no light key from the original fusel oils left. Temp is at 92.5 at 7.5 minutes.The boiling in the still looks foamy. Temperature reached 94.0 at 30 minutes. Foaming has subsided by 34 minutes. Voltage increased to 90V at 36 minutes in an attempt to see if the temperature will rise or if condensate collection will increase. Temperature was up to 94.5 after 45 minutes. Increasing the voltage seems to have increased the condensate collection a little, but not significantly. It is noted that at 46 minutes, vapor is escaping from the still. Trial stopped at 47 minutes to prevent more loss of residual. Temperature was 94.5C. There were three distinct liquid layers in the distillate, but only the top and bottom were recoverable. Two in steam stripped bottoms, two in steam stripped distillate, one in batch residual, two in steam stripped distillate (which was to be expected based on overhead temperature).
2/16	69362(B) 69363(DT) 69364(DB)	lab dried, steam stripped from 2/15/17	38	Temperature up to 92.6C after 6 minutes. Temperature up to 93.8C at 19.5 minutes. Some liquid is starting to escape from the seal at 35 minutes. Heat turned off after 38 minutes because of the escaping vapor (wiping the connection did not help). Condensate allowed to finish collecting until no longer dripping. Final Temp was 94.5. There was separation noted in the distillate. It looks like only two layers. Will separate using the separatory funnel.

Fusel Component	Wet: 90V Distillate	Wet: 90V Bottoms	Dry: 95V Distillate	Dry: 95V Bottoms	Lab Dried: 80V Distillate 1 (90min)	Lab Dried: 80V Distillate 2 (90min)	Lab Dried: 80V Bottoms (90min)	Low pH, 90 min: Distillate	Low pH, 90 min: Bottoms	High pH, 90 min: Bottoms (LAB)	Long Run D1	Long Run, D2	Long Run, D3	Long Run Bottoms	long run 2-8, Bottoms	long run 2-8, Distillate 1	long run 2-8, Distillate 2
(mg/L)	OD45534	OD45535	OD45543	OD45544	OD47695	OD47696	OD47697	OD49987	OD49988	OD50632	OD52290	OD52291	OD52292	OD52293	OD58330	OD58331	OD58332
Acetaldehyde	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000	<13000
Methanol	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000
Ethyl Acetate	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000	<20000
n-propyl	14410	<10000	163700	208900	11900	14790	<10000	182100	213100	206800	15050	14750	16460	<10000	<10000	13740	19940
Sec-butyl	76450	15610	73290	91880	77840	88660	17330	73060	98000	97510	91670	91810	106500	9686	<5000	89480	124700
Iso-Butyl	56350	22110	35290	99930	51100	70500	24460	38490	119000	124100	61390	73030	102700	16460	<10000	55980	103300
n-Butyl	<5000	<5000	<5000	11250	<5000	<5000	<5000	<5000	14850	15290	<5000	<5000	<5000	<5000	<5000	<5000	<5000
Active Amyl	45580	124800	<10000	53770	25180	50440	130200	<10000	72640	76330	31600	60220	102200	135100	137700	15140	46080
Iso-Amyl	110800	439400	<20000	155500	47740	107200	460200	<20000	210000	220500	62000	136300	265400	498400	507400	28990	81820
Total Fusel Oils	304400	606100	272700	621200	213800	332600	635600	299200	727700	740600	262200	377500	595700	660700	649300	203300	377400
Other Fusel Oils	**810**	**4180**	**420**	**-30**	**40**	**1010**	**3410**	**5550**	**110**	**70**	**490**	**1390**	**2440**	**1054**	**4200**	**-30**	**1560**

	Date	Type	Description	Refractive Index (Deg Brix)	Refractive Index (at 20C)	%Alcohol (%v/v +/- 0.14)	Ethanol in high fusel oils (%v/v)	$MFO
OD45531	1/23/2017	Wet	Feed	38.6	1.3970	pending	11.2	-
OD45532	1/23/2017	Wet	80V Distillate	26.0	1.3740	29.19	-	-
OD45533	1/23/2017	Wet	80V Bottoms	43.4	1.4064	pending	1.6	-
OD45534	1/24/2017	Wet	90V Distillate	26.0	1.3740	33.11	37.0	See Sheet 4
OD45535	1/24/2017	Wet	90 V Bottoms	43.0	1.4056	0.32	2.4	See Sheet 4
OD45536	1/25/2017	Wet	70V Distillate	24.5	1.3714	50.03	-	-
OD45537	1/25/2017	Wet	70V Bottoms	40.6	1.4008	3.27	-	-
OD45539	1/26/2017	Dry	90V Distillate	24.9	1.3721	-	37.1	-
OD45540	1/26/2017	Dry	90V Bottoms	35.1	1.3904	-	6.8	-
OD45541	1/27/2017	Dry	80V Distillate	23.9	1.3704	-	43.8	-
OD45542	1/27/2017	Dry	80V Bottoms	33.0	1.3865	-	11.5	-
OD45538	1/30/2017	Dry	Feed	31.0	1.3829	-	19.8	-
OD45543	1/30/2017	Dry	95V Distillate	24.4	1.3712	-	37.6	See Sheet 4
OD45544	1/30/2017	Dry	95V Bottoms	34.1	1.3885	-	9.0	See Sheet 4
OD47694	1/31/2017	Lab Dried	Feed	38.6	1.3970	-	10.8	-
OD47695	1/31/2017	Lab Dried	80V Distillate 1 (90min)	24.7	1.3718	-	44.4	See Sheet 4
OD47696	1/31/2017	Lab Dried	80V Distillate 2 (90min)	26.6	1.3750	-	26.9	See Sheet 4
OD47697	1/31/2017	Lab Dried	80V Bottoms (90min)	42.7	1.4050	-	1.9	See Sheet 4
OD47698	1/31/2017	Lab Dried	80V Distillate (45 min)	24.3	1.3711	-	53.2	-
OD47699	1/31/2017	Lab Dried	80V Bottoms (45 min)	42.3	1.4042	-	2.0	-
OD49987	2/1/2017	Dry	Low pH, 90 min: Distillate	24.7	1.3718	-	39.6	See Sheet 4
OD49988	2/1/2017	Dry	Low pH, 90 min: Bottoms	36.8	1.3935	-	4.2	See Sheet 4
OD50631	2/2/2017	Dry	High pH, 90 min: Distillate (LAB)	24.8	1.3719	-	37.6	pending
OD50632	2/2/2017	Dry	High pH, 90 min: Bottoms (LAB)	37.2	1.3943	-	2.9	See Sheet 4
OD52290	2/3/2017	wet	Long Run, D1	25.2	1.3726	-	40.8	See Sheet 4
OD52291	2/3/2017	Wet	Long Run, D2	26.7	1.2752	-	25.1	See Sheet 4
OD52292	2/3/2017	Wet	Long Run, D3	35.8	1.3916	7.22	-	See Sheet 4
OD52293	2/3/2017	Wet	Long Run Bottoms	43.7	1.4070	-	0.5	See Sheet 4
OD58326	2/7/2017	Lab Dried	high pH run, bottoms	36.8	1.3935	-	8.2	pending
OD58327	2/7/2017	Lab Dried	high pH run, Distillate	24.8	1.3719	-	37.0	-
OD58328	2/7/2017	Lab Dried	low pH run, bottoms	38.6	1.3968	-	5.4	pending
OD58329	2/7/2017	Lab Dried	low pH run, distillate	24.6	1.3716	-	37.6	-
OD58330	2/8/2017	Lab Dried	long run 2-8, Bottoms	44.0	1.4076	-	3.4	See Sheet 4
OD58331	2/8/2017	Lab Dried	long run 2-8, Distillate 1	23.8	1.3702	-	55.0	See Sheet 4
OD58332	2/8/2017	Lab Dried	long run 2-8, Distillate 2	27.0	1.3757	-	26.3	See Sheet 4
OD59881	2/8/2017	Lab Dried	long run 2-8, Distillate 3A	7.5	1.3440	9.90	-	-
OD59882	2/8/2017	Lab Dried	long run 2-8, Distillate 3B	4.8	1.3400	9.44	-	-
OD66211	2/14/2017	Wet	Steam Strip Bottoms 1	40.9	1.4014	-	3.0	See Sheet 2
OD66212	2/14/2017	Wet	Steam Strip Bottoms 2	2.8	1.3370	-	2.5	See Sheet 2
OD66213	2/14/2017	Wet	Steam Strip Distillate 1	28.7	1.3787	-	21.8	See Sheet 2
OD66214	2/14/2017	Wet	Steam Strip Distillate 2	11.9	1.3507	-	19.8	See Sheet 2
OD68804	2/15/2017	Wet	Stripped/Batch Bottoms	43.7	1.4070	-	0.8	See Sheet 2
OD68805	2/15/2017	Wet	Stripped/Batch Distillate Top	35.4	1.3909	-	6.5	See Sheet 2
OD68806	2/15/2017	Wet	Stripped/Batch Distillate Bottom	8.7	1.3459	-	7.6	See Sheet 2
OD68807	2/15/2017	Lab Dried	Steam Strip Bottoms 1	41.2	1.4020	-	2.2	See Sheet 2
OD68808	2/15/2017	Lab Dried	Steam Strip Bottoms 2	2.6	1.3368	-	2.2	See Sheet 2
OD68809	2/15/2017	Lab Dried	Steam Strip Distillate 1	31.1	1.3830	-	15.3	See Sheet 2
OD68810	2/15/2017	Lab Dried	Steam Strip Distillate 2	10.7	1.3489	-	16.8	See Sheet 2
OD69362	2/16/2017	Lab Dried	Stripped/Batch Bottoms	43.8	1.4072	-	-	pending
OD69363	2/16/2017	Lab Dried	Stripped/Batch Distillate Top	33.9	1.3881	-	-	pending
OD69364	2/16/2017	Lab Dried	Stripped/Batch Distillate Bottom	8.1	1.3449	-	-	pending

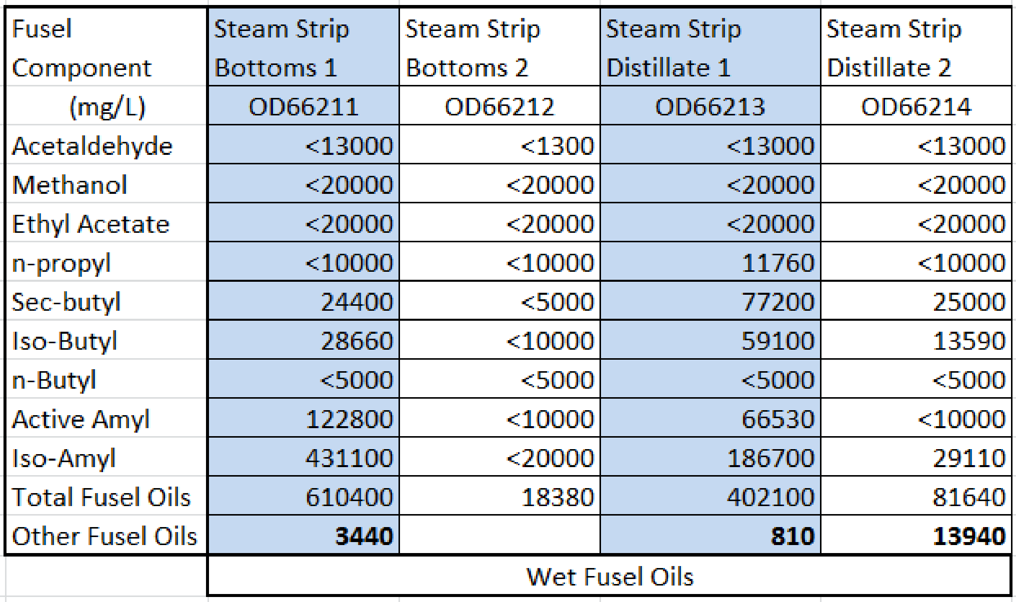
Appendix F: Full Lab Results for Sequential Distillation Trials

Fusel Oil Steam Stripper Spreadsheet



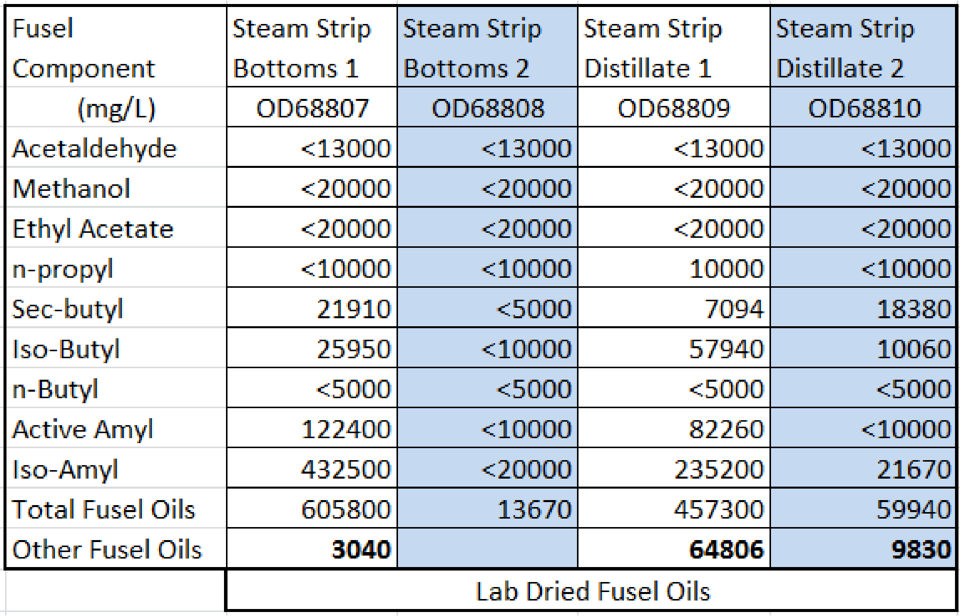
Date	Time of Run (min)*	Volume Base (mL)	Mass Base (g)	Average Temp at Heads (C)	Volume Distillate (mL)	Mass Distillate (g)	pH Distillate	Volume Bottoms (mL)	Mass Bottoms (g)	pH Bottoms	Notes
2/14/17	30.17	500	414.4	90.9	108, 20	93.1, 18.9	5.37, 6.30	325, 170	266.8, 165.4	4.66,4.13	The overhead temperature varied for the first 5-10 minutes of the run, but stayed mostly constant at 90.9 after that point. There was a noticible separation in both the bottoms and distillate.
2/15/17	30.92	500	517.9	90.7	~84, 44	71.2, 41.9	5.89, 6.59	315, 179	260.9, 176.3	7.34, 6.49	There were three layers in each the distillate and the bottoms, but only two of the three layers for each were recoverable. The overhead temperature was more constant on this run than on the first.

Steam Stripping of Wet Fusel Oils



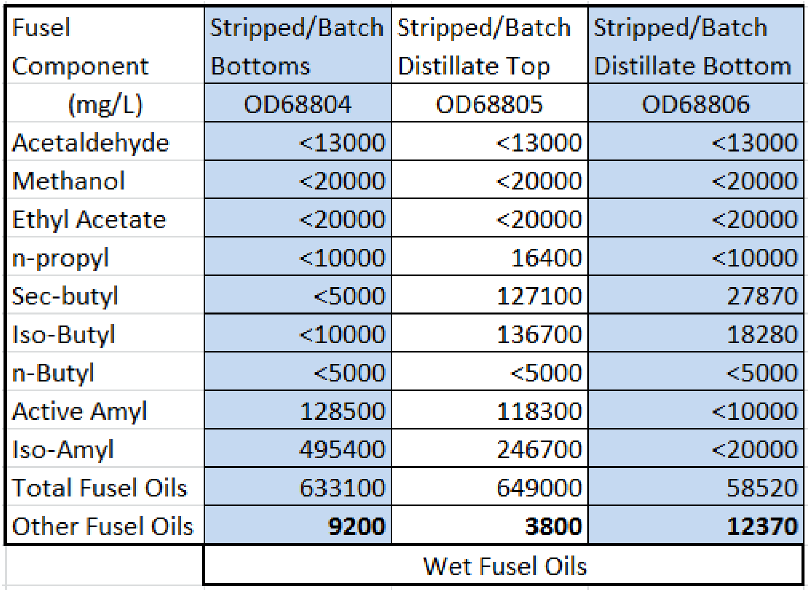
Fusel Component	Steam Strip Bottoms 1	Steam Strip Bottoms 2	Steam Strip Distillate 1	Steam Strip Distillate 2
(mg/L)	OD66211	OD66212	OD66213	OD66214
Acetaldehyde	<13000	<1300	<13000	<13000
Methanol	<20000	<20000	<20000	<20000
Ethyl Acetate	<20000	<20000	<20000	<20000
n-propyl	<10000	<10000	11760	<10000
Sec-butyl	24400	<5000	77200	25000
Iso-Butyl	28660	<10000	59100	13590
n-Butyl	<5000	<5000	<5000	<5000
Active Amyl	122800	<10000	66530	<10000
Iso-Amyl	431100	<20000	186700	29110
Total Fusel Oils	610400	18380	402100	81640
Other Fusel Oils	**3440**		**810**	**13940**
	Wet Fusel Oils			

Steam Stripping of Lab Dried Fusel Oils



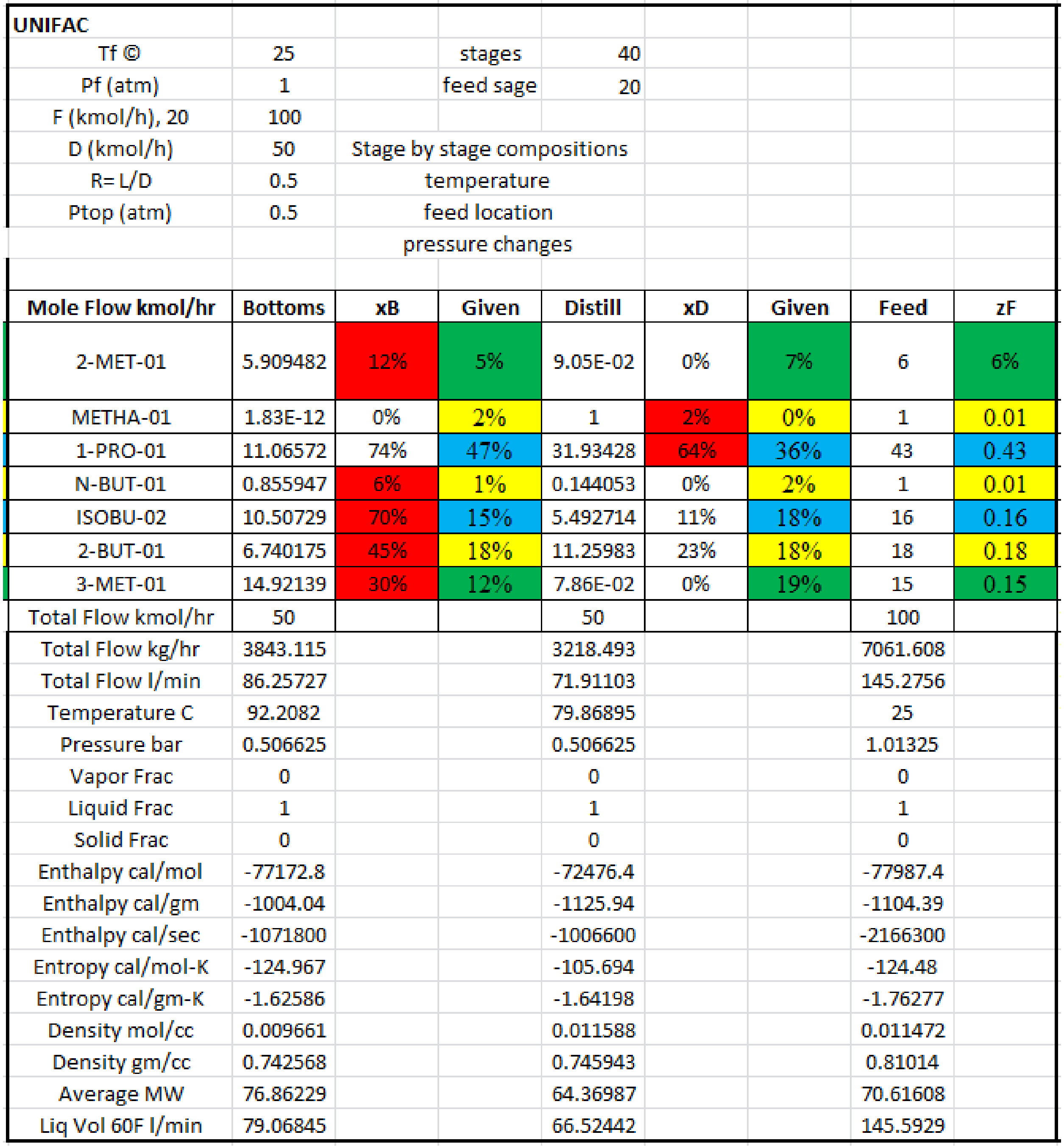
Fusel Component	Steam Strip Bottoms 1	Steam Strip Bottoms 2	Steam Strip Distillate 1	Steam Strip Distillate 2
(mg/L)	OD68807	OD68808	OD68809	OD68810
Acetaldehyde	<13000	<13000	<13000	<13000
Methanol	<20000	<20000	<20000	<20000
Ethyl Acetate	<20000	<20000	<20000	<20000
n-propyl	<10000	<10000	10000	<10000
Sec-butyl	21910	<5000	7094	18380
Iso-Butyl	25950	<10000	57940	10060
n-Butyl	<5000	<5000	<5000	<5000
Active Amyl	122400	<10000	82260	<10000
Iso-Amyl	432500	<20000	235200	21670
Total Fusel Oils	605800	13670	457300	59940
Other Fusel Oils	**3040**		**64806**	**9830**
	Lab Dried Fusel Oils			

Batch Distillation Results of the Steam Stripped Wet Fusil Oils

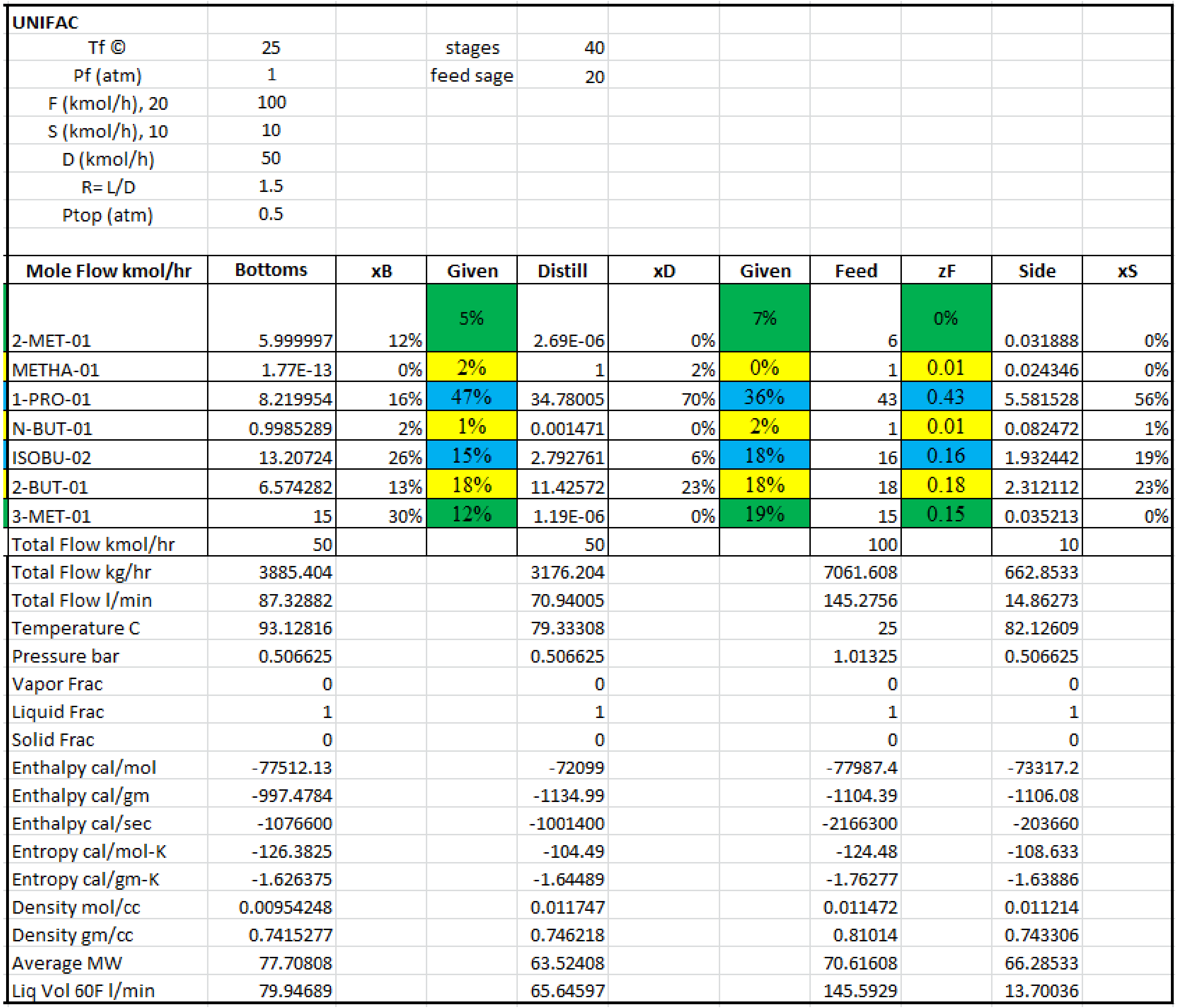


Fusel Component	Stripped/Batch Bottoms	Stripped/Batch Distillate Top	Stripped/Batch Distillate Bottom
(mg/L)	OD68804	OD68805	OD68806
Acetaldehyde	<13000	<13000	<13000
Methanol	<20000	<20000	<20000
Ethyl Acetate	<20000	<20000	<20000
n-propyl	<10000	16400	<10000
Sec-butyl	<5000	127100	27870
Iso-Butyl	<10000	136700	18280
n-Butyl	<5000	<5000	<5000
Active Amyl	128500	118300	<10000
Iso-Amyl	495400	246700	<20000
Total Fusel Oils	633100	649000	58520
Other Fusel Oils	**9200**	**3800**	**12370**
	Wet Fusel Oils		

Appendix G: Full Continuous Batch Data

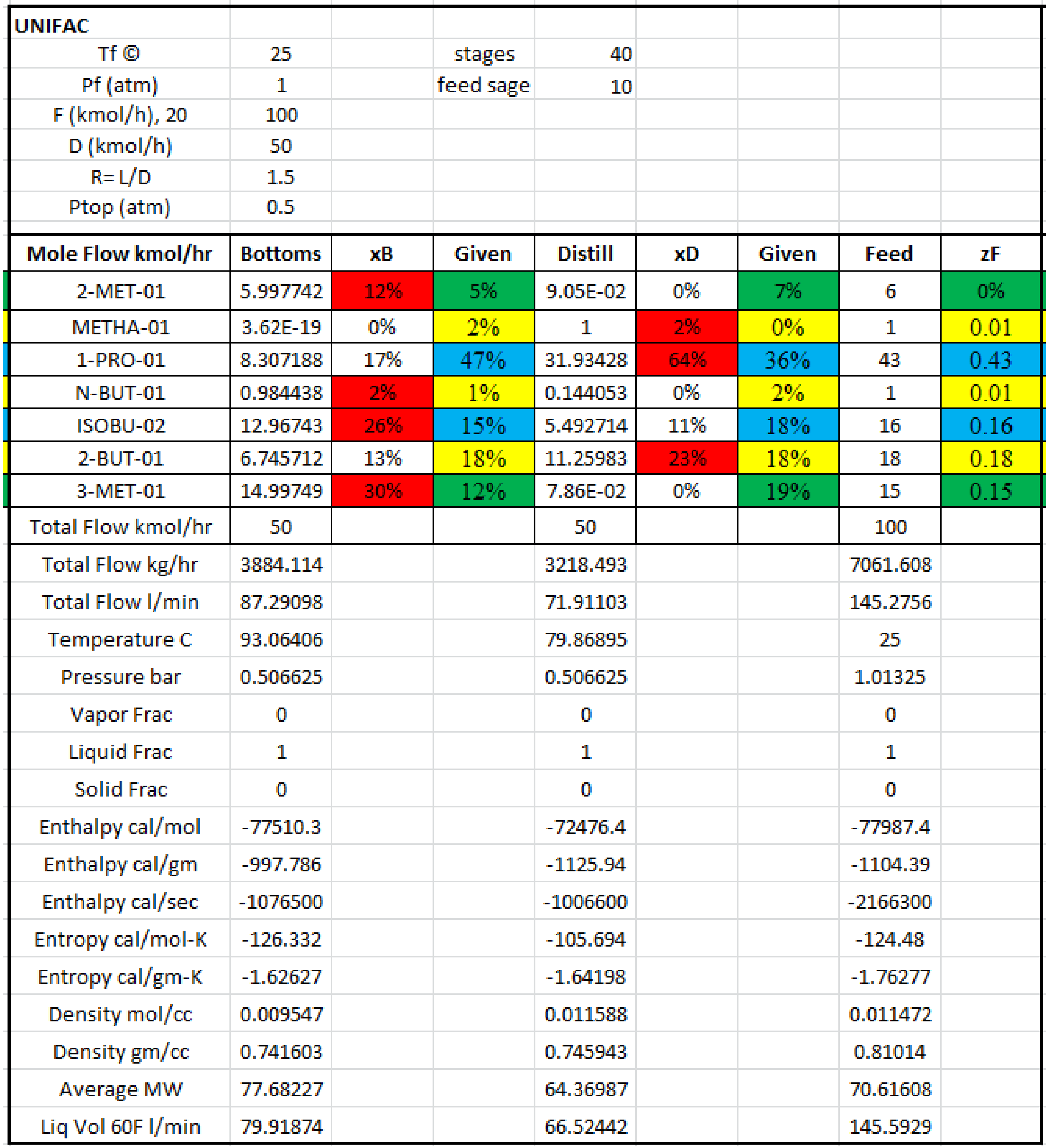


UNIFAC								
Tf ©	25		stages	40				
Pf (atm)	1		feed sage	20				
F (kmol/h), 20	100							
D (kmol/h)	50	Stage by stage compositions						
R= L/D	0.5	temperature						
Ptop (atm)	0.5	feed location						
		pressure changes						
Mole Flow kmol/hr	**Bottoms**	**xB**	**Given**	**Distill**	**xD**	**Given**	**Feed**	**zF**
2-MET-01	5.909482	12%	5%	9.05E-02	0%	7%	6	6%
METHA-01	1.83E-12	0%	2%	1	2%	0%	1	0.01
1-PRO-01	11.06572	74%	47%	31.93428	64%	36%	43	0.43
N-BUT-01	0.855947	6%	1%	0.144053	0%	2%	1	0.01
ISOBU-02	10.50729	70%	15%	5.492714	11%	18%	16	0.16
2-BUT-01	6.740175	45%	18%	11.25983	23%	18%	18	0.18
3-MET-01	14.92139	30%	12%	7.86E-02	0%	19%	15	0.15
Total Flow kmol/hr	50			50			100	
Total Flow kg/hr	3843.115			3218.493			7061.608	
Total Flow l/min	86.25727			71.91103			145.2756	
Temperature C	92.2082			79.86895			25	
Pressure bar	0.506625			0.506625			1.01325	
Vapor Frac	0			0			0	
Liquid Frac	1			1			1	
Solid Frac	0			0			0	
Enthalpy cal/mol	-77172.8			-72476.4			-77987.4	
Enthalpy cal/gm	-1004.04			-1125.94			-1104.39	
Enthalpy cal/sec	-1071800			-1006600			-2166300	
Entropy cal/mol-K	-124.967			-105.694			-124.48	
Entropy cal/gm-K	-1.62586			-1.64198			-1.76277	
Density mol/cc	0.009661			0.011588			0.011472	
Density gm/cc	0.742568			0.745943			0.81014	
Average MW	76.86229			64.36987			70.61608	
Liq Vol 60F l/min	79.06845			66.52442			145.5929	



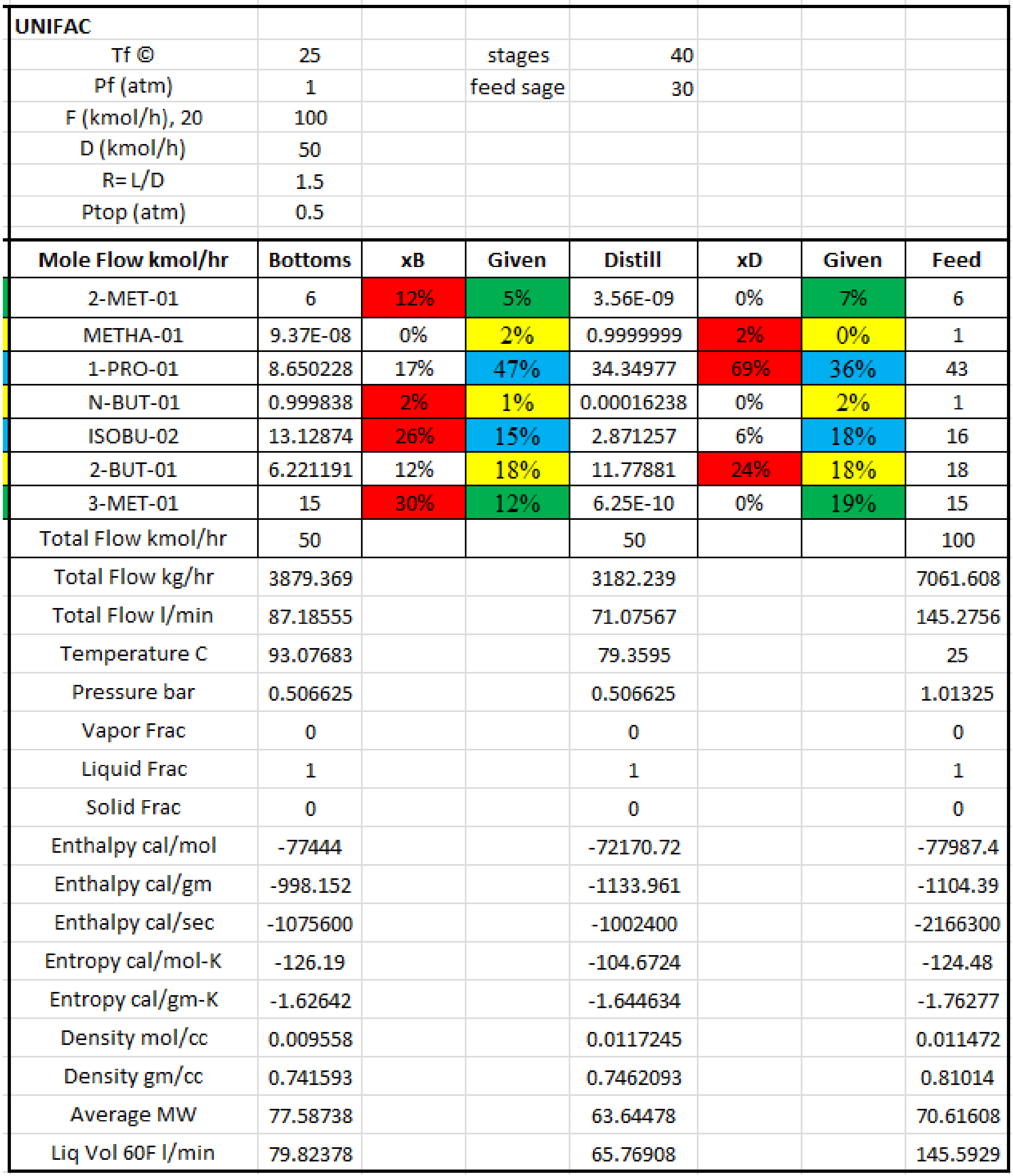
UNIFAC				
Tf ©	25		stages	40
Pf (atm)	1		feed sage	20
F (kmol/h), 20	100			
S (kmol/h), 10	10			
D (kmol/h)	50			
R= L/D	1.5			
Ptop (atm)	0.5			

Mole Flow kmol/hr	Bottoms	xB	Given	Distill	xD	Given	Feed	zF	Side	xS
2-MET-01	5.999997	12%	5%	2.69E-06	0%	7%	6	0%	0.031888	0%
METHA-01	1.77E-13	0%	2%	1	2%	0%	1	0.01	0.024346	0%
1-PRO-01	8.219954	16%	47%	34.78005	70%	36%	43	0.43	5.581528	56%
N-BUT-01	0.9985289	2%	1%	0.001471	0%	2%	1	0.01	0.082472	1%
ISOBU-02	13.20724	26%	15%	2.792761	6%	18%	16	0.16	1.932442	19%
2-BUT-01	6.574282	13%	18%	11.42572	23%	18%	18	0.18	2.312112	23%
3-MET-01	15	30%	12%	1.19E-06	0%	19%	15	0.15	0.035213	0%
Total Flow kmol/hr	50			50			100		10	
Total Flow kg/hr	3885.404			3176.204			7061.608		662.8533	
Total Flow l/min	87.32882			70.94005			145.2756		14.86273	
Temperature C	93.12816			79.33308			25		82.12609	
Pressure bar	0.506625			0.506625			1.01325		0.506625	
Vapor Frac	0			0			0		0	
Liquid Frac	1			1			1		1	
Solid Frac	0			0			0		0	
Enthalpy cal/mol	-77512.13			-72099			-77987.4		-73317.2	
Enthalpy cal/gm	-997.4784			-1134.99			-1104.39		-1106.08	
Enthalpy cal/sec	-1076600			-1001400			-2166300		-203660	
Entropy cal/mol-K	-126.3825			-104.49			-124.48		-108.633	
Entropy cal/gm-K	-1.626375			-1.64489			-1.76277		-1.63886	
Density mol/cc	0.00954248			0.011747			0.011472		0.011214	
Density gm/cc	0.7415277			0.746218			0.81014		0.743306	
Average MW	77.70808			63.52408			70.61608		66.28533	
Liq Vol 60F l/min	79.94689			65.64597			145.5929		13.70036	



UNIFAC				
Tf ©	25		stages	40
Pf (atm)	1		feed sage	10
F (kmol/h), 20	100			
D (kmol/h)	50			
R= L/D	1.5			
Ptop (atm)	0.5			

Mole Flow kmol/hr	Bottoms	xB	Given	Distill	xD	Given	Feed	zF
2-MET-01	5.997742	12%	5%	9.05E-02	0%	7%	6	0%
METHA-01	3.62E-19	0%	2%	1	2%	0%	1	0.01
1-PRO-01	8.307188	17%	47%	31.93428	64%	36%	43	0.43
N-BUT-01	0.984438	2%	1%	0.144053	0%	2%	1	0.01
ISOBU-02	12.96743	26%	15%	5.492714	11%	18%	16	0.16
2-BUT-01	6.745712	13%	18%	11.25983	23%	18%	18	0.18
3-MET-01	14.99749	30%	12%	7.86E-02	0%	19%	15	0.15
Total Flow kmol/hr	50			50			100	
Total Flow kg/hr	3884.114			3218.493			7061.608	
Total Flow l/min	87.29098			71.91103			145.2756	
Temperature C	93.06406			79.86895			25	
Pressure bar	0.506625			0.506625			1.01325	
Vapor Frac	0			0			0	
Liquid Frac	1			1			1	
Solid Frac	0			0			0	
Enthalpy cal/mol	-77510.3			-72476.4			-77987.4	
Enthalpy cal/gm	-997.786			-1125.94			-1104.39	
Enthalpy cal/sec	-1076500			-1006600			-2166300	
Entropy cal/mol-K	-126.332			-105.694			-124.48	
Entropy cal/gm-K	-1.62627			-1.64198			-1.76277	
Density mol/cc	0.009547			0.011588			0.011472	
Density gm/cc	0.741603			0.745943			0.81014	
Average MW	77.68227			64.36987			70.61608	
Liq Vol 60F l/min	79.91874			66.52442			145.5929	



UNIFAC							
Tf ©	25		stages	40			
Pf (atm)	1		feed sage	30			
F (kmol/h), 20	100						
D (kmol/h)	50						
R= L/D	1.5						
Ptop (atm)	0.5						

Mole Flow kmol/hr	**Bottoms**	**xB**	**Given**	**Distill**	**xD**	**Given**	**Feed**
2-MET-01	6	12%	5%	3.56E-09	0%	7%	6
METHA-01	9.37E-08	0%	2%	0.9999999	2%	0%	1
1-PRO-01	8.650228	17%	47%	34.34977	69%	36%	43
N-BUT-01	0.999838	2%	1%	0.00016238	0%	2%	1
ISOBU-02	13.12874	26%	15%	2.871257	6%	18%	16
2-BUT-01	6.221191	12%	18%	11.77881	24%	18%	18
3-MET-01	15	30%	12%	6.25E-10	0%	19%	15
Total Flow kmol/hr	50			50			100
Total Flow kg/hr	3879.369			3182.239			7061.608
Total Flow l/min	87.18555			71.07567			145.2756
Temperature C	93.07683			79.3595			25
Pressure bar	0.506625			0.506625			1.01325
Vapor Frac	0			0			0
Liquid Frac	1			1			1
Solid Frac	0			0			0
Enthalpy cal/mol	-77444			-72170.72			-77987.4
Enthalpy cal/gm	-998.152			-1133.961			-1104.39
Enthalpy cal/sec	-1075600			-1002400			-2166300
Entropy cal/mol-K	-126.19			-104.6724			-124.48
Entropy cal/gm-K	-1.62642			-1.644634			-1.76277
Density mol/cc	0.009558			0.0117245			0.011472
Density gm/cc	0.741593			0.7462093			0.81014
Average MW	77.58738			63.64478			70.61608
Liq Vol 60F l/min	79.82378			65.76908			145.5929

Component	**x_B**	**% of component in bottoms**	**x_D**	**% of component in distillate**	**z_F**
Active Amyl	12%	**100%**	0%	0%	6%
Methanol	0%	0%	2%	**100%**	1%
n-Propanol	16%	19%	70%	**81%**	43%
n-Butanol	2%	**100%**	0%	0%	1%
iso-Butanol	26%	83%	6%	**17%**	16%
sec-Butanol	13%	37%	23%	**63%**	18%
iso-Amyl	30%	**100%**	0%	0%	15%

Compositions for Continuous Simulation with L/D = 1.5 and Feed Stage = 20

Component	**x_B**	**% of component in bottoms**	**x_D**	**% of component in distillate**	**z_F**
Active Amyl	12%	**99%**	0%	1%	6%
Methanol	0%	0%	2%	**100%**	1%
n-Propanol	17%	21%	64%	**79%**	43%
n-Butanol	2%	**87%**	0%	13%	1%
iso-Butanol	26%	70%	11%	**30%**	16%
sec-Butanol	13%	37%	23%	**63%**	18%
iso-Amyl	30%	**99%**	0%	1%	15%

Compositions for Continuous Simulation with L/D = 1.5 and Feed Stage = 10

Component	**x_B**	**% of component in bottoms**	**x_D**	**% of component in distillate**	**z_F**
Active Amyl	12%	**100%**	0%	0%	6%
Methanol	0%	0%	2%	**100%**	1%
n-Propanol	17%	20%	69%	**80%**	43%
n-Butanol	2%	**100%**	0%	0%	1%
iso-Butanol	26%	82%	6%	**18%**	16%
sec-Butanol	12%	35%	24%	**65%**	18%
iso-Amyl	30%	**100%**	0%	0%	15%

Compositions for Continuous Simulation with L/D = 1.5 and Feed Stage = 30