# AGING OF WHISKEY SPIRITS IN BARRELS OF NON-TRADITIONAL VOLUME

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ABSTRACT

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In the aging of whiskey spirits, oak barrels provide vessels for containment which are semi-permeable to the spirit and to outside air. The barrel wood itself provides extractives derived from structural polymers which have been degraded during barrel construction. These extractives have a cumulative effect on the sensory characteristics of the aging spirit.

The traditional barrel for the aging of spirits ranges from 52-60 American gallons. Recent growth in the American craft distilled spirits industry has increased the use of reduced volume barrels ranging from 2-30 American gallons. These smaller barrels provide more rapid extraction and to some extent more rapid maturation.

The current study tracked extraction rates of 5 phenolic components from 2, 3, 5, and 10 gallon barrels confirming that extraction rate is tied to surface area to volume (SA/V) ratio. Volume loss was also monitored and rate of volume loss tied to SA/V ratio with greater losses in smaller volume containers. Extracts from oak spirals were examined and it was found that a variety of spirals may produce an extraction profile that is comparable to a barrel extract and that almost complete extraction was achieved in 10 days.

DEDICATION

This work is dedicated to my wife and children who moved our home and our life to allow me to pursue a dream.

# ACKNOWLEDGMENTS

I would like to most of all acknowledge the mentorship and inspiration provided to me by Dr. Kris Berglund, without whom I would never have gained the skills and knowledge I have come here to acquire, nor had such a great time doing it.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

# LIST OF SYMBOLS AND ABBREVIATIONS

%ABV - Percent Alcohol by Volume

TTB - Alcohol and Tobacco Tax and Trade Bureau

BAM - The Beverage Alcohol Manual of the TTB

LAB - Lactic acid bacteria

HPLC - High-performance-liquid-chromatography

LCMS - Liquid-chromatography-mass-spectrometry

GC - Gas-chromatography

GC-FID - Gas-chromatography with linked flame-ionization-detector

GC-MS - Gas chromatography with linked mass-spectrometer

EI - Electron ionization mode of mass spectrometer

SA/V - Surface area to volume ratio

NIST - National Institute of Science and Technology

2.1 - 2 gallon barrel, repetition 1

2.2 - 2 gallon barrel, repetition 2

3.1 - 3 gallon barrel, repetition 1

3.2 - 3 gallon barrel, repetition 2

5.1 - 5 gallon barrel, repetition 1

5.2 - 5 gallon barrel, repetition 2

10.1 - 10 gallon barrel, repetition 1

10.2 - 10 gallon barrel, repetition 2

A520 - 520 nanometer light for measurement of absorption

# REVIEW OF LITERATURE

## WHISKEY

Whiskey spirits are defined as Spirits distilled from a fermented mash of grain at less than 95% alcohol by volume (ABV) having the taste, aroma and characteristics generally attributed to whiskey and bottled at not less than 40% alcohol by volume (1). The various styles of whiskey spirit have documented historical lineage dating to the first recorded commercial transaction involving whisky (Scottish spelling) between the Benedictine monastery and Lindores Abbey in Fife, and the Court of King James IV at Holyrood, Edinburgh in 1494 (2). Individual standards of identity are established in the United States by the Alcohol and Tobacco Tax and Trade Bureau (TTB) under Code of Federal Regulations title 27. It publishes The Beverage Alcohol Manual (BAM) which establishes legal identities for spirits, techniques for their production and aging, and bottling and labeling rules (2,4).

## GRAIN PROCESSING

The initial processing of grain before fermentation and distillation is known as mashing. It constitutes a cooking process where the grain physical structure is disrupted, starches are released into an aqueous mixture, the starches are enzymatically hydrolyzed, and the mash is supplemented with nutrients to produce a healthy yeast fermentation environment. Starch extraction and hydrolysis follows the process shown in figure 1 (2,4,5,6).

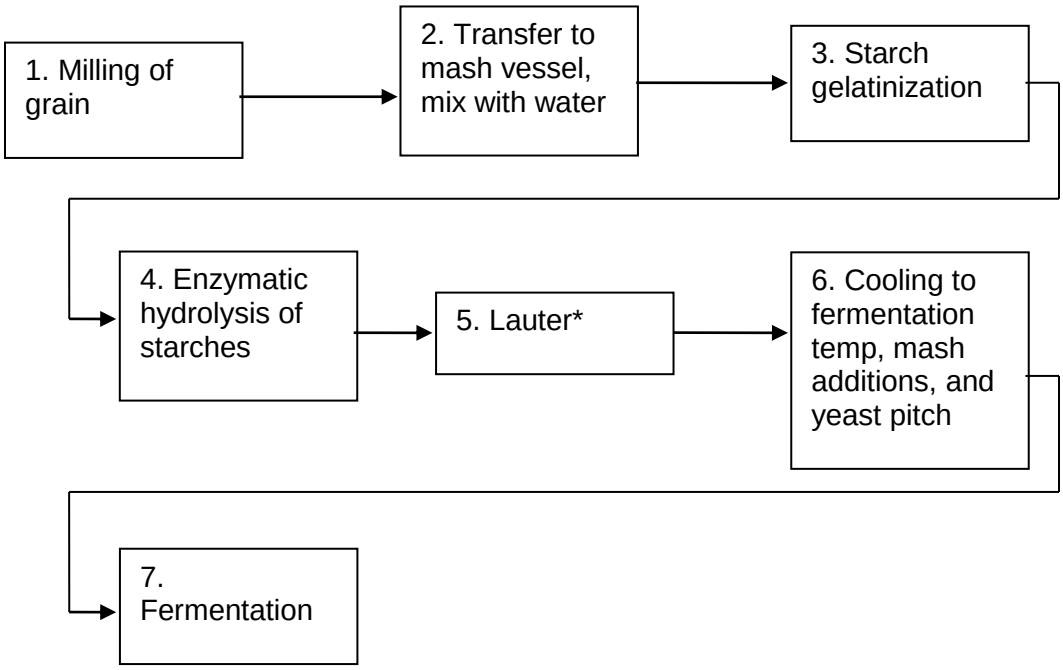


Figure 1: Grain processing flow chart

* Lautering is a process commonly employed in brewing that is used in the production of Scotch whiskies and some American whiskies (2,4,5,6).

1. **Milling** is conducted with the use of roller or hammer mills. Techniques employed later in the mashing process determine the type of mill and particle diameter. The destruction of the grain structure facilitates solubilization and subsequent hydrolysis of starches. Inadequate milling can cause reduced yields due to lack of starch extraction (5).
2. **Transfer and mixing**: Milled grain (grist) is commonly transferred to the mashing vessel (mash tun) using augers. As the grain is introduced to the vessel it is mixed with water. It is within the aqueous mixture (mash) that starch extraction takes place and enzyme activity is initiated.
3. **Gelatinization**: Starch molecules are housed in granular structures that are susceptible to rupture when exposed to aqueous environments at

elevated temperatures. Granule geometries vary in the variety of grains as do gelatinization temperatures, but in all cases heat treatment causes the swelling of the granule as water enters it, and eventual disruption of the structure releasing starch into the aqueous environment, making it accessible to the activity of hydrolytic enzymes (4,5,6).

4. **Enzymatic hydrolysis**: Yeast are unable to metabolize starch, but can consume glucose monomers, dimers (maltose), and trimers (maltotriose), the latter known as maltodextrins. Enzymes utilized in the process of mashing include: α-amylase, β-amylase, glucoamylase, limit dextrinase, and protease. Alpha and β-amylases, glucoamylase and limit dextrinase activities facilitate the breakdown of long unfermentable starch polymers to glucose and maltodextrins. Alpha and beta amylases work randomly on the α-1,4 bonds of the largely linear amylose starch molecule randomly hydrolyzing the polymer to dextrins of a variety of lengths from 2-glucose (maltose) to 5-glucose (maltopentaose). Glucoamylase hydrolyzes α-1,4 bonds at the reducing ends of short chain dextrins to produce glucose, and also has debranching activity on the α-1,6 side branches of the highly branched amylopectin starch. Limit dextrinase is a debranching enzyme whose activity cleaves α-1,6 bonds on the side branches of amylopectin. These enzymes are endogenous to malted barley which is often used in whiskey production but are also available commercially as isolates and are added to mash independently. Many whiskies are produced without malted barley and therefore enzymes must be added (4,5,6).

5. **Lautering** is a filtration process where the mash is spread over a screen bed in a vessel known as a lauter tun. Liquid is pulled through the grain bed and the screen from the bottom and recirculated over the top of the grain bed. This process creates a semi-uniform bed of grain solids which acts as a filter for the removal of small particulate matter. Once the liquid has reached a satisfactory level of clarity the liquid is diverted away from the lauter tun to another holding tank. This is universally used in the production of Scotch whiskey and is also utilized in American whiskey where the mashing process is conducted in a brewing facility. When mash is lautered and all solids removed it is referred to as wash. Many American distilleries ferment whiskey mash without the removal of grain solids.
6. **Cooling, mash additions, yeast pitching**: Grain is used as a source of mono, di and trisaccharides, for yeast fermentation and also provides some amino acids and lipids required for a healthy yeast life cycle. It is however, often the case that some trace minerals, salts, and free nitrogen are added to facilitate higher yields. Because the mashing process is conducted at elevated temperatures the mash must be cooled before the introduction of yeast (yeast pitch). This is achieved by the introduction of an aliquot of cool water, by cooling jackets containing water or glycol, or by passing the mash/wash through a heat exchange system. It is just after cooling that mash additions such as yeast nutrients and yeast is added. Yeast is often supplied in a dehydrated form and is rehydrated using warm water and/or an aliquot of the mash before it is introduced to the

fermentation vessel (4,5,6). Yeast selection can have a strong effect on the spirit and some distilleries maintain their own cultures in-house.

7. **Fermentation:** Many specialized distillery and brewery yeasts are available for the production of different styles of whiskey. These yeasts are stabile at higher temperatures than wild strains, and have been optimized for high alcohol yields and flavor profiles appropriate to whiskey production. Fermentation is allowed to proceed from 96 to 168hrs. It is during this time that ethyl alcohol and the large variety of alcohols, aldehydes, esters and acids that comprise the sensory qualities of a raw whiskey are produced by the yeast (4,5,6,7,8,9).

## WHISKEY DISTILLATION

Traditionally whiskeys have been distilled in a double or triple batch process, in what are known as alembic (English) or alambic (French) pot stills (11). The first alembic style spirits stills can be traced back to the 12$^{th}$ century where medicinal and plant extractive botanicals were distilled in monasteries by monks who became the founders of the early medicinal sciences and the sciences of brewing and distilling (10). Modern alembic stills are made of copper and resemble the traditional stills in many respects.

In alembic distillation, the fermented product is introduced to the pot (Fig. 2 A) where it is heated until boiling produces vapors which travel through the helmet (Fig. 2B), and to the condenser (Fig. 2D) via the spirit tube (Fig. 2C). The

liquid product of this first distillation is known as low wine and this initial distillation is known as stripping. From a fermented substrate of 7-10% it is expected that the low wines produced will have a percent alcohol by volume (%ABV) in the range of 20-35%. The low wines are reintroduced to the still and redistilled to a final %ABV of 60-79%ABV depending on the desired sensory qualities of the spirit (10,11,12). The product of the second distillation is the raw whiskey spirit and the final distillation is known as a finishing run or finishing distillation. In some cases this distillate is diluted with water and redistilled to refine the flavor profile. This is the simplest and the traditional style of whiskey distillation but not the only method. Larger facilities utilize continuous distillation columns and other technologies to increase alcohol concentration or increase throughput, but as this work is largely focused on the artisan industry, the alambic distillation method is most relevant (12,13,14).

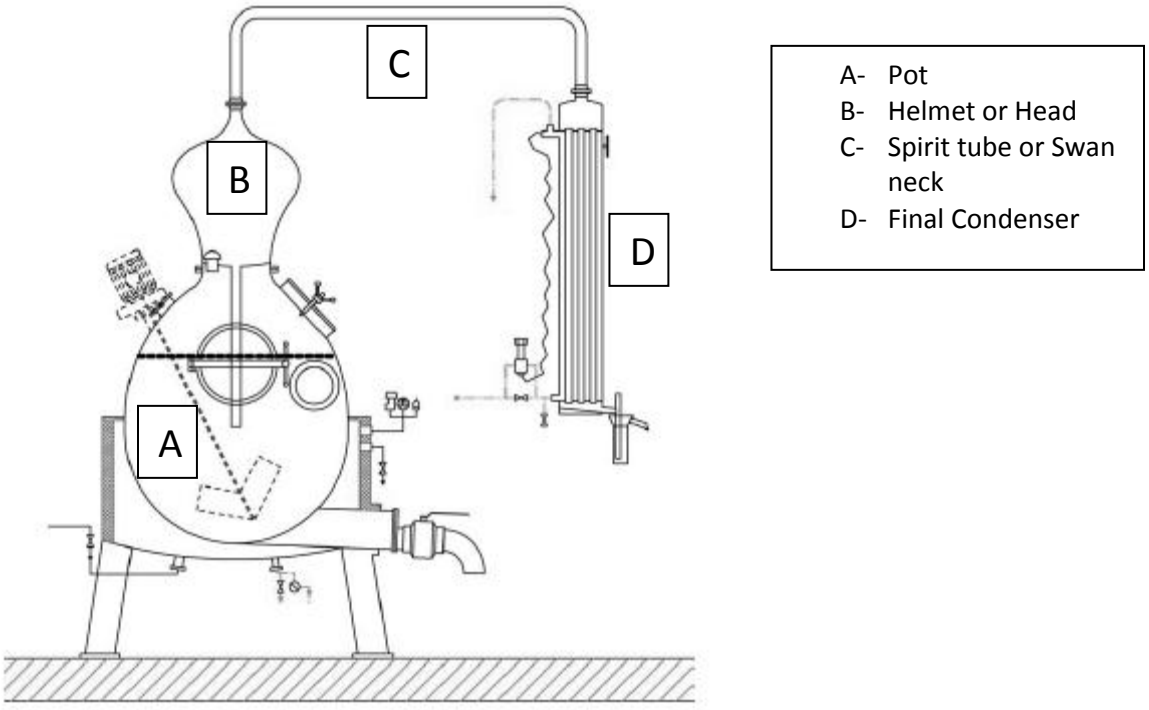


Figure 2: Modern steam jacket style, alambic distillery (Figure reproduced courtesy of Christian Carl Ing. Gmbh)

The batch process is characterized by a progression of chronological fractions during the course of a finishing distillation (14). Three primary fractions are observed. Chronologically they are known as the heads cut, the hearts cut, and the tails cut. Of these only the hearts cut constitutes potable spirit. The heads and tails consist of ethanol and water primarily but also contain high concentrations of alcohols, esters, fatty acids, and aldehydes that can produce unpleasant sensory qualities and/or cloud the spirit. These compounds are collectively known as congeners, and the high boiling compounds found in the tails are known as higher alcohols or fusel alcohols. The heads and tails are either disposed of or in some cases redistilled to recover some ethanol

(12,13,14). The heads fraction may vary from 85-95%ABV depending on the distillation dynamics and might potentially be utilized as a fuel additive after removal of water.

## UNAGED DISTILLATE

The hearts cut (also known as base spirit, white whiskey, or raw whiskey) is comprised primarily of ethanol and water, but also contains many other volatile compounds which contribute to the complex flavor of the finished spirit.

1. **Low boiling fraction/heads components** (Figure 3) consist of alcohols, aldehydes, and esters whose boiling points are lower than that of ethanol (78.6$^{o}$C), and are present in the first part of the distillation. They include: acetaldehyde, acetone, ethyl acetate, and methanol primarily. During the heads cut a large fraction of these compounds are removed but some concentrations are retained in the hearts cut where they contribute to the final sensory qualities of the spirit (10,11,13,14,15). As shown in Figure 3, the beginning portion of the run is characterized by extremely high concentrations of these compounds which quickly decrease. In this figure the hearts portion would begin at approximately minute 15.

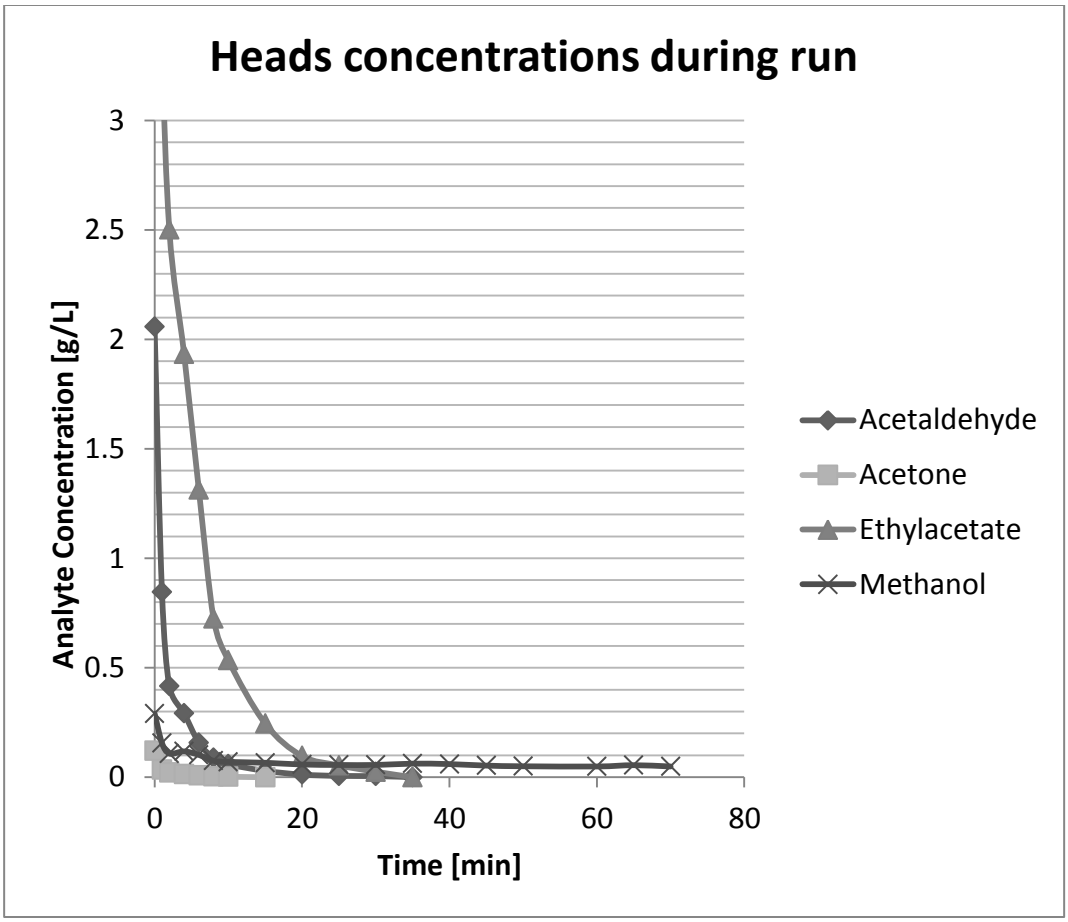


Figure 3: Showing the concentration of heads compounds over time in the distillation of a bourbon whiskey.

2. **High boiling fraction/tails components/higher alcohols/fusel alcohols** (Figure 4) are formed from catabolism of glucose and amino acids present in the mash or wash and have higher boiling points than that of ethanol. These include: propanol, isobutanol, isoamyl and active amyl alcohols and are present in both the hearts fraction and later in the tails fraction. At extremely high concentrations these compounds have unpleasant sensory impact but in concentrations as found in the spirit, they are essential for the characteristic flavor and aroma of

whiskey spirits, and their presence is necessary to produce sufficient maturation in aged whiskeys (10,11,13,14).

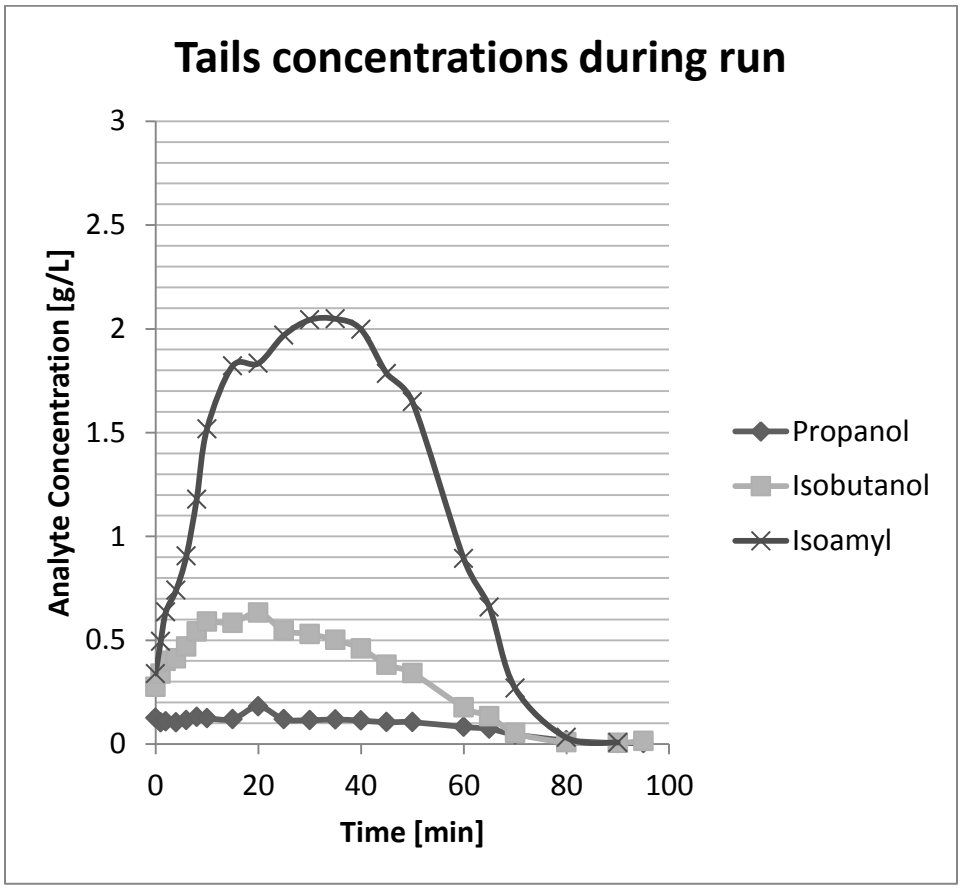


Figure 4: Showing the concentration of common higher alcohols during the distillation of a bourbon whiskey.

3. **Fatty acids/fusel oils** found in raw whiskey are derived from yeast cell walls, from the grain itself, are produced by yeast, or from microbial fermentations that often take place concurrently with the yeast fermentation. Common fatty acids include: acetic, propionic, isobutyric, butyric, isovaleric, lactic, hexanoic, octanoic, decanoic, dodecanoic,

and tetradecanoic. Although the boiling points of many of these acids far exceed the temperature in the pot during distillation, they are soluble in water/ethanol mixtures and travel through the distillation process with the vapor. They not only contribute directly to the character of the spirit but provide reaction substrate in the production of flavor esters during aging (15,16,17,18).

4. **Esters** are produced by yeast during fermentation and from the before mentioned fatty acids and alcohols during aging. Because ethyl alcohol is found in the highest concentration, the most common esters are fatty acid ethyl esters. They are found in higher concentrations where lautering does not take place as yeast produce higher congener levels in mash with higher solids content (65). Examples of esters commonly found in whiskies include: ethyl acetate (ethanol and acetic acid), ethyl butyrate (ethanol and butyric acid), ethyl hexanoate, etc. The major ethyl, isobutyl, and isoamyl esters of short-chain fatty acids have fruity aromas (15,16,19).
5. **Bacterial fermentation compounds** are produced by native flora which is present on the grain as it is brought into the distillery. At the artisan scale of whiskey production the mash is rarely boiled so no pasteurization step occurs and the fully prepared mash provides a hospitable environment for microbial fermentation. Some bacterially produced compounds such as butyric and lactic acids can contribute positively to flavor, while others such as acrolein and butanol can

produce acrid bitter flavors that are undesirable. The most commonly found microbial species are lactic acid bacteria (LAB) and their fermentation byproducts are considered to be an essential component in whiskey production. Some whiskey producers intentionally induce LAB to fermentations to control secondary fermentation, and ethyl lactate is a commonly found ester in such whiskies (20,21,22).

## WHISKEY FLAVOR AND FLAVOR CHEMISTRY

Flavor and aroma in whiskey spirits can be divided into several chemical categories based on derivation, sensory effects, and/or chemical composition. For the purposes of this work they will be discussed in chemical categories which will largely reflect their origins. The sources of flavor and aroma are grain, fermentation, distillation style, oak wood, and maturation chemistry. The major categories of chemical compounds responsible for the flavor, aroma, and general character of whiskey spirits are alcohols, aldehydes, volatile and non-volatile acids, esters, phenolics, and lactones  Over 1300 volatile components have been identified in alcoholic beverages since the 1960s and only major categories and specific compounds significant to this work will be discussed (66).

**Volatile compounds** (Table 1), including alcohols, aldehydes, and ketones comprise the highly volatile fraction in whiskey spirits. They are derived from fermentation of sugars and amino acids and are byproducts of biosynthesis and energy production in normal glycolytic metabolism (14,17,52,62). These

compounds were largely considered the most important for flavor and aroma of spirits before advances in analytical techniques showed that, while they play a major role, particularly in the profile of freshly distilled spirits, they are only one of many important categories of flavor and aroma active compounds (17,66). The alcohols whose boiling points exceed that of ethanol are collectively known in the industry as higher or fusel alcohols and are produced by metabolism of amino acids present in the medium (Erlich mechanism) or by synthesis from carbohydrates (66,68). While many of the descriptors utilized to describe the sensory qualities of these compounds are seemingly repugnant (seen in Table 1), they are important in the context of spirits for well rounded flavor and aroma. Odor thresholds for these compounds vary widely from 5.0mg/l (butanol) to 720mg/l (propanol) as examined in model whiskey and are found well in excess of these thresholds in many whiskey spirits (52).

Table 1: Some common volatile compounds, fermentation type, and substrate from which they are produced in whiskey spirits, and common sensory descriptors (40,52,68,69).

| Compound | Fermentation type | Substrate | Descriptor |
|---|---|---|---|
| Acetaldehyde | Yeast | Alanine, glucose | Solvent, fruit, floral, apple |
| Acetone | Yeast | glucose | Solvent |
| Glycerol | Yeast, Bacterial | Serine, glucose | Sweet |
| 1-Propanol | Yeast | 2-Amino-butyric acid, glucose | Solvent, chemical, antiseptic |
| 1-Butanol | Bacterial | N/A | Solvent, chemical |
| 2-Methyl-1-butanol | Yeast | Isoleucine, glucose | Solvent, chemical |
| 3-Methyl-1-butanol | Yeast | Leucine, glucose | Solvent, chemical |
| Isoamyl, active amyl alcohols | Yeast | Leucine, glucose | Solvent, chemical, antiseptic |

**Acids**, like the alcohols, aldehydes, and ketones, are largely produced in fermentation. Acids are separated categorically into short chain or volatile acids (acetic, propionic, butyric), and long chain or fatty acids (hexanoic, octanoic, decanoic, dodecanoic, tetradecanoic, and longer). It has been established in separate investigations that the concentrations of these acids is relatively consistent across multiple beverages regardless of fermentation substrate (52,64,68). These works were conducted to examine the assumption that higher levels of fatty acids would be found in grain fermentation due to grain oils, as compared to molasses or fruit (whiskey vs. cognac or rum), but this hypothesis proved to be false (52,64,68). Acetic, octanoic, and decanoic acids are known to

increase during barrel aging as they are extracted from oak and wood lipids are broken down (60).

While many fatty acids have boiling points far in excess of the boiling temperatures achieved in the production of distilled spirits, they are soluble in ethanol water mixtures and travel through the distillation within the vapor (52,66). In the context of the whiskey spirit they produce sensory descriptors such as sour, musty, soapy, grainy, and oily and are important for mouthfeel and body (17,40,52,66,70). Odor thresholds for this congener group vary from 3.4mg/l (butyric) to 26mg/l (acetic) in model whiskey solution and are found well in excess of these thresholds in many whiskey spirits (52).

**Esters**, are products of condensation reactions between alcohols and carboxylic acids and are heavily utilized in the flavoring industry due to their pleasant aromas. They are produced both by yeast during fermentation and during aging in the presence of oxygen (14,17,59,63,64). The presence of fermentation produced fatty acid ethyl esters in the raw spirit and after maturation is considered an essential component in the development of full complexity in flavor and aroma profiles of whiskey spirits. Major esters present in raw distillate include ethyl acetate, isoamyl acetate, butyl acetate, ethyl butyrate, ethyl hexanoate, ethyl lactate, ethyl octanoate, etc. They are responsible for pleasant aromas described as floral, fruity, pineapple, banana, apple, honey, flowery, and pear drops (40,63,65). The odor thresholds of these compounds varies from 0.15mg/l (ethyl-*n*-butyrate) to 17mg/l (ethyl acetate) in model whiskey solution and are found well in excess of these thresholds in many whiskey spirits (52).

**Phenolics and lactones**, are both derived from oak wood during aging of spirits. They are of great importance to the character of spirits which require a period of maturation, and a discussion of their derivation and importance follows.

WHITE OAK

Traditionally, oak aged spirits such as whiskey, dark rum, scotch and brandy are aged in white oak barrels of various species, *Quercus alba* (American oak) and *Quercus robur* (French oak) being the most common (23,24). Among the American oak species used *alba* is considered to be of the best quality but at least ten other species are utilized including: *Q. prinu, Q. bicolor, Q. muehlenbergii, Q. stellata, Q. macrocarpa, Q. lyrata* and *Q. durandii.* Among European or French oaks *robur* is considered to be of the highest quality with *Q. sessilis, q. petraea* and *Q. sessiflora* also commonly used (23,24,25).

White oak is particularly useful for liquid containment due to some unique anatomical structures (25,26). The first is the formation of tyloses, which are “bubble” like structures that partially occlude the vertical liquid conduction system of the wood. They are formed during tree death and are essential for the prevention of leakage from stave ends in the assembled barrel (27). In most other hard woods tylose formation is insufficient to prevent this leakage and barrels from such woods are therefore not liquid tight.

Another unique feature of white oak species is the presence of multiseriate compound medullary rays (25). Medullary rays function as part of the

lateral liquid conduction system of the living tree. They are impermeable to liquid from the outside and because of the geometry of cross-cutting during barrel production, prevent liquid loss from the sides of staves. While medullary rays themselves are not unique, the compound multseriate (spanning multiple cell layers) nature of white oak rays is a unique feature and one that is quite important for liquid containment in spirits and wine barrels (23,28,29). In white oak the rays are very densely packed and a molecule of liquid migrating from inside the barrel to the outside would encounter an average of 5 or more large rays in a straight path from the inside of the barrel to the outside (28).

Other features that are important in the consideration of woods for cooperage include flexibility of the wood and extractives content. White oak is suitably bendable for the shaping of the barrel bilge (the bulging center of the barrel shape). Many woods are brittle after seasoning making barrel shaping difficult or impossible (23,25,28).

American oak and European oak are of similar structure being composed of cellulose, lignin, and hemicellulose (29,30,31). None of these structural polymers are either extractable or soluble in their native forms. Heat treatment during barrel construction depolymerizes these compounds making their smaller subcomponents available for extraction. Over 100 extractable volatile components have been identified from heat treated oak wood by Nishimura *et al*. (1983). Among those components are: 35 aliphatic compounds, 54 aromatic compounds, furans, and terpenes. At least 7 fatty acids have been identified as well (16,24,25).

Only heartwood is used for barrel construction. The heart of American white oak is composed of 49-52% cellulose, 31-33% lignin, 22% hemicelluloses, and a 7-11% fraction extractable by hot water or ethyl ether (30). Cellulose, lignin, and hemicelluloses are largely insoluble without some form of treatment, but the extractable fraction is made up largely of phenolic extractives, derived from ellagitannins which have astringent sensory qualities (32,33). Cellulose is considered to be the framework of the wood, hemicelluloses the matrix, and lignin the solidifying encrustant (25). Cellulose is a polymer of glucose. Wood hemicelluloses are polymers of pentoses and hexoses among other sugars and acids. They form polyoses which can consist of one unit (homopolymer) such as xylans or two or more units (heteropolymer) such as glucomannans (glucose-mannose dimer) (30,31).

Lignin is a three dimensional, hydrophobic polymer structure that is highly branched. Its structural precursors (p-coumaric alcohol, synapyl alcohol, coniferyl alcohol among others) are assembled from glucose via the shikimic acid metabolic pathway (31). Polymerization is random and spontaneous leading to the uniquely heterogeneous nature of the lignin molecule, with no repeating structural base (31). As lignin is formed it is forced to fill in the spaces between other structural elements of the cell wall where it lends strength and density (28,30,31). Neither cellulose, hemicellulose, nor lignin has the ability to directly affect flavor or aroma of wine or spirits in their native forms as they are insoluble. The degradation of structural polymers during barrel production yields a large variety of flavor and aroma active components which are largely responsible for

the characteristic flavors, aromas, and colors found in oak aged spirits (23-26,28,32,33).

## OAK BARRELS

Many standards of identity for spirits require minimum aging time in oak barrels that range from 1-3 years but may last as long as 12-25 years at the discretion of the producer (24). Oak barrels impart flavor, aroma, and color to spirits that are completely clear at the time of distillation, and lacking many of the most familiar and desirable sensory qualities of aged spirits. Freshly distilled whiskey may have some unpleasant characteristics that require maturation time to moderate some of their pungency and acquire many of the traditional flavors that are desirable in a mature product (33). Bottled spirits are often blends from barrels which have been aged for the legal minimum time period and those which have been aged for longer periods.

Barrels for aging of spirits are constructed of staves cross cut and quarter sawn from mature white oak trees. In American cooperage the staves are then kiln dried, stacked outdoors and exposed to the elements in a curing process which takes up to 3 years (34). During outdoor seasoning the staves are exposed to the elements which have a variety of effects. Rain and sun exposure cause structural degradation, which allows for the native extractable phenolic fraction of the wood to be washed away, removing astringent flavors, and for structural damage to make the wood more permeable to liquid (53-56). It has also been

found that white rot fungi found on the surface of staves during seasoning may contribute to structural degradation and release of free phenolic compounds from structural precursors, such as lignin (57,58). The period of seasoning is characterized by reduction in soluble tannins, increase in low molecular weight phenolics, and total decrease in wood moisture (23,28,53,54,55)

After the period of seasoning, staves are cleaned, steam treated to increase flexibility and the barrels are formed. Once formed the interior of the barrel is subjected to heat treatment. In European barrel construction this takes the form of toasting while in American bourbon barrels this is a high heat, gas fired charring. Whiskies are aged in both toasted and charred barrels, but standards of identity for some American whiskies dictate charred barrels (1). Heat treatment has the effect of breaking down structural polymers, making them available for extraction (33). Lignin breakdown yields such aromatic compounds as aldehydes and acids, including vanillin, vanillic acid and syringaldehyde (26,35). The products of lignin decomposition have low sensory thresholds and are therefore considered quite important to the sensory qualities of finished spirit (24,26,33).

Charring with its higher temperature has been found to result in higher concentrations of aromatic aldehydes derived from lignin, in the spirit (24). In American oak barrels the charring process is responsible for the production of volatile phenols such as guaiacol and syringol, and the total phenolic content of the oak wood is increased (36,37,38,39). The intense flame heat of charring penetrates beyond the surface of the wood causing thermal degradation

reactions behind the char layer. The consequent degradation of the wood structure facilitates liquid penetration and extraction from these deeper layers (24). It has been established that some desirable components are at highest concentrations as deep as 6mm beneath the char layer (28).

The effects of charring have been categorized thusly:

1. production of a char layer with adsorbent qualities which may remove undesirable flavor congeners and catalyze reactions;
2. Beneath the char layer a thermal gradient is produced which constitutes a variety of heat treatments due to temperature differences at different layers during heat exposure. In this layer lignin is thermally degraded releasing flavor/aroma active components such as vanillin and making them available for extraction;
3. The total polyphenolic extract is increased due to disruption of wood structure and consequent increase in surface area, and phenolic contents are increased as certain compounds are produced (36,41).

Cellulose and hemicellulose degradation, specifically furfural formation is often accompanied by the production of other components which are noted for their caramel and toasted aromas (43,44,45). It has also been shown that Maillard reaction byproducts may be contributing factors to oak aged spirit sensory profiles in combination with sugar pyrolysis byproducts (40,43).

For the purposes of this study it is lignin degradation components that are of primary interest. The following four pathways for the origin of lignin

degradation products have been established and verified (24), although others have been proposed (46,47,26,42,48):

1. degradation of lignin to aromatic phenolics due to heat treatment of staves (charring/toasting);
2. extraction of lignin degradation components and lignin from the wood;
3. release of aromatics by ethanolysis of lignin;
4. further conversion of compounds present in the spirit (24);

Table 2: Confirmed phenolic components extracted from white oak by spirits and model spirits or wines

| **Compound** | **Sensory descriptors** |
|---|---|
| Vanillin | vanilla |
| Acetovanillone | vanilla |
| Eugenol | spice, parsley |
| Isoeugenol | spice, parsley |
| Guaiacol | clove |
| Ethylguiacol | sweet, medicinal |
| Vinylguiacol | clove, smokey, spicey |
| *Trans-β*-methyl-γ-octalactone | nutty, smoke, astringent |
| *Cis-β*-methyl-γ-octalactone | nutty, smoke, coconut, woody |
| Cinnamaldehyde | cinnamon |
| Syringaldehyde | sour |
| Coniferaldehyde | |
| Sinapaldehyde | |
| Syringic acid | |
| p-coumaric acid | balsamic |
| Benzoic acid | |
| Cinnamic acid | Honey floral |

In addition to the production of desirable extractive components, heat treatment is responsible for the elimination of some unpleasant sensory qualities.

*Trans*-2-nonenal in untreated wood, likely the byproduct of auto-oxidation of linoleic acid has been found to yield rancid, sawdust aroma to spirits exposed to untreated oak (49). This quality is almost completely eliminated after toasting or charring.

## OAK EXTRACTS AND CONTRIBUTORS TO AROMA AND FLAVOR

As early as 1960 Russian researchers had begun to identify and establish the importance of some aromatic compounds found in oak aged spirits, and their relationship to oak lignin. The first components identified were vanillin, syringaldehyde, coniferaldehyde, and *p*-hydroxybenzaldehyde in brandy, all lignin degradation components (24). Baldwin *et al*. (1967) were able to isolate the same components in whiskies. Since then hundreds of components have been isolated and examined from a variety of spirits.

The traditional barrel used for aging ranges from 52-59 gallons. The surface area to volume ratio of this sized barrel is calculated at roughly 90cm$^2$/Liter (28). This number however takes only the surface into account, and underestimates the three dimensional migration into and out of barrel wood. The barrel-spirit interface is the site of extraction of phenolic components, and migration of ethanol and water out of the barrel and it has been theorized that the maturation process might be accelerated in smaller barrels (28,34,36).

Work conducted by Conner *et. al.* showed that Scotch whiskey aged in six liter barrels not only extracted phenolic components at a faster rate, but that the

spirit itself showed markers of aging in less time. It was theorized that the reduced maturation time was due to increased wood extract and greater oxidation by higher exposure to oxygen due to greater head space in the barrel. This was in part due to the fact that greater evaporation takes place in smaller barrels but also because large sample volumes drawn from the small barrels produced reduced fill volume more quickly than natural migration from the barrel would have (50). Analytical methods employed in the study required large sample volumes and conditions in the small barrels were affected by this. In the case of this study it was deemed that smaller casks were inappropriate for the Scotch whiskey industry. It is important to note that casks utilized in this case were not heat treated and it is known that raw oak is not ideal for aging spirits (39,41). This constitutes the only published work on alternative barrel sizes to date.

Migration of oxygen into the barrel is an essential component in maturation of spirits, fueling important oxidation reactions, and it has been determined that migration occurs at what is referred to as the ullage, or the headspace above the spirit (28,50). As evaporation occurs and the fill level decreases, oak not in contact with liquid spirit dries, contracts, and becomes more porous to the entry of outside air (28). Oxygen present in the barrel fuels oxidation reactions that are essential in the production of mature spirits. It is for this reason that spirits barrels are rarely “topped off” as are wine barrels. Additionally the concentration of flavors that is the consequence of evaporation is an important factor in maturation. Average volume loss from traditional 52-55gal

barrels is 5% per year with some variation from environmental conditions (26,28,50).

While much work has been conducted in the evaluation of aging and maturing effects in oaked spirits, it has failed to produce quantifiable quality standards as many components are present in very low concentrations and indeed many act synergistically to produce combined flavor effects that are not easily quantified. In fact the presence of low concentrations of a variety of phenolic extractives often produce flavor effects that are as pronounced as those from relatively higher concentrations of, for example, fatty acid ethyl esters. These factors combine to create great difficulty in producing so called quality standards for oak aged spirits (40,33,50,51,52).

It is however, known that the presence of certain components is necessary for their individual contributions to flavor and through concentrations sufficient to support reactions. Extractives that have in past work been quantified and examined for sensory threshold have been established in a variety of studies to be important to the finishing of spirits (32,33,40,41,50). For the purposes of this study, 5 of these components (vanillin: 4-hydroxy-3-methoxybenzaldehyde, eugenol: 4-allyl-2-methoxyphenol, guaiacol: 2-methoxyphenol, 2-methoxy-4-methylphenol, and syringaldehyde: 4-hydroxy-3,5-dimethoxybenzaldehhyde) have been chosen for examination. Substances were chosen based on data present in past work, and relative ease of quantification on available equipment. Acetovanillone and isoeugenol were also examined for possible tracking as were both conformations of oak lactone, but with none of these compounds was it

possible to achieve adequate peak separation utilizing the method designed for the purposes of this work.

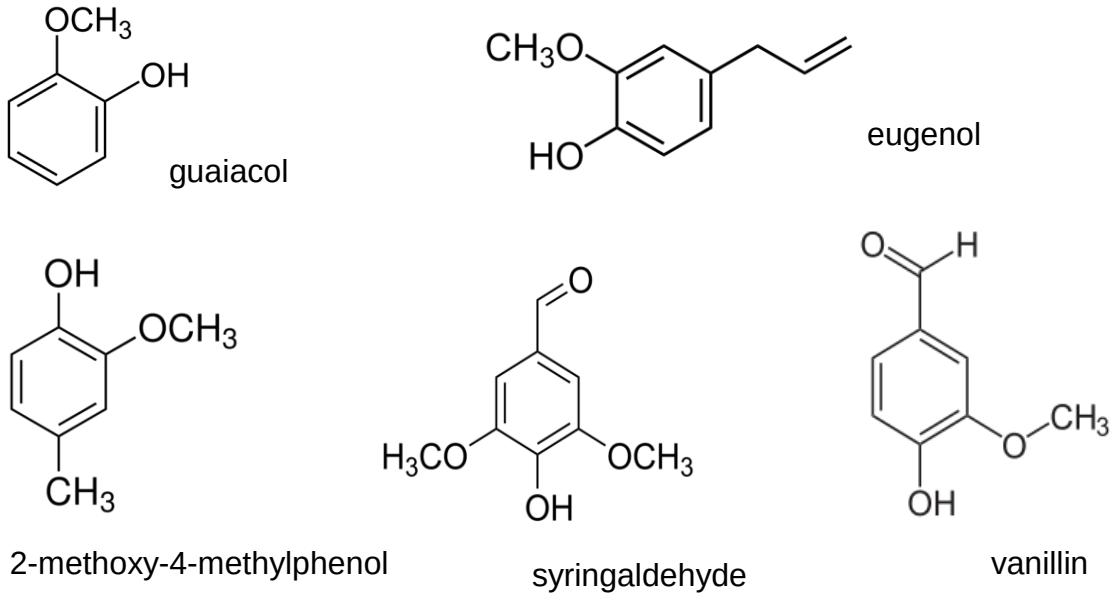


Figure 5: Chemical structure of the phenolic components chosen for the current study

AGING

While the mechanisms of aging have been examined, they have not been completely elucidated and therefore no reliable chemical or physical index exists which can be relied upon to predict maturity, or to accurately track the process of maturation. Environmental conditions in barrel storage facilities (rack houses) are not controlled which leads to differences in aging effects in the variety of climatic

conditions in which whiskies are aged (24,36,34). The sensory qualities derived from the maturation process vary due to the following contributors:

1. The variety of whiskeys is barreled at different alcohol concentrations ranging from 55-75%ABV, which affects the extraction profile and process of evaporation (23,24,28,26,34).
2. There are variations in the wood itself due to environmental growth factors, which leads to differences in lignin concentration and structure, and therefore phenolic concentration and differences in porosity due to wood density variation. Slow growth wood with higher density has higher lignin concentration (48,51,53-55).
3. Some whiskey producing countries employ barrels previously used for the aging of whiskey or wine, while others are legally required to use new barrels (23).
4. A large variety of barrel heat treatments are available including various levels of charring (used for American whiskeys), dark, medium and light toasting (used for some American whiskeys, for wine, and for many whiskeys of The British Isles) (33).
5. Environmental conditions such as temperature and humidity have great impact on the aging process within the barrel (33,34,35).

While large producers are able to minimize variations by blending whiskies from many barrels, smaller artisan producers are subject to the seasonal variation of grain and wood composition.

The period of aging is responsible for a large proportion of the characteristic sensory qualities that are sought in aged spirits. It is also characterized by loss of proof through evaporation of ethanol through the wood and consequent reduction in total volume (33). The barrel acts as a semi-permeable membrane which allows evaporation from the cask and migration of air into the barrel, because of its porous structure. Changes in the spirit during oak aging have been categorized by Nishimura and Matsuyama into 7 categories thusly (24):

1. direct extraction of wood components;
2. decomposition of the macromolecules forming the framework of wood, such as lignin, cellulose and hemicelluloses, followed by elution into the spirits;
3. reactions of wood components with components of the unaged distillates;
4. reactions involving only the extracted wood materials;
5. reactions involving only the distillate components;
6. evaporation of the low-boiling compounds through the wood of the cask;
7. formation of stable molecular clusters of ethanol and water;

## ANALYTICAL METHODS FOR THE EXAMINATION OF OAK EXTRACTION

Analytical methods which have been employed in previous work for the examination of aging in oak include High-Performance-Liquid-Chromatography

(HPLC), HPLC coupled with Mass Spectrometry (LCMS), Gas-Chromatography with Flame Ionization Detection (GC-FID), GC-Mass-Spectrometry (GC-MS), and Spectrophotometry. These techniques have been utilized for the examination of a variety of components and some standardization of some techniques has occurred over the past decades.

**HPLC and LCMS** are useful for the analysis of non-volatile compounds (71,72). They are often employed in mash and fermentation analysis as these methods of detection are extremely effective for sugars, acids, and solvents in concentrations at or above 0.1-0.5g/L. They are less commonly used in freshly distilled spirits analysis as the primary constituents of spirits being volatile, are better suited to GC or GCMS analysis. After aging in barrels however a number of nonvolatile compounds are solubilized in the spirit and compounds such as vanillin, vanillic acid, gallic acid, and syringaldehyde are detectable using HPLC/LCMS after extraction and concentration (71,72).

**GC-FID** is the primary method for analysis of alcohols, aldehydes, ketones, acids, fatty acids, esters, and phenolics (73,74). In GC analysis samples are volatilized before introduction to the separations column and therefore it is appropriate to the analysis of volatile compounds. For the purpose of this study GC analysis was employed for examination of the congener compounds which include acetaldehyde, acetone, ethyl acetate, methanol, 1-propanol, isobutanol, isoamyl, and active amyl alcohols. Active and iso amyl alcohols eluted simultaneously and therefore their concentrations are reported collectively as amyl alcohols. Methods were drawn from the literature.

**GCMS** has been utilized for the identification and quantification of both compounds native to the fresh distillate and those that accumulate and are formed in the aging product. The sensitivity of Electron Impact detection allows for detection and quantification of compounds in much lower concentrations than GC-FID, and coupling with the National Institute of Science and Technology (NIST) library allows for preidentification without the purchase of expensive standards. For the purposes of this study GCMS was utilized for the detection and quantification of phenolic extractives from the oak barrels.

## CURRENT STUDY

### JUSTIFICATION OF RESEARCH

The understanding of any process requires the understanding of its underlying elements. While much work has been done to elucidate the macro-process of whiskey ageing and to determine the subcomponents that must be present to produce a fully mature spirit, the work has largely been focused on the traditional industry and for the most part has been conducted on whiskies of the British Isles. It is difficult to compare results from work conducted on these whiskeys as they are almost exclusively aged in barrels that have previously been used for the ageing of bourbon. This means that many compounds which are commonly found as major contributors to the sensory qualities of American whiskies are absent, or present in very low concentrations having been previously extracted in the aforementioned bourbon spirit.

A newer and smaller industry than the traditional large production model has begun to grow in the U.S. and other whiskey producing countries. One of the outgrowths of this new industry has been the use of alternative methods that attempt to produce spirits that are of equal quality but require less time for maturation than the traditional. This is due to pressure from the start-up capital requirements in the building of a distilling operation and the length of time required before a matured spirit may be bottled and sold.

It was the objective of this study to begin to develop an understanding of oak extraction rate as it relates to surface area to volume ratio (SA/V), and to obtain this understanding with industry typical processes. The artisan industry has not established itself yet as an institution and therefore has limited resources with which to fund research and development and is employing production techniques about which little is known.

As stated previously the traditional size of spirits barrels ranges from 52-59 gallons. In the growing artisan spirits industry many producers have taken to the use of smaller barrels and other alternatives for faster extraction through higher surface area to volume ratio, and potentially more rapid aging. While a body of research exists examining the processes of aging in traditional barrels, little information is available examining conditions in non-traditional barrels and little or no information is available on the actual extraction rates of smaller barrels for specific oak components. The current study was undertaken to quantify the rate of extraction for: guaiacol, eugenol, 2-methoxy-4-methylphenol, vanillin, and

syringaldehyde from 2, 3, 5, and 10 gallon barrels over the course of 200 days. Duplicates of each barrel size were utilized.

In an attempt to track extraction from another alternative oaking substrate, oaking spirals were obtained from an industry source, introduced to the same spirit in a sealed glass ehrlenmeyer flask and the extraction of the same compounds was examined. In the manufacturer's recommendations it is noted that full extraction takes place within 6 weeks. Dosages are given for wine but not for spirits so dosages were utilized that fell within the range of recommendation for wine which is 1.3-2.6 cm per gallon of wine. Oak spirals are sold as an alternative to barrels which are more rapid and yet comparable to barrels. They are cut from heart wood in the same manner as are barrel staves. The spirals offer a large surface area and rapid infiltration of the spirit into the wood. They are offered in 8, 9, and 48 inch lengths for use in glass carboys, 50 gallon spent or fully extracted barrels, and 1000 gallon tanks respectively.

The spirals are exposed to a variety of heat treatments as it is known that in the heat treatment of a barrel a temperature gradient is produced with different concentrations of compounds appearing in higher concentrations at different depths. The heat treatment attempts to allow the producer to mimic the gradient in the barrel and customize extraction.

In the original experiment design quadruplicate barrels were to be used and tracked over the course of 500 days. Duplicates of each sized barrel would be filled with two separate whiskey types which would be tracked individually.

During the course of the tracking period all samples from the triplicate and quadruplicate barrels were destroyed before analysis could take place, and only samples from the first 200 days of the first two sets of barrels were undamaged. Data from this period and sample set is presented herein.

## MATERIALS AND METHODS

### WHISKEY AND BARRELS

Whiskey was produced from a mash of 79% corn and 21% wheat, mashed and distilled using typical industry practices and then diluted to 62% alcohol by volume with water before filling the barrels.

American oak barrels were purchased from a well recognized supplier to the artisan spirits industry. The barrels chosen were level 3 char, often employed in the production of American whiskey spirits. The barrels were filled with water at 70$^{o}$C and the water emptied before spirits were introduced, as recommended by the manufacturer. This caused the wood staves to swell and the barrel to become more liquid tight to prevent leakage of spirits. Duplicates of 2, 3, 5, and 10 gallon barrels were filled on June 5, 2010 and stored at environmental temperatures in a non-temperature controlled warehouse, again as is commonly done in industry. The barrels were sampled at days 2, 7, 14, 28, 42, 56, 70, 98, and 202. For sampling, two milliliters were removed from each barrel, held in GC vials at refrigeration temperature (4$^{o}$C) and analyzed when equipment availability allowed. In an attempt to minimize variation in the barrels, samples were

removed after gentle agitation. Whiskey and ambient temperatures were recorded but not controlled. Final volumes and %ABV (alcohol by volume) were measured to establish evaporation rate.

ANALYSIS

For analysis of volatile congener concentrations, a Shimadzu gas chromatograph with auto-injector and flame ionization detector (FID) was utilized. An Agilent Stabilwax column with fused-silica capillary column, 30M long, with 0.25mm inner diameter and 0.25μm film thickness was injected with 0.4μL injection with 20:1 split, held at 33$^{o}$C for 1 minute and then temperature increased at 9/min to 110$^{o}$C, held for 1min and reduced to 33$^{o}$C. Helium was used as a carrier gas. External standards were prepared and a standard curve produced which was used to calculate concentrations. Standards were run monthly to ensure that changes in column response were taken into account. This method yielded quantitative analysis of volatile components.

For analysis of oak extractives an Agilent GC was utilized with auto-injector, and linked MS in electron ionization (EI) mode. An Agilent DB-Wax column with the same liner and dimensions as those listed for the GC was injected with 5μL splitless injection, held at 40$^{o}$C for 5min, increased at 5$^{o}$/min to 100$^{o}$C, and then at 2$^{o}$/min to 210$^{o}$C, held for 45min and cooled to 40$^{o}$C. Helium was used as carrier gas with 1.5mL/min initial flow, 11.93psi pressure, and average velocity of 44cm/sec. The injector was held at 250$^{o}$C and the GC to MS transfer line was held at 240$^{o}$C. Purge flow of 50.0mL/min was held for 2.0 min. A

14.5 minute solvent delay (data acquisition delay) was necessary as the initial volatile components (ethanol and volatile congeners) had the effect of decreasing the total sensitivity of the detector during the run, due to the large injection volume, and high concentrations. The ion signals were detected over the range of 10-350 and preidentification of components was performed with the National Institute of Science and Technology (NIST) mass-spectral library. These identifications were confirmed using external GC grade standards purchased from Sigma Aldritch.

Standard curves were produced with the external standards and used to calculate concentration from peak areas. Standard solutions were mixed using each analyte individually in 62%ABV and water (the concentration at which the barrels were filled). A standard was mixed using 20mg/l of each analyte and a 5 part dilution series was conducted yielding concentrations of: 0.0001g/L, 0.0002g/L, 0.00025g/L, 0.0005g/L, 0.002g/L, 0.005g/L, and 0.02g/L. The dilution procedure was conducted in triplicate. A four point standard curve was produced using the initial dilution set and then confirmed using the subsequent two sets. Where any variation above 0.5% occurred standards were remixed. All standards were stored below $0^{o}$C, and the 0.02mg/l standard was rerun before analysis of any samples, to confirm column response.

While common practice in industry for GCMS analysis of oak extractives employs extraction and concentration of phenolic components before analysis, this methodology was not utilized as it would have required larger sample volumes (10-1000ml). In research these processes were conducted to increase

peak separation. Larger sample volumes would have significantly affected the SA/V ratio by within the barrel by decreasing the spirit volume over time, and therefore artificially decreasing extraction. Instead, a large volume injection combined with a relatively slow temperature profile was utilized to produce the necessary peak separation and allow for smaller sample volumes (2 ml). A method was adapted from the literature to minimize the sample volume and hence the effect of sampling on volume and therefore spirit/barrel interactions. Compounds were chosen for analysis by consistent peak separation and good quality peaks.

A spectrophotometer was utilized for absorbance data. Plastic cuvets were purchased from Sigma Aldritch with a 1cm path length. Absorbance was collected with the unaged distillate in the reference cell. Unaged distillate was stored in Pyrex containers in darkness. Two milliliters of whiskey was removed from each cask, measured and returned to the barrel.

An Anton Paar densitometer was used for analysis of %ABV at the beginning and end of the study. This is an industry standard analytical method.

## RESULTS

DATA KEY

Barrels are named by size and repetition

Barrel 2.1: 2 gallon barrel, repetition 1

Barrel 3.1: 3 gallon barrel, repetition 1

Barrel 10.2: 10 gallon barrel, repetition 2, etc.

## VOLATILE CONGENERS

Concentrations of some volatile congeners within the barreled spirit increased, in some cases quite drastically during the period of study (Table 3). The changes in apparent concentrations of some compounds can likely be attributed to the nature of aging in the barrel. Where decreases in higher alcohols are found (around day 50) this may be due to the production of esters with fatty acids, where the concentration of the alcohol appears to decrease as it is consumed by reaction. The slight increases toward day 200 are likely due to evaporation of water and ethanol from the barrel and concentration of the remaining compounds in the spirit. These two processes proceed simultaneously as the same evaporation which causes apparent increases, allows more air to penetrate into the barrel fueling production of esters.

In the case of ethyl acetate a much more drastic change in concentration is apparent. For this study it was not possible to quantify acetic acid as it eluted during sensor acquisition delay. Acquisition delay was necessary because some volatile components (ethanol, amyl alcohols, acetic acid) were present in such high relative concentrations that they had the effect of overwhelming the sensor and reducing sensitivity to compounds eluting later in relatively lower concentrations. The sensor was not turned on until after these compounds had eluted. With both ethanol and acetate in this high concentration category, the increase in ethyl acetate may be explained by the presence of ample substrate for the production of the resulting ester. While this is a likely explanation, no clear

trend is apparent that relates to barrel size, although the greatest increase appears in a 2 gallon barrel while the least increases appear in the 10 gallon barrels.

Table 3: Selected congener increases per barrel from day 0 to day 202

| Barrel | Ethyl acetate | Isobutanol | Amyl alcohols |
|---|---|---|---|
| 2.1 | 130% | 27% | 28% |
| 2.2 | 114% | 31% | 32% |
| 3.1 | 95% | 31% | 31% |
| 3.2 | 118% | 29% | 28% |
| 5.1 | 120% | 26% | 26% |
| 5.2 | 110% | 24% | 23% |
| 10.1 | 76% | 23% | 23% |
| 10.2 | 38% | 23% | 24% |

The variation in methanol is not so easily explained (Figures 6-13). In all but barrels 5.2 and 10.2 the trends are remarkably similar, with a 3-4 fold increase beginning at day 84 and returning to original levels by day 202. Ordinarily high concentrations of methanol in fruit spirits are due to demethylation processes related to structural polymers such as cellulose in fermentation. General increase trends in congener content during barrel ageing are attributed to evaporation and concentration. While lignolytic activity of ethanol is reported in the literature, lignin is not methylated as heavily as cellulose. Cellulosic ethanolysis has been reported causing increases in carbohydrate concentration of whiskey spirits, which might be the cause of the increases in methanol concentration at certain points during tracking as cellulose is heavily methylated and oak wood is approximately 50% cellulose.

In this study the concentration eventually returned to almost its starting point. It is unknown in this case what the mechanism of change might be, unless methyl esters were produced toward the end of the aging period consuming methanol and lowering apparent concentrations. It is also possible that more methanol diffused out of the barrel as its concentration rose. Its molecular weight (MW) being 32 falls between ethanol (MW: 46) and water (MW: 18). Further examination of such trends would be invaluable for the understanding of the ageing process.

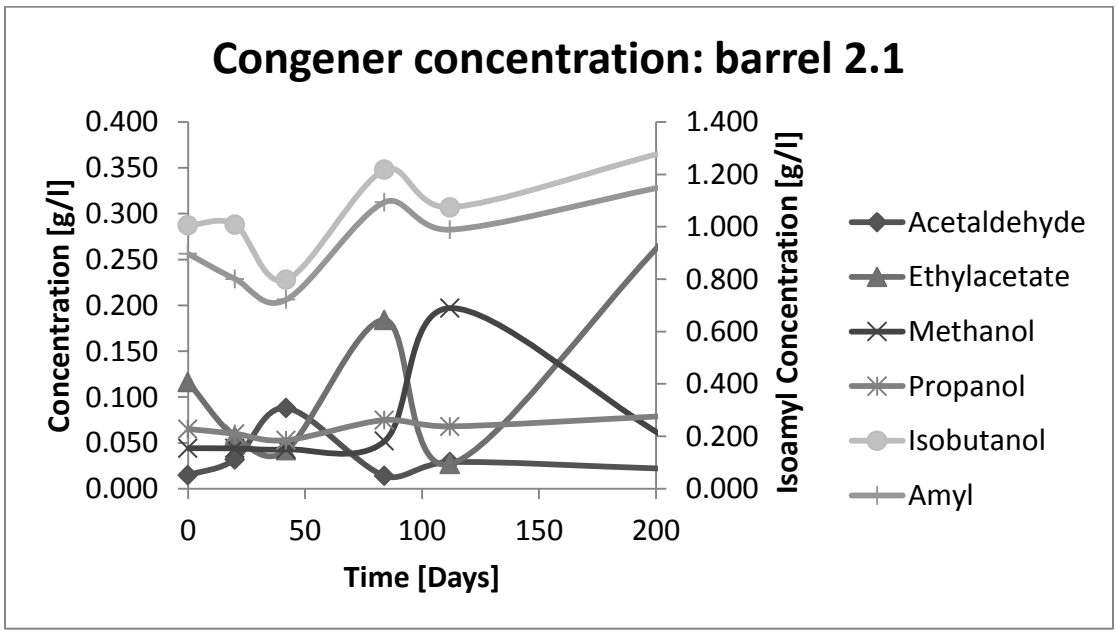


Figure 6: Concentrations of selected congeners in barrel 2.1 over 202 days.

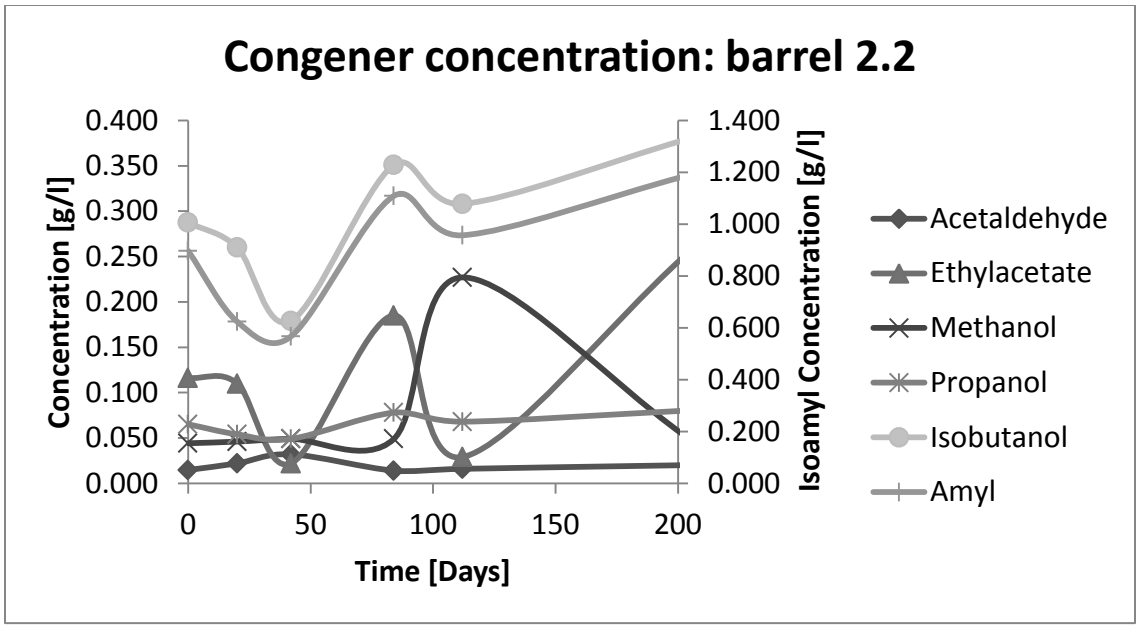


Figure 7: Concentrations of selected congeners in barrel 2.2 over 202 days.

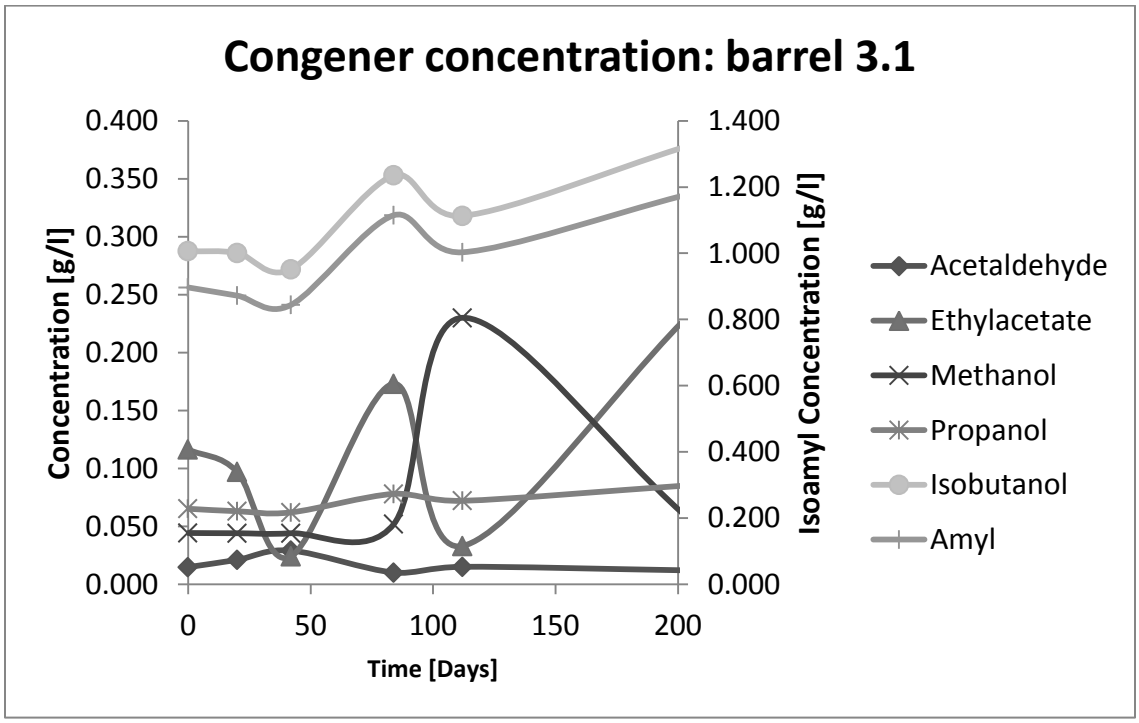


Figure 8: Concentrations of selected congeners in barrel 3.1 over 202 days.

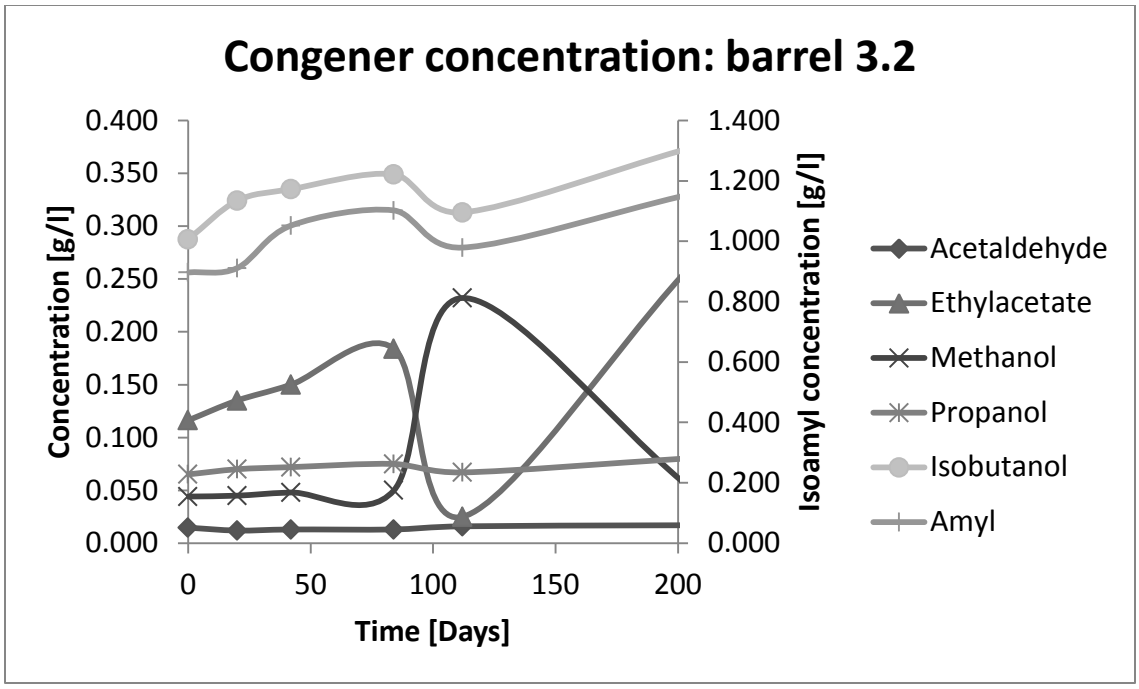


Figure 9: Concentrations of selected congeners in barrel 3.2 over 202 days.

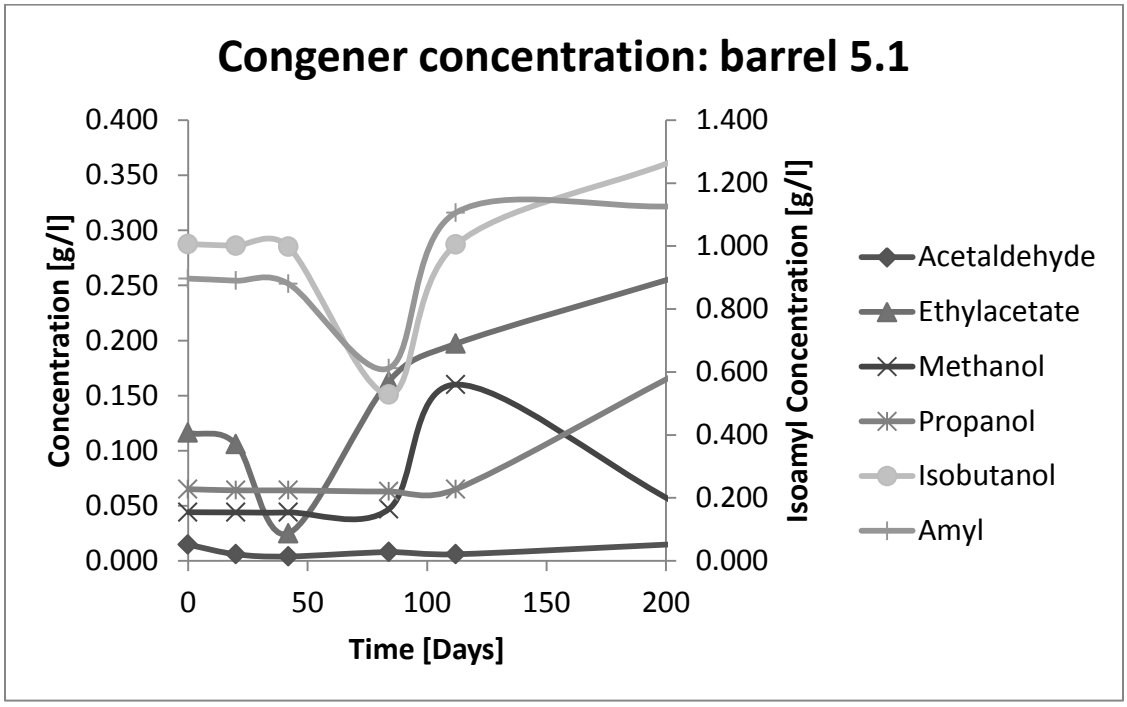


Figure 10: Concentrations of selected congeners in barrel 5.1 over 202 days.

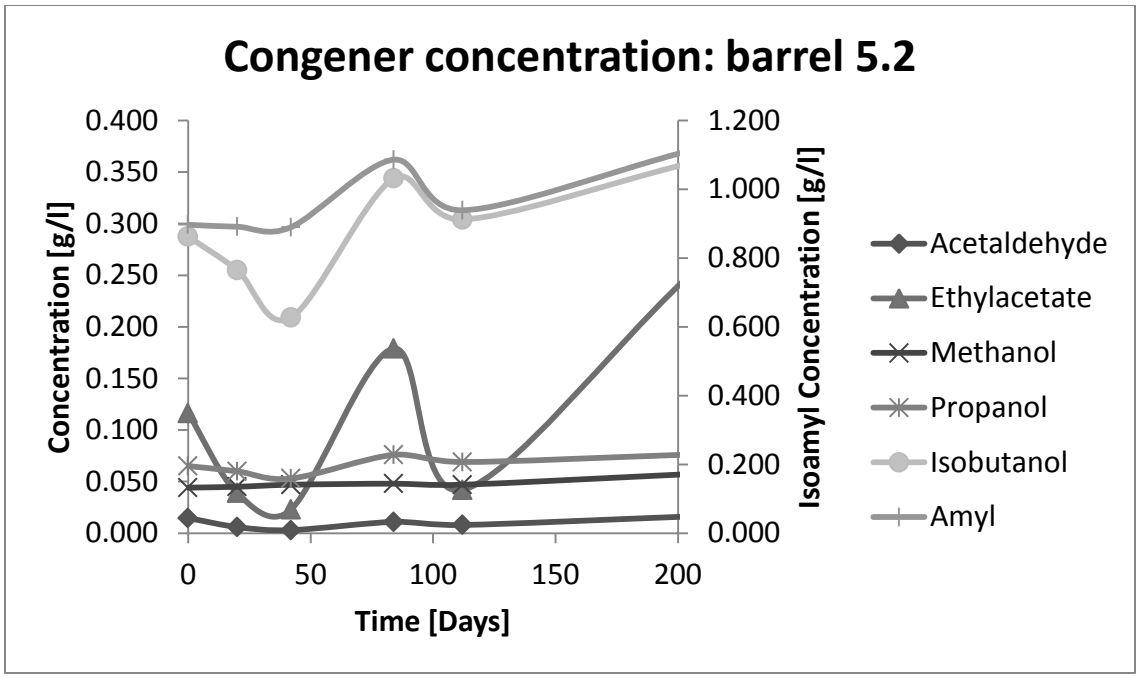


Figure 11: Concentrations of selected congeners in barrel 5.2 over 202 days.

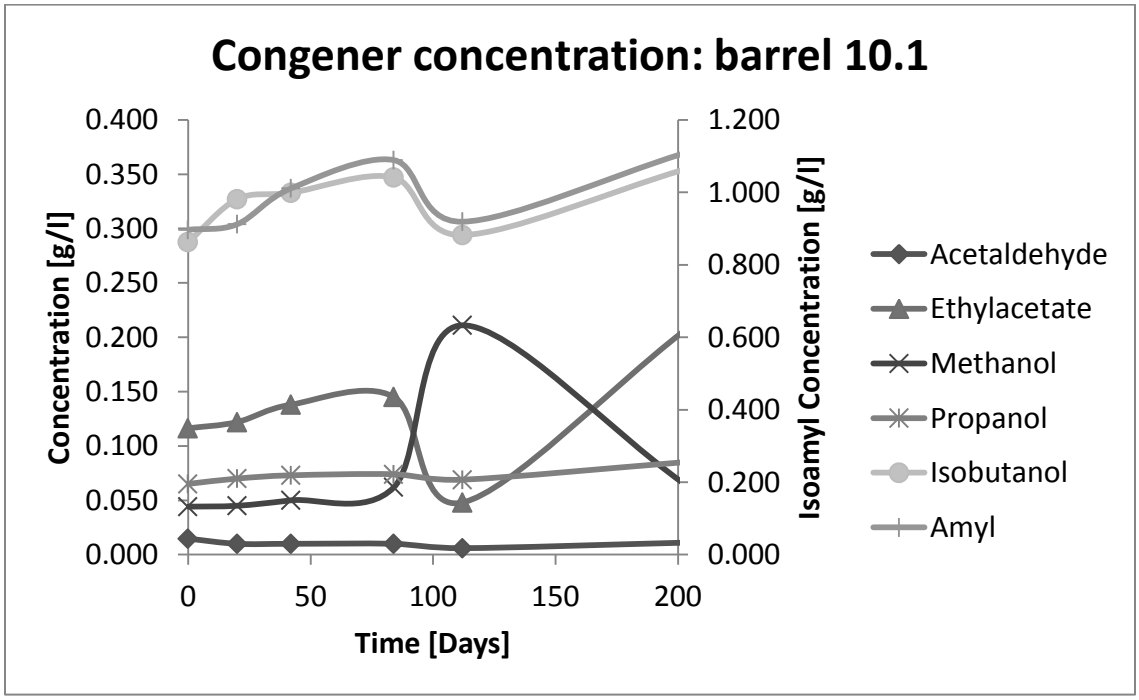


Figure 12: Concentrations of selected congeners in barrel 10.1 over 202 days.

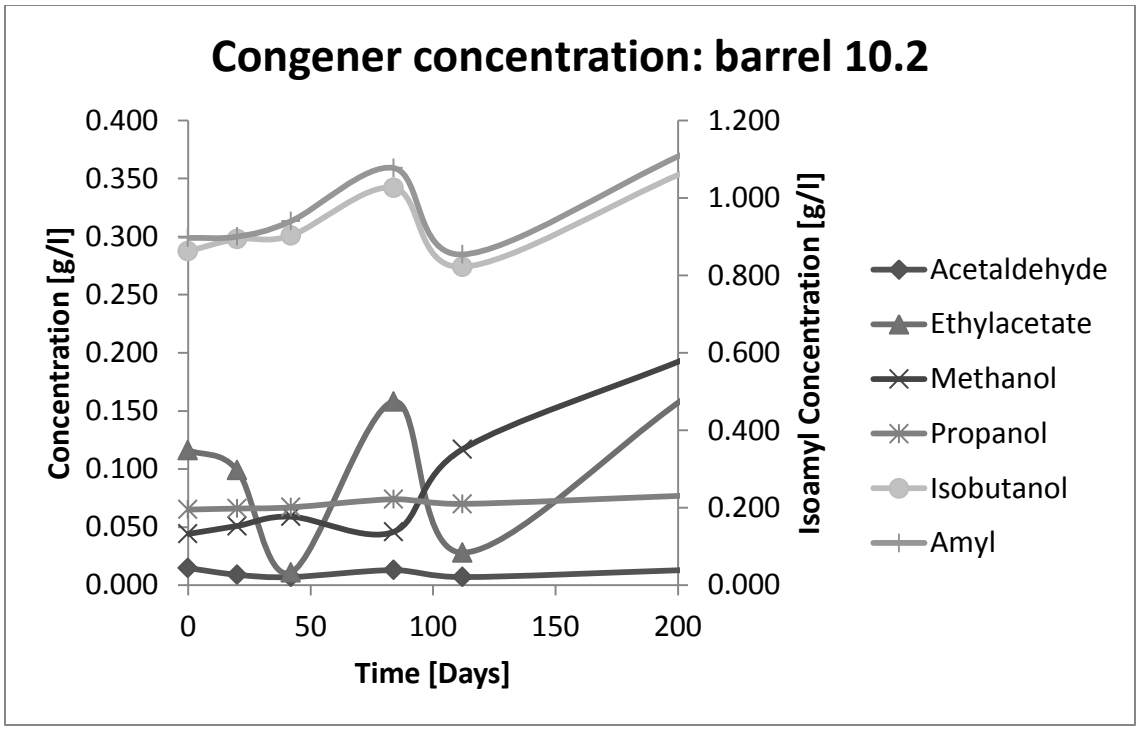


Figure 13: Concentrations of selected congeners in barrel 10.2 over 202 days.

ABSORBANCE

Absorbance data trended upward during the study for all barrels. Absorbance at A520 has been utilized by MacDougall in the development of a uniform color scales for whiskies. From the data presented in Figure 14 it is apparent that absorbance may be valuable for tracking barrel extraction. This might take the form of empirical data collected and employed in QAQC facilities in industry, but may also warrant further examination in a laboratory setting. This methodology for barrel tracking has not been suggested in the literature or examined for its utility. With the prevalence of affordable and portable spectrophotometric devices this could become a valuable technology in the production setting.

The upward absorbance trend does not follow the same pattern of increase as was observed in the oak extraction rates in 2 and 3 gallon barrels (Figures 15-19). It is unknown what components within the spirit are responsible for the absorbance at this wavelength. Thousands of aromatic substances have been isolated from whiskeys any or all of which collectively might be responsible for the effect, and more data would be required to ascertain of what value this data might be in production. Absorbance data was collected for A350 as well but by day 10 all barrels had reached a plateau at an absorbance value of 2, and was therefore not continued.

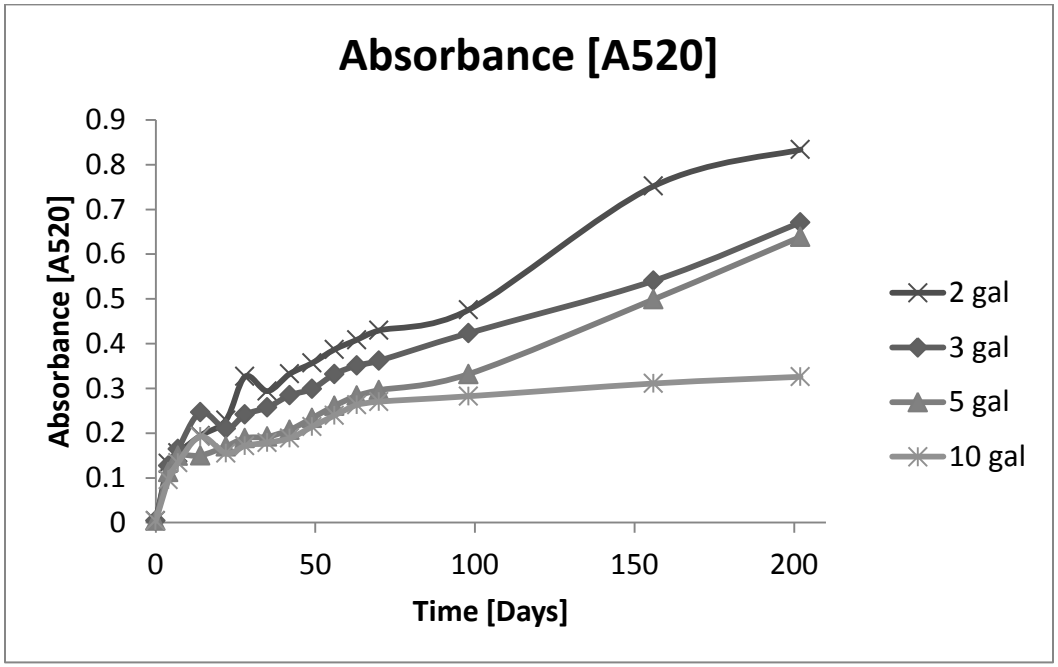


Figure14: Averaged duplicate absorbance data for all barrels, day 0 to day 202 measured at 520nm.

## BARREL EXTRACTION

Oak extraction data is presented in Figures 15-18. For each of the compounds analyzed extraction occurred faster at smaller barrel volumes. One interesting phenomena noted was a latent period in extraction during the first 40 days in 2 and 3 gallon barrels. Between days 40 and 60 the 2 and 3 gallon barrels displayed a rapid increase in concentration of each phenolic compounds. It is unknown why the smaller barrels would display this pattern but it is also interesting to note that after this period of rapid extraction the flavor of the spirit could be considered over extracted with the flavor of oak in these spirits becoming overwhelming. The 5-10 gallon barrel produced a more gradual and consistent increase in concentration during the full 202 days, for all compounds, with no latent period.

It is a known feature of oak ageing that spirit migrates into and out of the wood staves. Migration of liquid into the barrel wood and back into the container with solubilized phenolic constituents is the method of extraction. The barrel stave thickness becomes slightly greater as the barrel volume grows and it is possible that the smaller staves in the 2 and 3 gallon barrels were affected differently by heat treatment causing the change in extraction activity. Heat treatment is an uncontrolled factor in this study and so its affect on the available extractive content.

In the construction of a 55gal barrel, staves are produced from many trees and potentially multiple subspecies of *Quercus* and the average 50 gallon barrel

is constructed of 55 staves. This random sampling of staves has the effect of minimizing specific effects from differing growth conditions of the individual trees on the sensory qualities of the spirit. Because there are fewer staves utilized in the construction of smaller barrels there is more opportunity for the effects of an individual growth condition to influence the extraction profile of the whiskey. Additionally in the large production setting whiskeys are blended from many barrels, again reducing the impact of individual growth factors on the sensory qualities of whiskeys. The artisan producer does not have access to this large volume of aged product for blending and may be subject to greater impact from individual trees on the sensory qualities of their products.

Table 4 shows final concentrations from this study compared with that collected in previously published research. Very few studies exist which display concentrations of multiple compounds extracted from new American oak in American whiskeys. These concentrations were comparable in some cases and far higher in others to those values found in the literature. Again, this points to the lack of data in this area of research and the need for further data.

Most published extraction data has been collected from the Scotch whiskey industry which utilizes barrels previously used for the ageing of bourbon whiskey. This means that many of the compounds expected in American whiskeys will not appear in Scotch or Irish as they have been extracted in previous use and their extraction profiles cannot be compared. Additionally, because the standards of identity for some spirits allow for blending with neutral spirits, blending of spirits aged for a variety of periods in barrels and activated

carbon treatments for the removal of certain compounds, even within the category of American whiskies it is difficult to determine the value of such comparisons. Each of the references below characterized whiskeys aged in 55 gallon barrels.

Table 4: Concentrations of phenolic components [g/l] as reported in published research and in the current study (CS) in 2, 3, 5, and 10 gallon barrels (CS 2, CS 3, etc.)

| | **Guaiacol** | **Eugenol** | **Vanillin** |
|---|---|---|---|
| Ref. 82 | 0.00005 | 0.00024 | 0.00213 |
| Ref. 83 | | ~0.00033 | ~0.0042 |
| Ref. 84 | | | 0.00094 |
| Ref. 85 | 0.00005 | | |
| Ref. 89 | 0.003760 | 0.000583 | 0.008130 |
| CS 2 | 0.0048 | 0.0020 | 0.0094 |
| CS 3 | 0.0031 | 0.0014 | 0.0084 |
| CS 5 | 0.0024 | 0.0013 | 0.0049 |
| CS 10 | 0.0021 | 0.0008 | 0.0031 |

*(Ref 82: characterized a 3yr bourbon, Ref 83: characterized 10yr Scotch, Ref 84: characterized American bourbon, Ref 85 characterized American whiskey, Ref 89 characterized commercial rye whiskey).

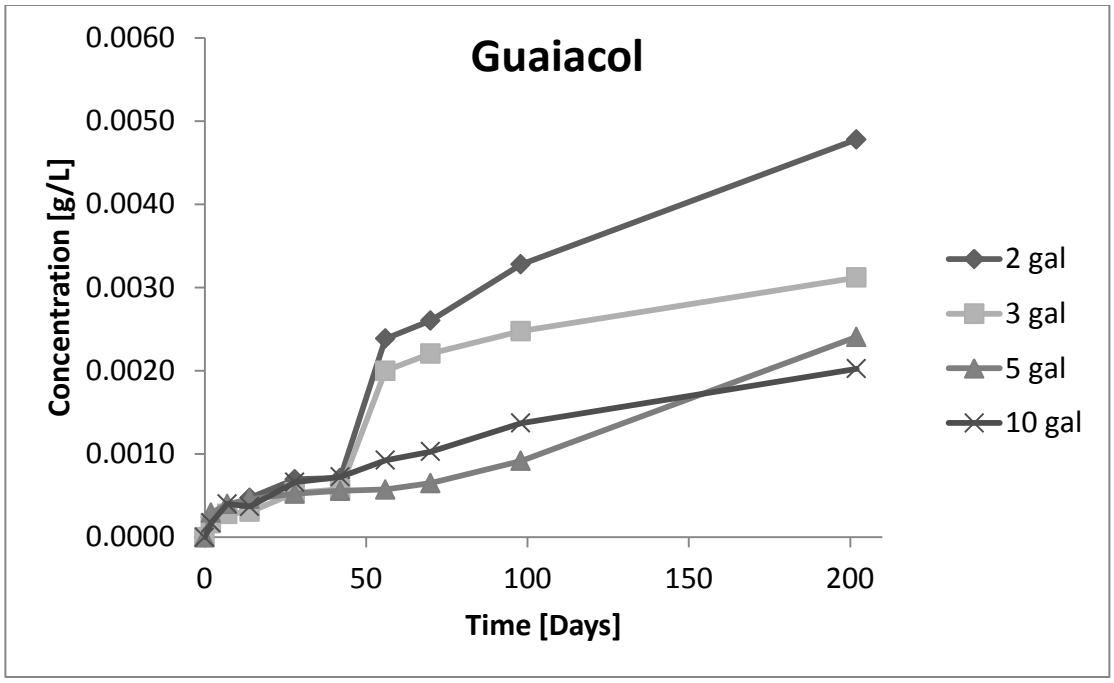


Figure 15: Averaged duplicate concentrations of guaiacol over 202 days in all barrels.

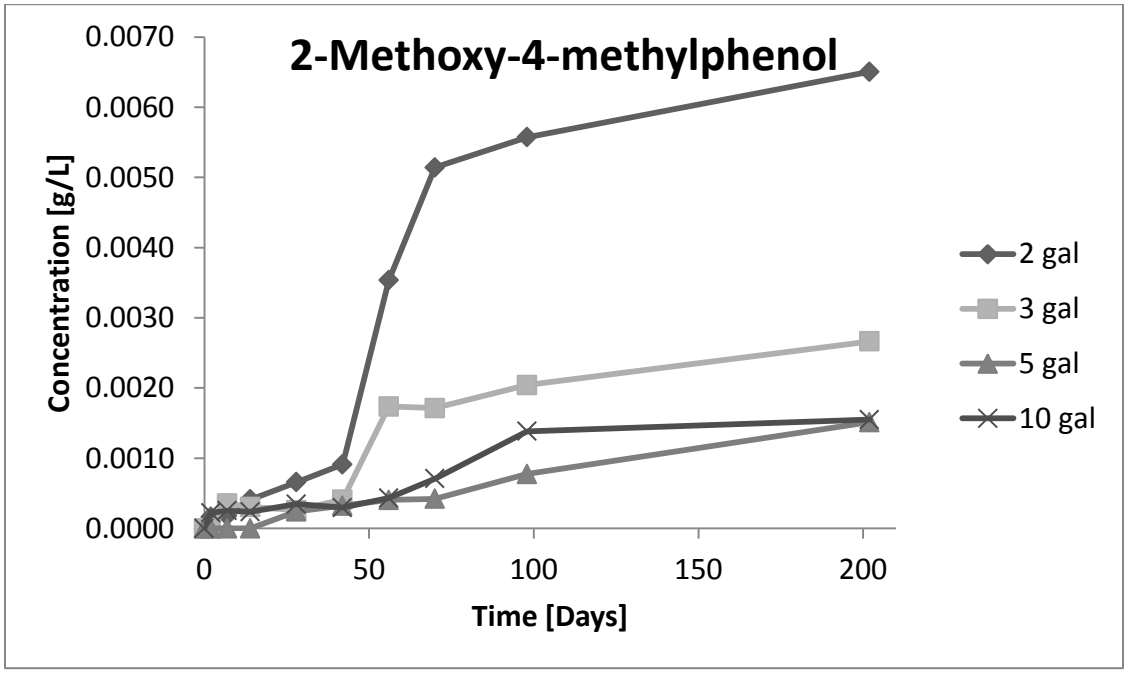


Figure 16: Averaged duplicate concentrations of 2-Methoxy-4-methylphenol over 202 days in all barrels

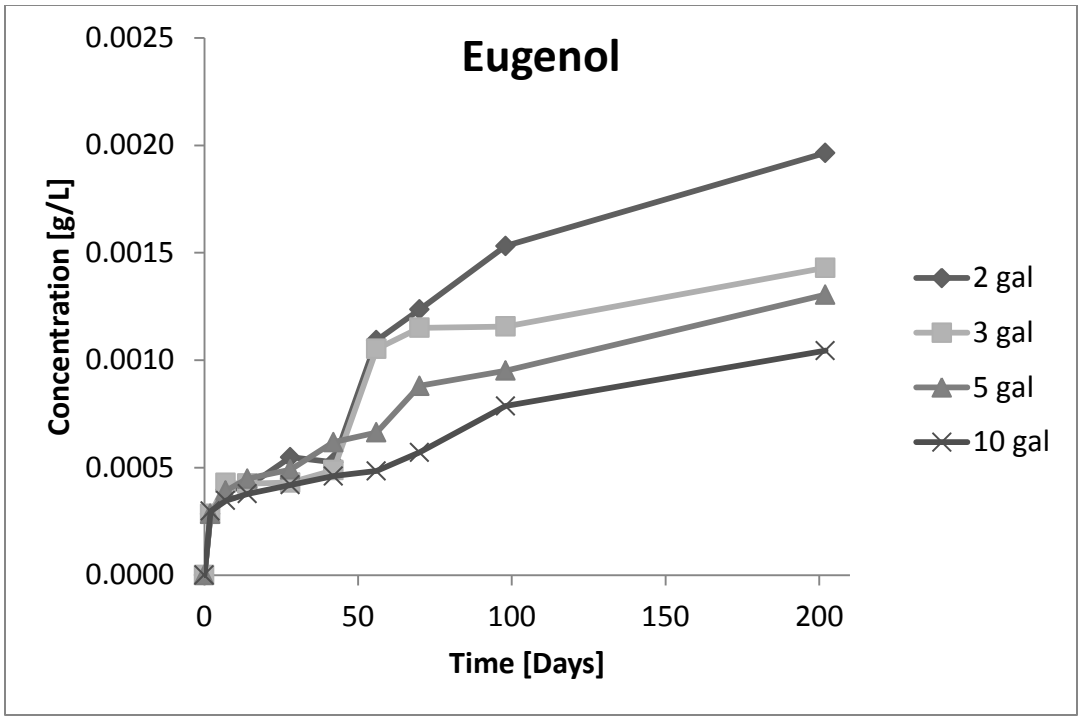


Figure 17: Averaged duplicate concentrations of eugenol over 202 days in all barrels

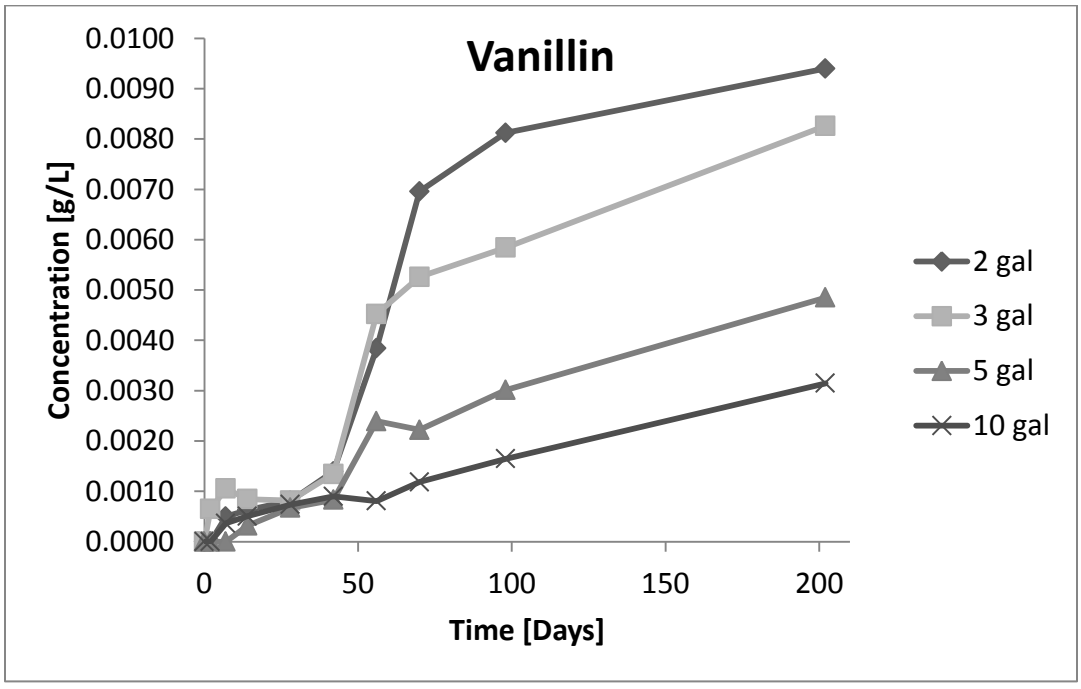


Figure 18: Averaged duplicate concentrations of vanillin over 202 days in all barrels

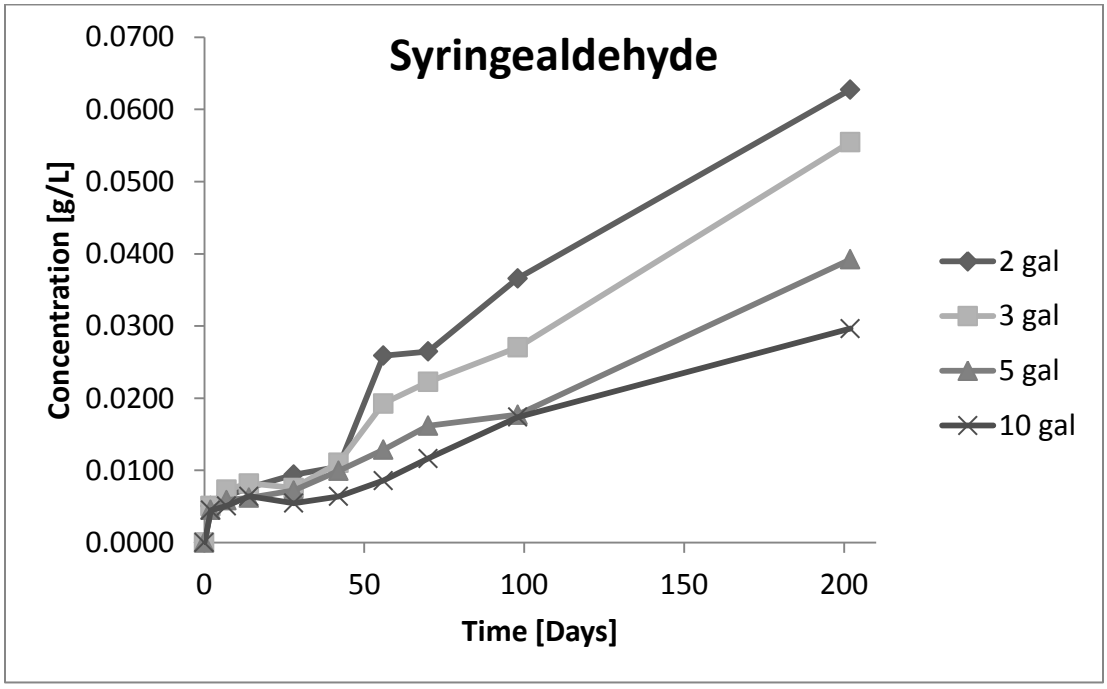


Figure 19: Averaged duplicate concentrations of syringaldehyde over 202 days in all barrels

SPIRAL EXTRACTION

The manufacturer states that full extraction is achieved with oak spirals within 6 weeks, but this recommendation is designed for wines. For the trials conducted in the current study it would appear that the extraction time required for wine might be greater than that required by spirits, as the concentration change from hour 160 (day 7) to hour 600 (day 25) is not significantly greater for any extractive compound. The manufacturer's recommended dosages have been calculated as 1.3 to 2.6 cm per gallon of wine. No dosages are offered for spirits so this wine recommendation was utilized in the design of these trials.

Because these extractions were conducted in glass containers, no changes were observed in volatile congener concentration or volume and alcohol concentration. Therefore, following traditional rationale it is not possible in this manner to produce an aged spirit. Extraction of oak components takes place but the required esterification reactions will not take place in the absence of the dynamic environment provided by the barrel and the oxygen infiltration that occurs there. It is possible that some form of oxygen sparge might be utilized to catalyze the required reactions in the presence of the oak extract from spirals but this would require a good deal of development as oxygen sparge might also catalyze the production of undesirable compounds, or excessive concentrations of desirable ones such as ethyl acetate.

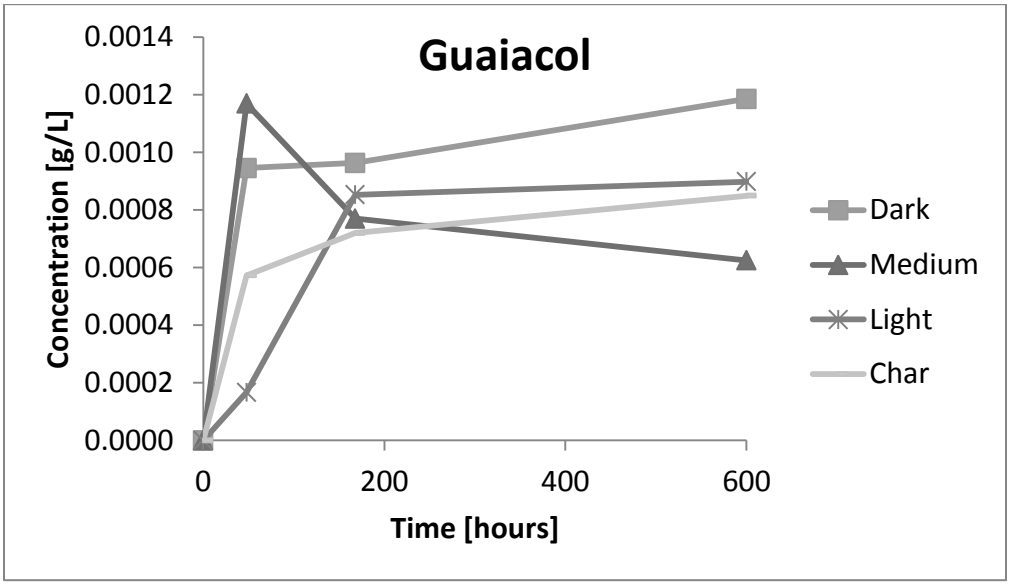


Figure 20: Concentrations of guaiacol extracted from oak spirals by whiskey spirit, over 600 hours (25 days)

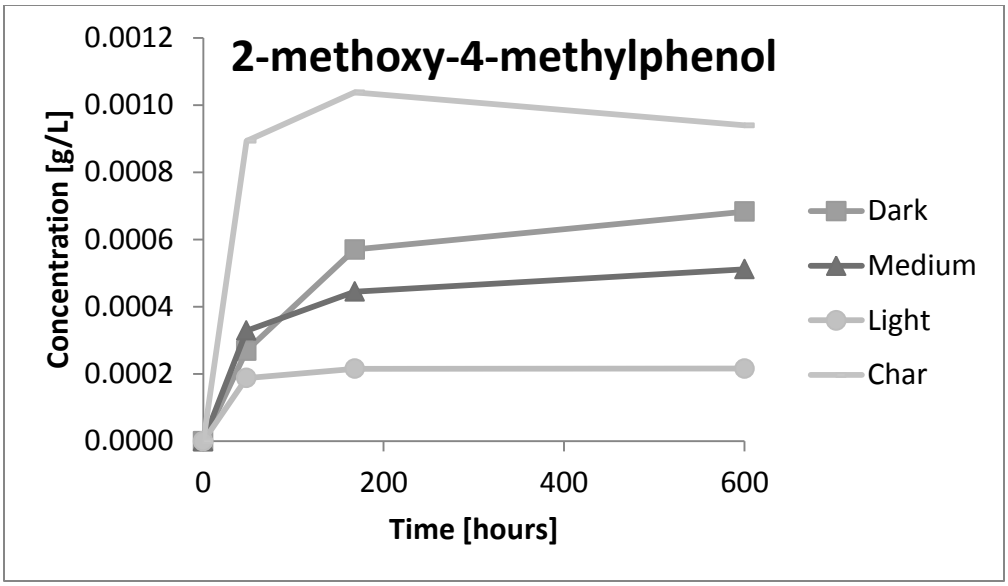


Figure 21: Concentrations of 2-methoxy-4-methylphenol extracted from oak spirals by whiskey spirit, over 600 hours (25 days)

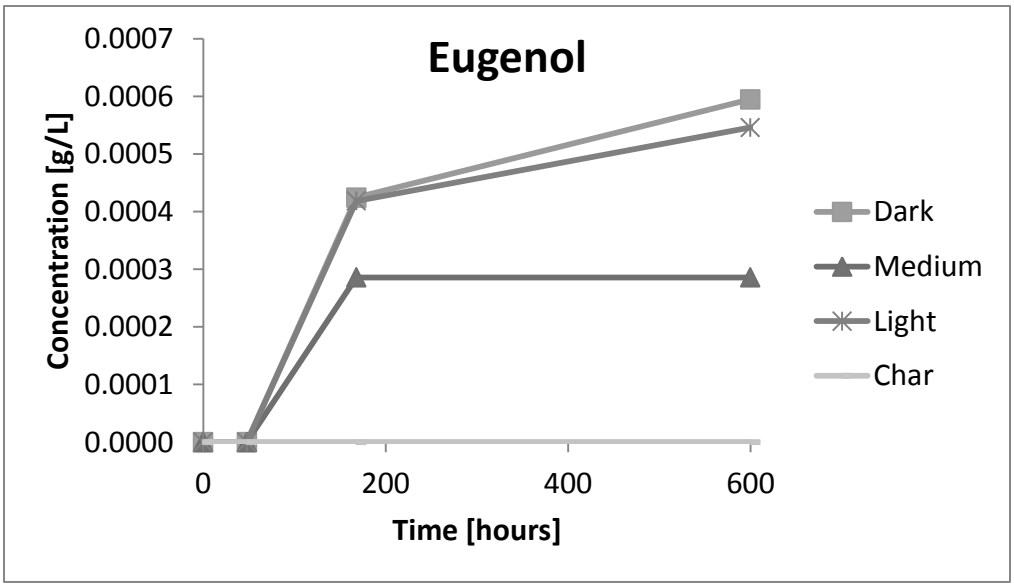


Figure 22: Concentrations of eugenol extracted from oak spirals by whiskey spirit, over 600 hours (25 days)

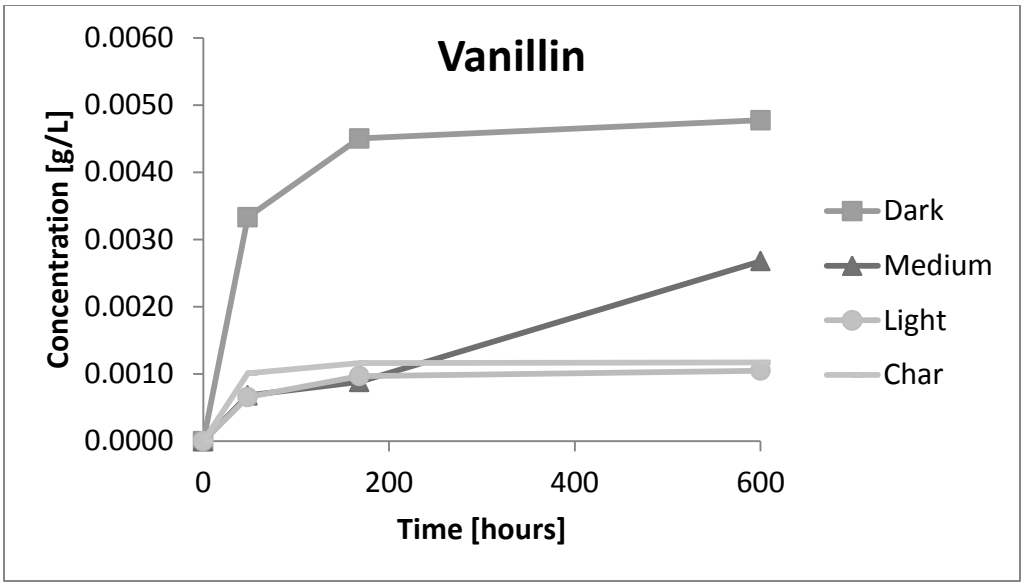


Figure 23: Concentrations of vanillin extracted from oak spirals by whiskey spirit, over 600 hours (25 days)

For the extraction trials displayed above the dose was calculated individually for each heat treatment spiral type and each was exposed in the recommended dose individually. The recommendation of the manufacturer is to dose the beverage with the variety of heat treatments for a total oak dose containing each of the treatments. The concentrations of compounds within oak wood differs with exposure to heat at different intensities and times and manufacturers claim to be able to customize flavor extracts of oak in this way. In the barrel this takes the form of the natural temperature gradient that is produced in the depth of the stave during charring, but with spirals this must be reproduced by the use of the variety of treatments and spirals must be combined to mimic the total extractive profile of the barrel.

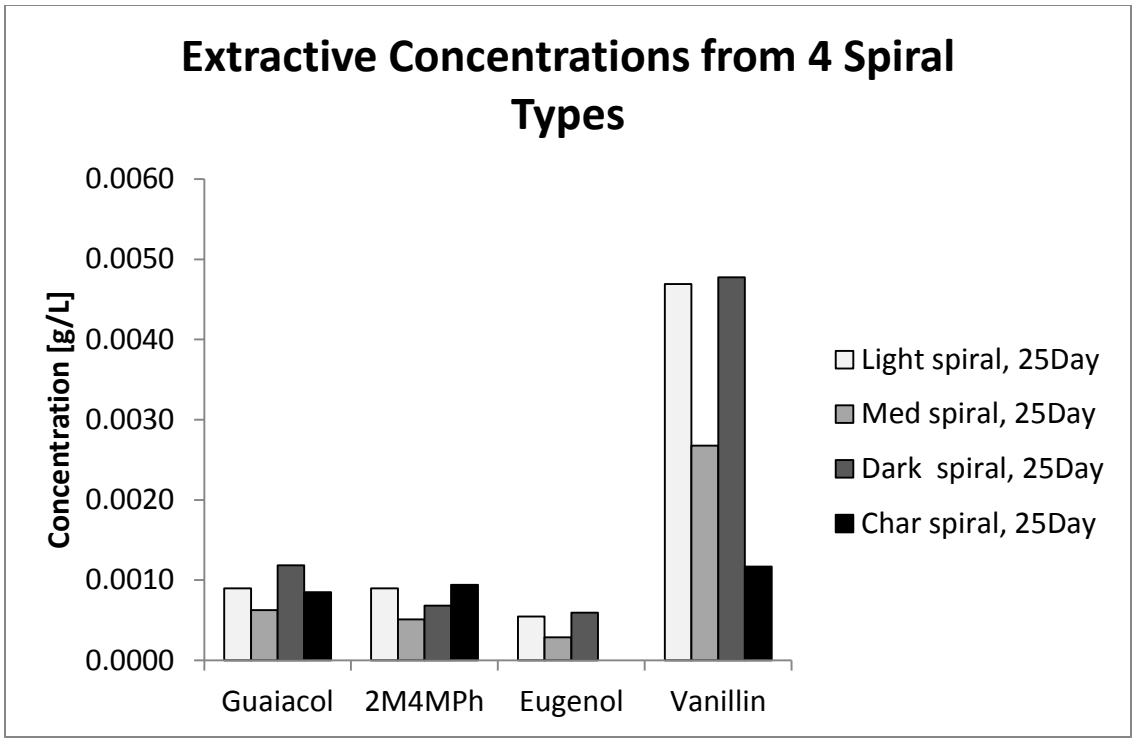


Figure 24: Final concentrations 4 compounds extracted from oak spirals by whiskey spirits

When extraction from the variety of spirals was compared to the extractive levels in the 5 and 10 gallon barrels it was noted that for guaiacol, 2-methoxy-4-methylphenol, and eugenol were higher from the barrels while vanillin extraction was comparable to some treatment types. The 5 and 10 gallon barrels were the most pleasing in terms of sensory characteristics at day 270 and so comparison with those products would seem to be sensible. The sensory characteristics of the spiral extractions were universally unpleasant as the oak was not integrated into the spirit and/or its flavor and aroma profile. This highlights the fact that while extraction is important it is a contributor to ageing and must be coupled with the reactions that take place in the barrel.

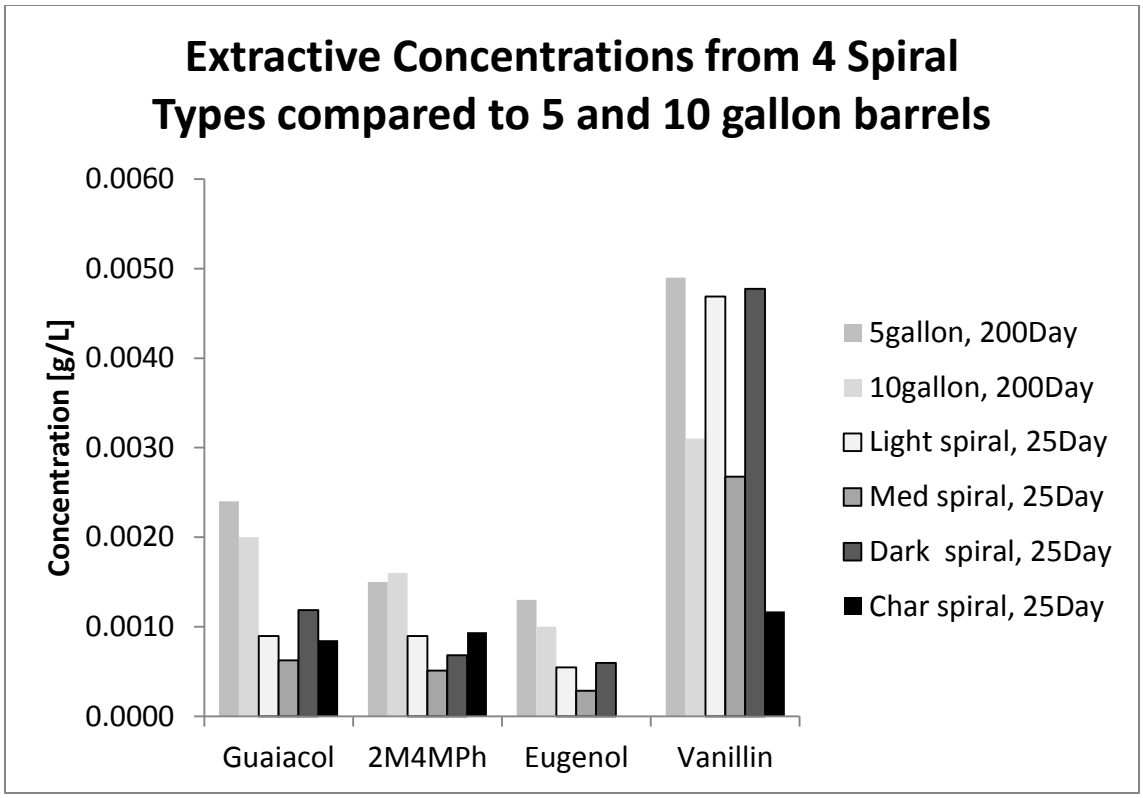


Figure 25: Concentrations of 4 compounds extracted from oak spirals compared to those extracted from 5 and 10 gallon barrels

When the final concentrations of each compound was divided by the number of available heat treatments to simulate extraction from a variety of spirals, the total extractive profile more closely resembled that of the 5 and 10 gallon barrels as shown in Figure 27 below. This would seem to reinforce the manufacturer's assertion that a total barrel extract might be approximated using spirals if all of the heat treatments are utilized. The important thing to note is that the presence of some form of catalyst would be necessary to form the requisite esters and other complex compounds that produce maturity in a finished spirit.

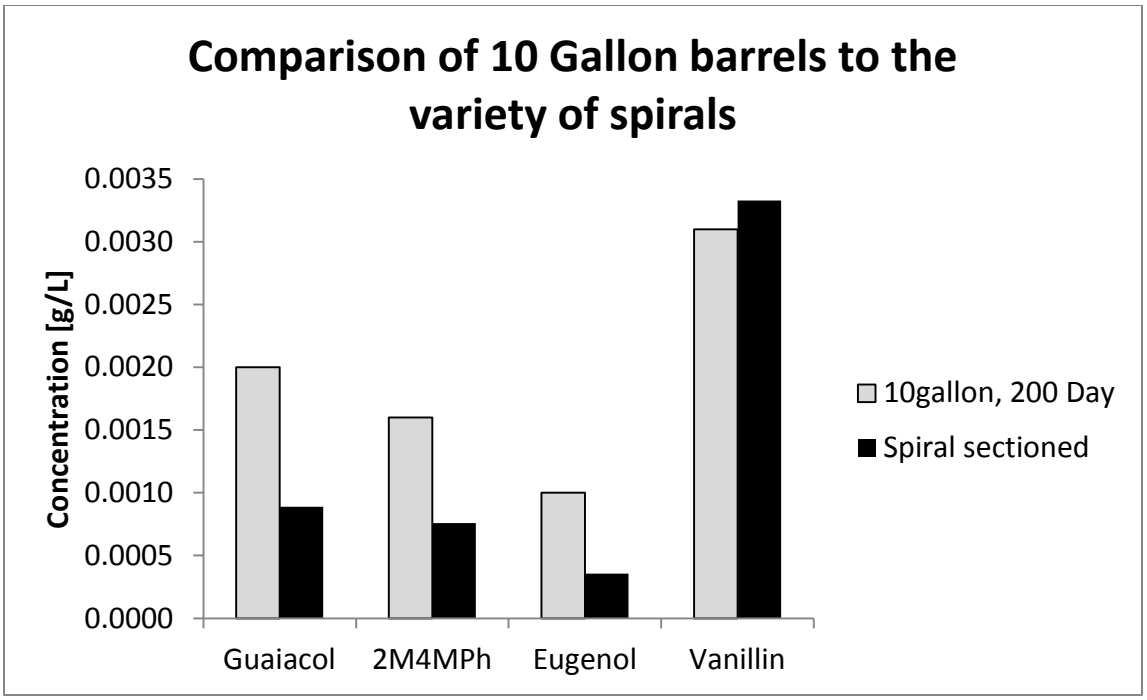


Figure 26: Concentrations of 4 compounds extracted from oak spirals combined and corrected for manufacturer recommended treatment, compared to those extracted from 10 gallon barrels

SENSORY THRESHOLDS

Extraction data is valuable as it contributes to the body of knowledge surrounding the extremely complex processes that are required to produce mature and complex spirits within the barrel system. It is however also valuable to examine the data in the context of the spirit itself and the sensory affects that can be expected from the extract. As such the extraction data is presented below in combination with information from the literature on the sensory thresholds of the compounds within the ethanol and water matrix.

A good deal of work has been conducted by a variety of research groups examining aroma and flavor thresholds in spirits of bottling and barreling strength (40%ABV and ~60%ABV respectively). Table 5 displays some of this literature information. It is important to note that for the compounds examined, the aroma thresholds as reported have already been exceeded within the first week of exposure to new American oak barrels. Lee *et al*. has reported the flavor threshold for vanillin to be 0.1mg/L at 40%ABV (40-45% is the strength range at which spirits are ordinarily bottled) (40). Spirits are aged in the barrel at 58-62%ABV so a concentration of 0.15-0.2mg/L is required within the barrel to exceed the flavor threshold within the bottle, once water has been added to achieve bottling strength (40,87,90,91).

Table 5: Reported flavor and aroma thresholds for some compounds of interest, in mg/L (40, 82, 85, 88, 89, 90, 91)

| - | Guiacol | Eugenol | Vanillin | Syr-aldehyde |
|---|---|---|---|---|
| Aroma Threshold, 40% | 0.0069 | 0.0071 | 0.022 | |
| Flavor Threshold | 27 | 50 | 0.1 | 15 |

Table 6: Day at which each barrel concentration exceeded reported taste thresholds for syringaldehyde (0.02g/L) and combined threshold for vanillin and syringaldehyde (0.003g/L) corrected for concentration after dilution to bottling proof (40%ABV).

| Barrel Size | Day to surpass Syringealdehyde Threshold | Day to surpass Syr/Van Threshold |
|---|---|---|
| 2 | 56 | 7 |
| 3 | 70 | 7 |
| 5 | 150 | 14 |
| 10 | 202 | 7 |

Table 6 displays the importance of synergistic taste thresholds by showing the day at which each barrel size exceeded the individual taste threshold for syringaldehyde and the day at which the barrels exceeded the synergistic combined thresholds for syringaldehyde and vanillin. Only 5 compounds have been examined in this study and individually neither eugenol or guaiacol concentrations exceed their flavor thresholds while both vanillin and syringaldehyde exceed thresholds by the end of the study. It is known that synergistically, phenolic compounds in combination have lower sensory thresholds and that the combined sensory descriptors are reminiscent of the individual components as is the case for syringaldehyde and vanillin (40). All compounds exceed their aroma thresholds very early on.

It must also be noted that in the case of spirits in particular, the differentiation between aroma and taste threshold is less clear than in solid foods. Aroma itself is a major contributor to the flavor experience and the contents of spirits are volatile. Orthonasal sensation becomes the major contributor to the taste/flavor experience as spirit volatilizes once in contact with the pallet. Normal human body temperature exceeds the boiling point of ethanol and thus the volatilization of spirits within the mouth and experience of aroma within the orthonasal cavity is part of the taste experience.

In terms of extraction levels and sensory threshold comparisons it may be said that the best use of the barrel may not be to fill it and wait for the completion of the aging process, but to fill it and extract enough flavor/aroma active components to cross some sensory thresholds, then transfer the spirit to another

container, and refill the original barrel with fresh spirit and extract again to the same sensory threshold. It is a rule of thumb in industry that for each refilling of a barrel it will take twice as long to achieve the same level of extraction. This may constitute a more sustainable and economically viable production method as barrels are one of the major cost contributors to distillery operations.

Taking the data in Figure 27 below in the context of synergistic taste thresholds of some phenolic components it is clear that that the taste threshold might be passed quite quickly. Lee *et al*. reported synergistic thresholds of 2mg/L for vanillin and syringaldehyde, and 4mg/L for ferulic acid, vanillic acid, syringic acid, sinapic acid, and vanillin. While only the first encompasses compounds tracked for this study, the second gives some further context and provides a range. In all of the barrels the concentration at which these thresholds would be reached, even after dilution for bottling, has been achieved by day 14.

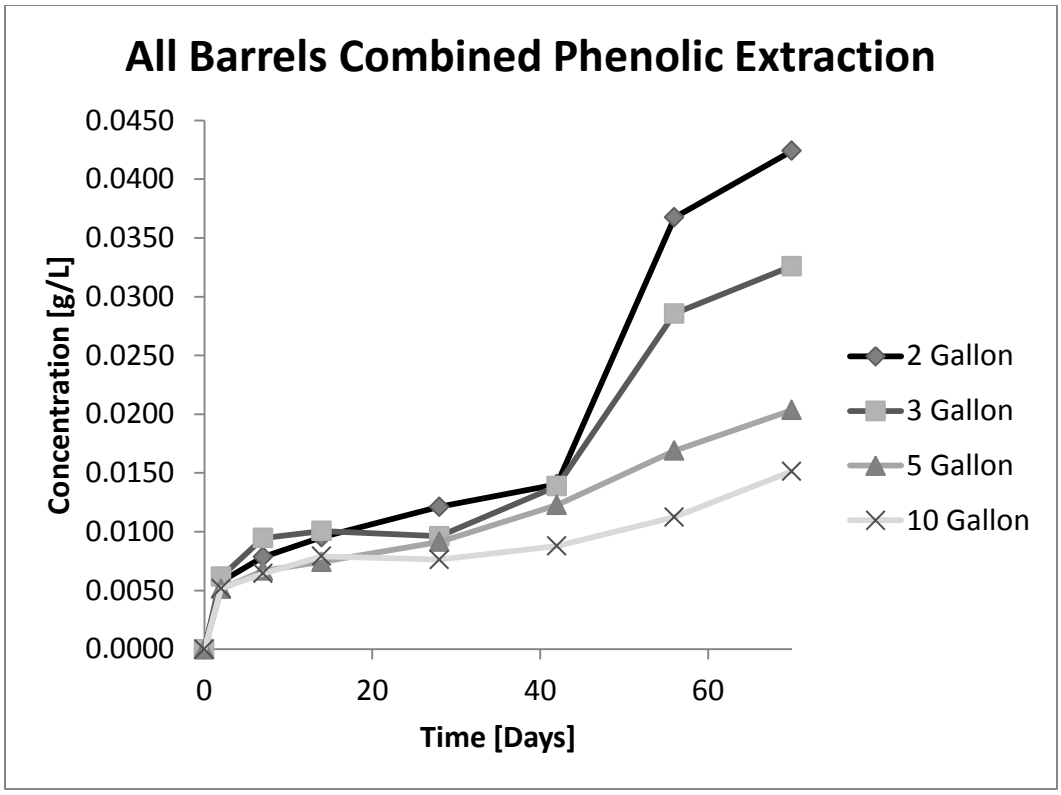


Figure 27: Combined concentrations of all 5 phenolic compounds in 2, 3, 5, and 10 gallon barrels over 70 days.

VOLUME LOSSES

Percent volume loss was not measured at the same end point as the final extraction data was taken. The volume loss and data presented on it was collected at day 270 when it was discovered that samples had been destroyed.

Angel's share is an industry term used to describe percent volume lost from the barrel due to evaporation. Angel's share increased as SA/V ratio increased. Volume loss ranged from 8% in 10 gallon barrels to 28% in 2 gallon during the 270 day period. It is noted that when percent of total volume lost as ethanol was compared, it was found that 2-3 gallon barrels lost 64.96% and

63.67% respectively, while in 5-10 gallon barrels 80.54% and 83.21% was lost as ethanol respectively. A greater proportion of the volume loss was lost as ethanol in larger barrels. Evaporation from the barrel is affected by humidity in the environment. It is generally accepted that greater humidity produces greater ethanol loss, as water must migrate against atmospheric osmotic pressure. Ethanol concentration in the barrel can rise if humidity is low (water preferentially migrating out) and decrease if humidity is high (ethanol preferentially migrating out). Both water and ethanol are lost but the change in ethanol concentration is dependent on the relative rate of loss of each. Water with the molecular weight 18 (MW) diffuses faster than ethanol or even air. Ethanol with its MW of 46 takes longer than water and in fact, unlike water, does not diffuse against a gradient as the atmosphere is usually almost free of ethanol. In this study, it would appear that headspace conditions in the variety of barrel sizes also has an effect on migration of ethanol from the barrel.

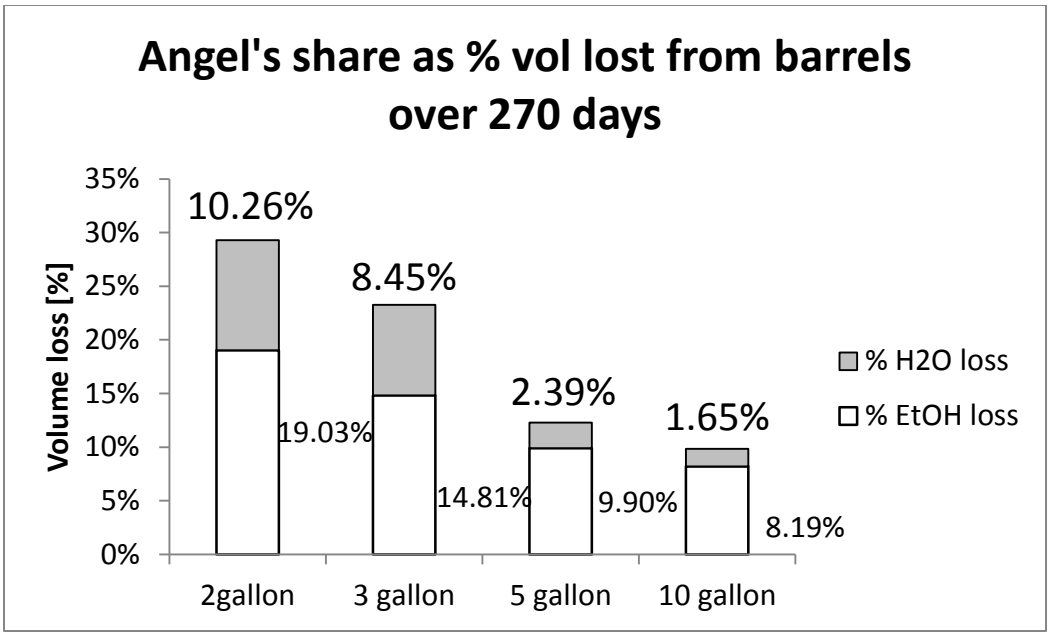


Figure 28: Angel's share reported as percent volume lost from the variety of barrels over 270 days

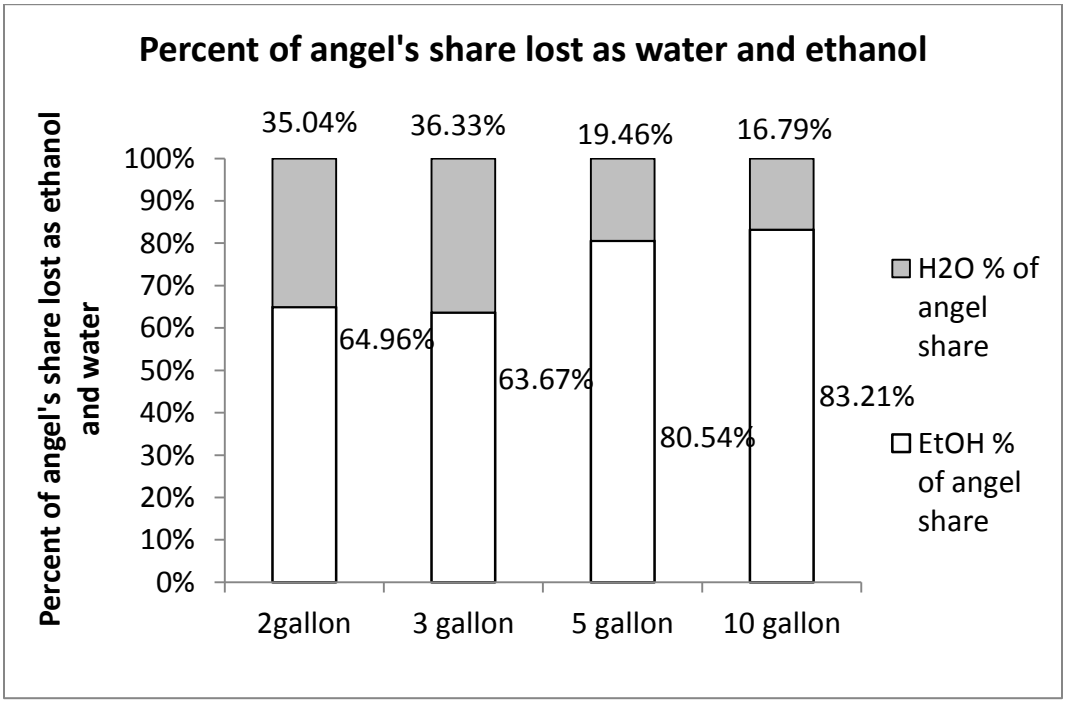


Figure 29: Angels share showing percent lost in ethanol and water during the 270 day period

When volume lost as ethanol was plotted over barrel volume capacity it was found that the resulting curve showed potential as a predictor of evaporation of ethanol from a variety of barrel sizes. It is important to note that evaporation is highly dependent on environmental conditions, so such a curve could be most useful to extrapolate empirically measured loss from one barrel size, to larger or smaller barrels before use, in similar environmental conditions within a facility. The primary point to this however is that there appears to be some connection between the percent of volume lost as ethanol and the barrel size. This might be a useful tool for the producer to determine how barrel size would affect whiskey volume, proof and ageing dynamics over time.

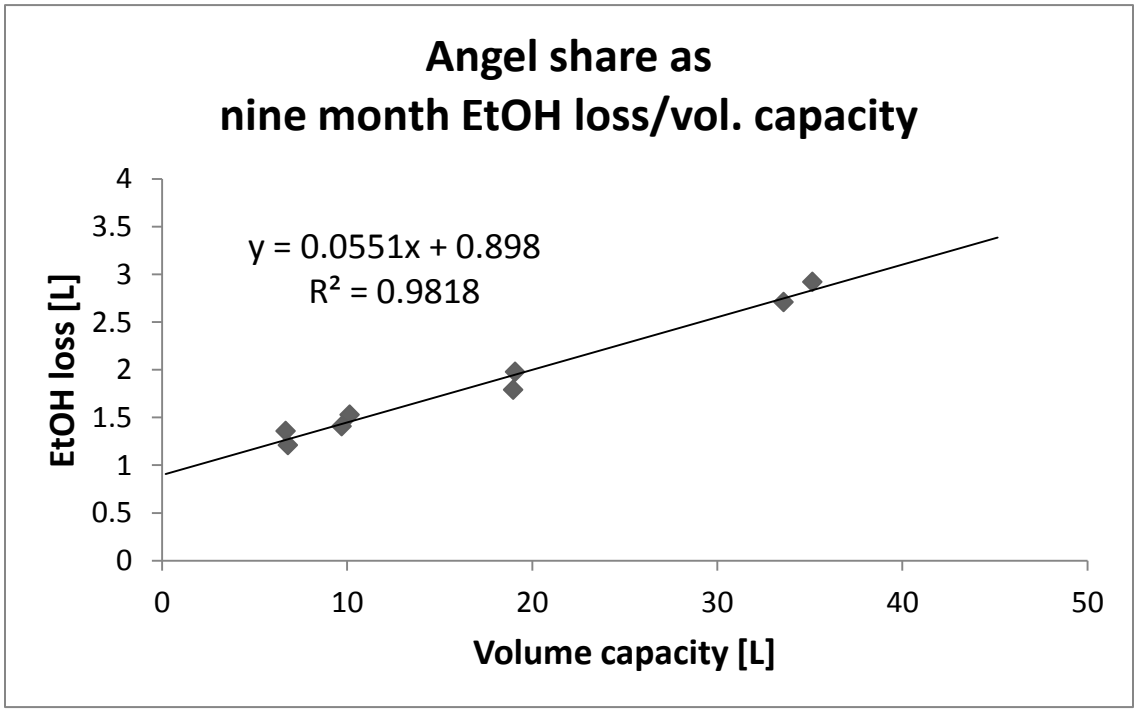


Figure 30: Angel's share plotted as ethanol loss over volume

SURFACE AREA TO VOLUME RATIOS

Vernon Singleton in 1974 provided some SA/V ratio calculations for barrels based on a variety of geometries, including: cube, sphere, frustum, and cylinder. The frustum data are plotted below as drawn from his tables (28).

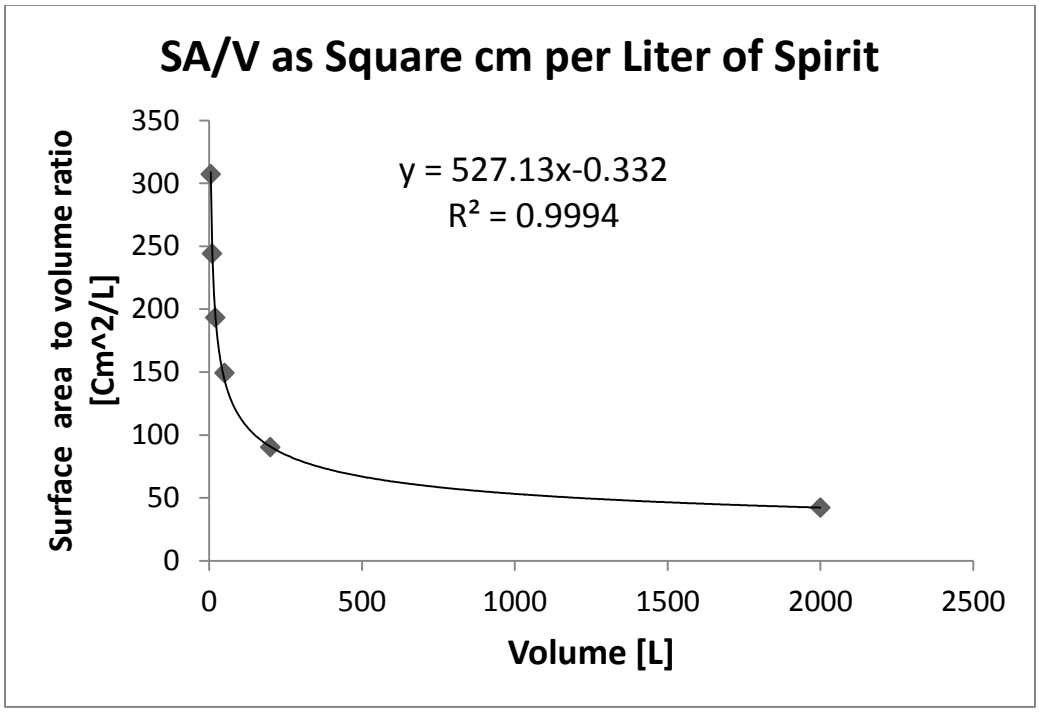


Figure 31: SA/V over volume as drawn from tables presented by Singleton in 1974

Using the equation derived from this data and the actual measured volumes of the barrels utilized in this study, the SA/V of the variety of barrels is presented below.

Table 7: SA/V of barrels utilized in this study as derived from equation above and actual volumes, in $cm^2$/Liter of fill.

| | 2 gal | 3 gal | 5 gal | 10 gal | 50 gal |
|---|---|---|---|---|---|
| SA/V Ratio | 280 | 246 | 198 | 163 | 90 |

The 2 dimensional view of SA/V is valuable as a baseline but does not take into account the fact that spirit is not only in contact with the surface of the barrel but migrates into the wood. This means that the SA/V ratio will be higher than calculations regarding 2 dimensional geometry estimate. Workers have examined migration and found that spirits may return to the barrel from as deep as 6mm within the barrel staves. This would increase the functional SA/V. Additionally heat treatment creates physical changes in the wood structure. The surface of the wood in direct contact with flames for charring has a charcoal layer on it. Similar to activated carbon, charcoal has a very high surface area although this layer would have lower phenolic concentrations, and these factors should be taken into account as well.

It is obvious from the extraction data above that higher SA/V produces faster extraction. Further examination of the total 3 dimensional SA/V would be valuable to quantify this.

## ADDITIONAL COMPOUNDS

Tables 5-7 show other compounds that were identified in the barreled whiskey during the course of analysis. These compounds correspond to those found in previous research and are either widely known to be present in whiskies (acids and esters) or have at least been identified in other research (phenolics). No quantification was conducted on any of the following compounds.

Table 8: Fatty acids identified using NIST library and their retention times, unquantified results

| **Compound** | **Retention Time** |
|---|---|
| Acetic | 12.6 |
| Butanoic | 14.376 |
| Formic | 13.292 |
| Decanoic | 12.814 |
| Dodecanoic | 15.553 |
| Octanoic | 21.321 |

Table 9: Fatty acid ethyl esters (AEE) identified using NIST library and their retention times, unquantified results

| **Compound** | **Retention Time** |
|---|---|
| Decanoic AEE | 12.814 |
| Dodecanoic AEE | 17.018 |
| Tetradecanoic AEE | 21.328 |
| Pentadecanoic AEE | 21.832 |
| Hexadecanoic AEE | 25.397 |
| Octadecanoic AEE | 22.157 |
| Oleic AEE | 29.465 |
| Linoleic AEE | 29.481 |
| Acetic-2-phenylethyl ester | 16.497 |

Table 10: Other compounds identified using NIST library and their retention times, unquantified results

| **Compound** | **Retention Time** |
|---|---|
| Phenol | 21.01 |
| Phenylethyl alcohol | 19.22 |
| Homovanillyl alcohol | 33.507 |
| 2-Furanmethanol | 14.964 |
| 2,6-dimethoxy phenol | 25.68 |
| 4-Ethyl guaiacol | 20.5 |
| 4-Vinyl guaiacol | 24.448 |
| Butylated hydroxytoluene | 17.217 |
| Acetosyringone | 49.851 |
| Syringol | |
| Xylose | 14.244 |
| *Cis*- 3-methyl-4-octanolide | |
| *Trans*-3-methyl-4-octanolide | |

## CONCLUSIONS

The current study has begun the process of characterization of extraction from non-traditional barrel sizes. This represents a starting point for an area of research which should be considered useful to a segment of the American distilled spirits industry that utilizes these barrels to produce spirits rather than or in addition to traditional barrels.

It may be said of the extraction data, that it is confirmed that extraction rate is coupled to SA/V ratio, and that faster and sometimes greater extraction is possible as SA/V increases. Guaiacol concentrations were as much as 100 times higher than those found in some literature, and comparable to others (82-85,89). Eugenol concentrations were 10 times higher than those found in some literature and slightly less than double those found in others (82-85,89). Vanillin concentrations were comparable to some at the 10 gallon size and comparable to others at the 2 gallon size (82-85,89).

This not only points to the great variation in concentration between styles of whiskey, it also emphasizes the great variation between studies and the difficulty with standardization of such compounds for whiskey spirits. While it is clear that smaller barrels lead to faster extraction and in some cases higher concentrations it is difficult to establish target concentrations. A larger body of knowledge is available for the scotch whiskey industry which utilizes barrels which have been used once for the aging of bourbon. Used barrels lead to lower concentration of some oak extractives and therefore are not as useful in the context of the American artisan whiskey industry.

Further study would be useful for the elucidation of the total aging process in alternative barrels. For this, the use of a concentration and extraction method might be necessary to examine concentrations on a longer time scale. Because of the large angel's share from 2 and 3 gallon barrels they must be considered unfeasible for use in industry for anything other than rapid examination of certain oak characters in trial whiskies. As such, barrels of 10, 20, and 30 gallons might be examined for extraction and aging character and in the context of the larger barrels, larger samples appropriate to extraction and concentration would be possible. It would be useful to compare these in the laboratory setting to conditions in traditional barrels, however this becomes problematic as the time required to conduct such studies is measured in years. This may be a primary reason such research has not been completed to date. In past studies samples are taken from bottles of commercial products or from barrels within the commercial setting. This means that the researchers had little control over the ageing process and sampling was not conducted over time within individual barrels.

To further elucidate the total aging process it would be advisable to track production of esters during aging. It was noted that volatile congeners increased and decreased at different points in the aging process. While it may be posited that this was coupled to ester production and evaporation processes it would be useful to track these processes more closely to determine whether this was the case. This would provide a more coherent understanding of processes as they relate to one another.

In addition to the above suggestions, sensory data coupled to extraction rate and concentration would be helpful. It was noted that the 2 and 3 gallon barrels were over extracted and their sensory qualities were poor. Other barrels in the series tasted over extracted at certain points but by the end of the study at day 270, both 5 and 10 gallon barrels had developed some characteristics of mature whiskies and their sensory qualities had begun to improve. While this is a subjective judgment of the author, samples were compared to industry products and found to have some qualities in common that had been lacking at previous time points. This is an important feature as it points to the fact that while extraction is an important process, time is required to incorporate the extracted compounds into the spirit to produce maturity. It is also important to note that while over extraction is possible, even higher than normal concentrations of extractives may be fully integrated into the spirit given enough time.

With further examination it might be possible to establish a spectrophotometric procedure to allow producers to estimate total extraction during the aging period. This might provide a quick standard by which a variety of barrels might be compared for blending purposes. Affordable spectrophotometric units are now available which could be employed in a production setting for tracking of extractives. This might be linked to particular markers of aging such as ethyl esters and oak extractives and used to supplement current techniques which rely largely on sensory analysis.

This work should be considered a preliminary examination of an extremely complex system. Much research has been conducted to determine the

categories of compounds which are significant contributors to ageing, but the ongoing process itself within the barrel is still largely unknown. With a small but high growth industry emerging in the U.S. this kind of information will become valuable to inexperienced producers.

# APPENDICES

APPENDIX 1

PROCESS GC TABLES FOR FIGURES 3 AND 4

Table 11: Volatile congener concentrations during the distillation of bourbon whiskey, from which data for Figures 3 and 4 is drawn

| Time | Acetaldehyde | Acetone | Ethylacetate | Methanol | Propanol | Isobutanol | Isoamyl |
|---|---|---|---|---|---|---|---|
| 0 | 2.058 | 0.121 | 5.634 | 0.291 | 0.126 | 0.275 | 0.339 |
| 1 | 0.846 | 0.034 | 3.426 | 0.156 | 0.104 | 0.338 | 0.494 |
| 2 | 0.416 | 0.021 | 2.502 | 0.108 | 0.109 | 0.4 | 0.636 |
| 4 | 0.292 | 0.014 | 1.933 | 0.118 | 0.104 | 0.413 | 0.741 |
| 6 | 0.158 | 0.008 | 1.314 | 0.102 | 0.114 | 0.47 | 0.906 |
| 8 | 0.088 | 0.004 | 0.725 | 0.075 | 0.13 | 0.542 | 1.178 |
| 10 | 0.059 | 0.002 | 0.534 | 0.07 | 0.124 | 0.589 | 1.517 |
| 15 | 0.029 | 0 | 0.245 | 0.066 | 0.12 | 0.584 | 1.821 |
| 20 | 0.012 | | 0.097 | 0.058 | 0.181 | 0.632 | 1.833 |
| 25 | 0.006 | | 0.054 | 0.056 | 0.119 | 0.547 | 1.969 |
| 30 | 0.005 | | 0.025 | 0.056 | 0.115 | 0.53 | 2.043 |
| 35 | 0 | | 0 | 0.062 | 0.118 | 0.501 | 2.048 |
| 40 | | | | 0.06 | 0.113 | 0.46 | 1.997 |
| 45 | | | | 0.053 | 0.105 | 0.381 | 1.785 |
| 50 | | | | 0.05 | 0.105 | 0.342 | 1.649 |
| 60 | | | | 0.049 | 0.082 | 0.176 | 0.893 |
| 65 | | | | 0.055 | 0.073 | 0.134 | 0.659 |
| 70 | | | | 0.049 | 0.046 | 0.053 | 0.269 |
| 80 | | | | 0.036 | 0.017 | 0.008 | 0.031 |
| 90 | | | | 0.031 | 0.004 | 0.005 | 0.007 |
| 95 | | | | 0.024 | 0.004 | 0.015 | |

APPENDIX 2

TABLES FROM WHICH FUSEL DATA IS DRAWN

Table 12: Volatile congener development over 202 days in barrel 2.1

| 2.1 | | | | | | |
|---|---|---|---|---|---|---|
| **Time** | **Acetaldehyde** | **Acetone** | **Ethylacetate** | **Methanol** | **Propanol** | **Isobutanol** |
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 |
| 20 | 0.032 | 0.002 | 0.057 | 0.044 | 0.06 | 0.288 |
| 42 | 0.088 | 0 | 0.042 | 0.043 | 0.053 | 0.228 |
| 84 | 0.014 | 0.007 | 0.184 | 0.052 | 0.075 | 0.348 |
| 112 | 0.029 | 0 | 0.027 | 0.197 | 0.068 | 0.307 |
| 202 | 0.022 | 0.009 | 0.267 | 0.059 | 0.079 | 0.366 |

Table 13: Volatile congener development over 202 days in barrel 2.2

| | 2.2 | | | | | | |
|---|---|---|---|---|---|---|---|
| **Time** | **Acetaldehyde** | **Acetone** | **Ethyl acetate** | **Methanol** | **Propanol** | **Isobutanol** | **Amyl** |
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 | 0.897 |
| 20 | 0.022 | 0.001 | 0.11 | 0.046 | 0.054 | 0.26 | 0.624 |
| 42 | 0.032 | | 0.022 | 0.049 | 0.049 | 0.179 | 0.567 |
| 84 | 0.014 | 0.006 | 0.185 | 0.049 | 0.078 | 0.351 | 1.109 |
| 112 | 0.016 | | 0.029 | 0.227 | 0.068 | 0.308 | 0.957 |
| 202 | 0.02 | 0.009 | 0.249 | 0.054 | 0.08 | 0.378 | 1.183 |

Table 14: Volatile congener development over 202 days in barrel 3.1

| 3.1 | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Time** | **Acetaldehyde** | **Acetone** | **Ethyl acetate** | **Methanol** | **Propanol** | **Isobutanol** | **Amyl** |
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 | 0.897 |
| 20 | 0.021 | 0 | 0.097 | 0.044 | 0.063 | 0.286 | 0.872 |
| 42 | 0.029 | 0 | 0.024 | 0.044 | 0.062 | 0.272 | 0.844 |
| 84 | 0.01 | 0.007 | 0.173 | 0.052 | 0.078 | 0.353 | 1.115 |
| 112 | 0.015 | 0 | 0.033 | 0.23 | 0.072 | 0.318 | 1.003 |
| 202 | 0.012 | 0.012 | 0.227 | 0.061 | 0.085 | 0.377 | 1.174 |

Table 15: Volatile congener development over 202 days in barrel 3.2

3.2

| Time | Acetaldehyde | Acetone | Ethyl acetate | Methanol | Propanol | Isobutanol | Amyl |
|---|---|---|---|---|---|---|---|
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 | 0.897 |
| 20 | 0.012 | 0 | 0.135 | 0.045 | 0.07 | 0.324 | 0.911 |
| 42 | 0.013 | 0 | 0.15 | 0.048 | 0.072 | 0.335 | 1.052 |
| 84 | 0.013 | 0.007 | 0.184 | 0.05 | 0.075 | 0.349 | 1.102 |
| 112 | 0.016 | 0 | 0.025 | 0.232 | 0.067 | 0.313 | 0.979 |
| 202 | 0.017 | 0.008 | 0.254 | 0.058 | 0.08 | 0.372 | 1.15 |

Table 16: Volatile congener development over 202 days in barrel 5.1

5.1

| Time | Acetaldehyde | Acetone | Ethyl acetate | Methanol | Propanol | Isobutanol | Amyl |
|---|---|---|---|---|---|---|---|
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 | 0.897 |
| 20 | 0.006 | 0.001 | 0.106 | 0.044 | 0.064 | 0.286 | 0.89 |
| 42 | 0.004 | 0 | 0.025 | 0.044 | 0.064 | 0.285 | 0.88 |
| 84 | 0.008 | 0.006 | 0.163 | 0.047 | 0.063 | 0.151 | 0.612 |
| 112 | 0.006 | 0 | 0.197 | 0.16 | 0.065 | 0.287 | 1.106 |
| 202 | 0.015 | 0.005 | 0.256 | 0.055 | 0.167 | 0.362 | 1.126 |

Table 17: Volatile congener development over 202 days in barrel 5.2

5.2

| Time | Acetaldehyde | Acetone | Ethyl acetate | Methanol | Propanol | Isobutanol | Amyl |
|---|---|---|---|---|---|---|---|
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 | 0.897 |
| 20 | 0.006 | 0 | 0.039 | 0.045 | 0.06 | 0.255 | 0.891 |
| 42 | 0.003 | 0 | 0.023 | 0.047 | 0.053 | 0.209 | 0.89 |
| 84 | 0.011 | 0.004 | 0.179 | 0.048 | 0.076 | 0.344 | 1.086 |
| 112 | 0.008 | 0 | 0.042 | 0.047 | 0.069 | 0.304 | 0.939 |
| 202 | 0.016 | 0.007 | 0.244 | 0.057 | 0.076 | 0.357 | 1.107 |

Table 18: Volatile congener development over 202 days in barrel 10.1

10.1

| Time | Acetaldehyde | Acetone | Ethyl acetate | Methanol | Propanol | Isobutanol | Amyl |
|---|---|---|---|---|---|---|---|
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 | 0.897 |
| 20 | 0.01 | 0 | 0.122 | 0.045 | 0.07 | 0.327 | 0.912 |
| 42 | 0.01 | 0 | 0.138 | 0.05 | 0.073 | 0.333 | 1.011 |
| 84 | 0.01 | 0 | 0.145 | 0.062 | 0.074 | 0.347 | 1.089 |
| 112 | 0.006 | 0 | 0.048 | 0.211 | 0.069 | 0.294 | 0.919 |
| 202 | 0.011 | 0.007 | 0.205 | 0.066 | 0.085 | 0.354 | 1.107 |

Table19: Volatile congener development over 202 days in barrel 10.2

10.2

| Time | Acetaldehyde | Acetone | Ethyl acetate | Methanol | Propanol | Isobutanol | Amyl |
|---|---|---|---|---|---|---|---|
| 0 | 0.015 | 0.002 | 0.116 | 0.044 | 0.065 | 0.288 | 0.897 |
| 20 | 0.009 | 0.002 | 0.099 | 0.051 | 0.066 | 0.298 | 0.9 |
| 42 | 0.007 | 0.003 | 0.011 | 0.059 | 0.067 | 0.301 | 0.94 |
| 84 | 0.013 | 0.003 | 0.158 | 0.046 | 0.074 | 0.342 | 1.077 |
| 112 | 0.007 | | 0.028 | 0.117 | 0.07 | 0.274 | 0.854 |
| 202 | 0.013 | 0.003 | 0.16 | 0.194 | 0.077 | 0.355 | 1.113 |

APPENDIX 3

TABLES FROM WHICH ABSORBANCE AND BARREL EXTRACTION DATA IS DRAWN

Table 20: Absorbance data from all barrels at wavelength A520 over 202 days

| 2.1 | 2.2 | 3.1 | 3.2 | 5.1 | 5.2 | 10.1 | 10.2 |
|---|---|---|---|---|---|---|---|
| 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 | 0.004 |
| 0.126 | 0.138 | 0.15 | 0.105 | 0.116 | 0.11 | 0.106 | 0.085 |
| 0.148 | 0.163 | 0.192 | 0.137 | 0.16 | 0.139 | 0.149 | 0.119 |
| 0.189 | 0.2 | 0.226 | 0.267 | 0.159 | 0.141 | 0.201 | 0.184 |
| 0.222 | 0.236 | 0.239 | 0.181 | 0.179 | 0.162 | 0.169 | 0.141 |
| 0.298 | 0.355 | 0.262 | 0.221 | 0.194 | 0.184 | 0.188 | 0.155 |
| 0.31 | 0.278 | 0.282 | 0.233 | 0.197 | 0.187 | 0.197 | 0.161 |
| 0.344 | 0.321 | 0.318 | 0.251 | 0.22 | 0.195 | 0.208 | 0.169 |
| 0.357 | 0.356 | 0.336 | 0.262 | 0.243 | 0.224 | 0.239 | 0.19 |
| 0.39 | 0.384 | 0.364 | 0.3 | 0.279 | 0.243 | 0.26 | 0.219 |
| 0.414 | 0.403 | 0.388 | 0.314 | 0.296 | 0.271 | 0.283 | 0.243 |
| 0.435 | 0.424 | 0.399 | 0.325 | 0.308 | 0.284 | 0.284 | 0.257 |
| 0.501 | 0.45 | 0.43 | 0.417 | 0.354 | 0.31 | 0.292 | 0.273 |
| 0.706 | 0.798 | 0.551 | 0.53 | 0.492 | 0.506 | 0.301 | 0.321 |
| 0.845 | 0.822 | 0.667 | 0.675 | 0.635 | 0.642 | 0.32 | 0.332 |

APPENDIX 4: EXTRACTION DATA FROM BARRELS OVER 202 DAYS

Table 21: Guaiacol extraction data from all barrels over 202 days

| Size [gal] | Time[Days] | Guaiacol | Guaiacol 2 | Avg |
|---|---|---|---|---|
| 2 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 2 | 0.0003 | 0.0002 | 0.0002 |
| 2 | 7 | 0.0004 | 0.0003 | 0.0003 |
| 2 | 14 | 0.0005 | 0.0005 | 0.0005 |
| 2 | 28 | 0.0007 | 0.0007 | 0.0007 |
| 2 | 42 | 0.0007 | 0.0007 | 0.0007 |
| 2 | 56 | 0.0023 | 0.0025 | 0.0024 |
| 2 | 70 | 0.0027 | 0.0025 | 0.0026 |
| 2 | 98 | 0.0031 | 0.0035 | 0.0033 |
| 2 | 202 | 0.0044 | 0.0052 | 0.0048 |
| 3 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 3 | 2 | 0.0002 | 0.0002 | 0.0002 |
| 3 | 7 | 0.0003 | 0.0003 | 0.0003 |
| 3 | 14 | 0.0003 | 0.0004 | 0.0003 |
| 3 | 28 | 0.0004 | 0.0007 | 0.0005 |
| 3 | 42 | 0.0004 | 0.0007 | 0.0006 |
| 3 | 56 | 0.0020 | 0.0020 | 0.0020 |
| 3 | 70 | 0.0021 | 0.0023 | 0.0022 |
| 3 | 98 | 0.0024 | 0.0025 | 0.0025 |
| 3 | 202 | 0.0034 | 0.0028 | 0.0031 |
| 5 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 2 | 0.0002 | 0.0004 | 0.0003 |
| 5 | 7 | 0.0003 | 0.0005 | 0.0004 |
| 5 | 14 | 0.0004 | 0.0005 | 0.0005 |
| 5 | 28 | 0.0005 | 0.0005 | 0.0005 |
| 5 | 42 | 0.0006 | 0.0005 | 0.0006 |
| 5 | 56 | 0.0006 | 0.0005 | 0.0006 |
| 5 | 70 | 0.0007 | 0.0006 | 0.0006 |
| 5 | 98 | 0.0009 | 0.0009 | 0.0009 |
| 5 | 202 | 0.0027 | 0.0021 | 0.0024 |
| 10 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 10 | 2 | 0.0002 | 0.0002 | 0.0002 |
| 10 | 7 | 0.0004 | 0.0003 | 0.0004 |
| 10 | 14 | 0.0004 | 0.0004 | 0.0004 |
| 10 | 28 | 0.0006 | 0.0007 | 0.0007 |
| 10 | 42 | 0.0007 | 0.0007 | 0.0007 |
| 10 | 56 | 0.0010 | 0.0009 | 0.0009 |
| 10 | 70 | 0.0011 | 0.0010 | 0.0010 |
| 10 | 98 | 0.0013 | 0.0015 | 0.0014 |
| 10 | 202 | 0.0021 | 0.0019 | 0.0020 |

Table 22: 2-methoxy-4-methylphenol extraction data from all barrels over 202 days

| Size [gal] | Time[Days] | 2M4Mph | 2M4Mph 2 | Avg |
|---|---|---|---|---|
| 2 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 2 | 0.0001 | 0.0002 | 0.0002 |
| 2 | 7 | 0.0001 | 0.0003 | 0.0002 |
| 2 | 14 | 0.0002 | 0.0007 | 0.0004 |
| 2 | 28 | 0.0007 | 0.0007 | 0.0007 |
| 2 | 42 | 0.0009 | 0.0010 | 0.0009 |
| 2 | 56 | 0.0034 | 0.0037 | 0.0035 |
| 2 | 70 | 0.0046 | 0.0057 | 0.0051 |
| 2 | 98 | 0.0049 | 0.0062 | 0.0056 |
| 2 | 202 | 0.0059 | 0.0071 | 0.0065 |
| 3 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 3 | 2 | 0.0000 | 0.0000 | 0.0000 |
| 3 | 7 | 0.0004 | 0.0003 | 0.0004 |
| 3 | 14 | 0.0003 | 0.0003 | 0.0003 |
| 3 | 28 | 0.0002 | 0.0003 | 0.0003 |
| 3 | 42 | 0.0004 | 0.0004 | 0.0004 |
| 3 | 56 | 0.0018 | 0.0017 | 0.0017 |
| 3 | 70 | 0.0020 | 0.0014 | 0.0017 |
| 3 | 98 | 0.0022 | 0.0019 | 0.0020 |
| 3 | 202 | 0.0031 | 0.0022 | 0.0027 |
| 5 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 2 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 7 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 14 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 28 | 0.0003 | 0.0002 | 0.0002 |
| 5 | 42 | 0.0004 | 0.0002 | 0.0003 |
| 5 | 56 | 0.0005 | 0.0003 | 0.0004 |
| 5 | 70 | 0.0004 | 0.0004 | 0.0004 |
| 5 | 98 | 0.0010 | 0.0005 | 0.0008 |
| 5 | 202 | 0.0017 | 0.0013 | 0.0015 |
| 10 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 10 | 2 | 0.0003 | 0.0002 | 0.0002 |
| 10 | 7 | 0.0003 | 0.0002 | 0.0003 |
| 10 | 14 | 0.0002 | 0.0002 | 0.0002 |
| 10 | 28 | 0.0003 | 0.0004 | 0.0003 |
| 10 | 42 | 0.0002 | 0.0003 | 0.0003 |
| 10 | 56 | 0.0004 | 0.0004 | 0.0004 |
| 10 | 70 | 0.0007 | 0.0007 | 0.0007 |
| 10 | 98 | 0.0015 | 0.0013 | 0.0014 |
| 10 | 202 | 0.0016 | 0.0015 | 0.0016 |

Table 23: Eugenol extraction data from all barrels over 202 days

| Size [gal] | Time[Days] | Eugenol | Eugenol 2 | Avg |
|---|---|---|---|---|
| 2 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 2 | 0.0003 | 0.0003 | 0.0003 |
| 2 | 7 | 0.0004 | 0.0004 | 0.0004 |
| 2 | 14 | 0.0004 | 0.0004 | 0.0004 |
| 2 | 28 | 0.0005 | 0.0006 | 0.0005 |
| 2 | 42 | 0.0005 | 0.0005 | 0.0005 |
| 2 | 56 | 0.0010 | 0.0012 | 0.0011 |
| 2 | 70 | 0.0011 | 0.0013 | 0.0012 |
| 2 | 98 | 0.0016 | 0.0015 | 0.0015 |
| 2 | 202 | 0.0021 | 0.0018 | 0.0020 |
| 3 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 3 | 2 | 0.0003 | 0.0003 | 0.0003 |
| 3 | 7 | 0.0005 | 0.0004 | 0.0004 |
| 3 | 14 | 0.0003 | 0.0005 | 0.0004 |
| 3 | 28 | 0.0004 | 0.0004 | 0.0004 |
| 3 | 42 | 0.0005 | 0.0005 | 0.0005 |
| 3 | 56 | 0.0011 | 0.0010 | 0.0011 |
| 3 | 70 | 0.0012 | 0.0011 | 0.0012 |
| 3 | 98 | 0.0013 | 0.0011 | 0.0012 |
| 3 | 202 | 0.0015 | 0.0013 | 0.0014 |
| 5 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 2 | 0.0003 | 0.0003 | 0.0003 |
| 5 | 7 | 0.0003 | 0.0005 | 0.0004 |
| 5 | 14 | 0.0004 | 0.0005 | 0.0004 |
| 5 | 28 | 0.0004 | 0.0005 | 0.0005 |
| 5 | 42 | 0.0005 | 0.0007 | 0.0006 |
| 5 | 56 | 0.0006 | 0.0007 | 0.0007 |
| 5 | 70 | 0.0008 | 0.0010 | 0.0009 |
| 5 | 98 | 0.0009 | 0.0010 | 0.0010 |
| 5 | 202 | 0.0013 | 0.0013 | 0.0013 |
| 10 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 10 | 2 | 0.0003 | 0.0003 | 0.0003 |
| 10 | 7 | 0.0004 | 0.0003 | 0.0003 |
| 10 | 14 | 0.0004 | 0.0004 | 0.0004 |
| 10 | 28 | 0.0004 | 0.0004 | 0.0004 |
| 10 | 42 | 0.0004 | 0.0005 | 0.0005 |
| 10 | 56 | 0.0005 | 0.0005 | 0.0005 |
| 10 | 70 | 0.0006 | 0.0005 | 0.0006 |
| 10 | 98 | 0.0008 | 0.0008 | 0.0008 |
| 10 | 202 | 0.0011 | 0.0010 | 0.0010 |

Table 24: Vanillin extraction data from all barrels over 202 days

| Size [gal] | Time[Days] | Vanillin | Vanillin 2 | Avg |
|---|---|---|---|---|
| 2 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 2 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 7 | 0.0002 | 0.0008 | 0.0005 |
| 2 | 14 | 0.0004 | 0.0009 | 0.0006 |
| 2 | 28 | 0.0007 | 0.0009 | 0.0008 |
| 2 | 42 | 0.0014 | 0.0014 | 0.0014 |
| 2 | 56 | 0.0033 | 0.0044 | 0.0038 |
| 2 | 70 | 0.0062 | 0.0077 | 0.0070 |
| 2 | 98 | 0.0077 | 0.0085 | 0.0081 |
| 2 | 202 | 0.0091 | 0.0097 | 0.0094 |
| 3 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 3 | 2 | 0.0000 | 0.0013 | 0.0006 |
| 3 | 7 | 0.0010 | 0.0011 | 0.0011 |
| 3 | 14 | 0.0011 | 0.0006 | 0.0008 |
| 3 | 28 | 0.0009 | 0.0008 | 0.0008 |
| 3 | 42 | 0.0014 | 0.0013 | 0.0013 |
| 3 | 56 | 0.0045 | 0.0045 | 0.0045 |
| 3 | 70 | 0.0053 | 0.0052 | 0.0053 |
| 3 | 98 | 0.0058 | 0.0058 | 0.0058 |
| 3 | 202 | 0.0087 | 0.0078 | 0.0083 |
| 5 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 2 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 7 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 14 | 0.0002 | 0.0004 | 0.0003 |
| 5 | 28 | 0.0006 | 0.0008 | 0.0007 |
| 5 | 42 | 0.0007 | 0.0009 | 0.0008 |
| 5 | 56 | 0.0017 | 0.0031 | 0.0024 |
| 5 | 70 | 0.0019 | 0.0025 | 0.0022 |
| 5 | 98 | 0.0023 | 0.0037 | 0.0030 |
| 5 | 202 | 0.0047 | 0.0050 | 0.0049 |
| 10 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 10 | 2 | 0.0000 | 0.0000 | 0.0000 |
| 10 | 7 | 0.0004 | 0.0003 | 0.0004 |
| 10 | 14 | 0.0005 | 0.0005 | 0.0005 |
| 10 | 28 | 0.0008 | 0.0007 | 0.0007 |
| 10 | 42 | 0.0009 | 0.0009 | 0.0009 |
| 10 | 56 | 0.0007 | 0.0009 | 0.0008 |
| 10 | 70 | 0.0013 | 0.0011 | 0.0012 |
| 10 | 98 | 0.0018 | 0.0015 | 0.0016 |
| 10 | 202 | 0.0030 | 0.0033 | 0.0031 |

Table 25: Syringaldehyde extraction data from all barrels over 202 days

| Size [gal] | Time[Days] | Syringealdehyde | Syringealdehyde 2 | Avg |
|---|---|---|---|---|
| 2 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 2 | 2 | 0.0051 | 0.0050 | 0.0051 |
| 2 | 7 | 0.0059 | 0.0069 | 0.0064 |
| 2 | 14 | 0.0070 | 0.0082 | 0.0076 |
| 2 | 28 | 0.0088 | 0.0100 | 0.0094 |
| 2 | 42 | 0.0103 | 0.0107 | 0.0105 |
| 2 | 56 | 0.0218 | 0.0300 | 0.0259 |
| 2 | 70 | 0.0225 | 0.0304 | 0.0265 |
| 2 | 98 | 0.0333 | 0.0399 | 0.0366 |
| 2 | 202 | 0.0677 | 0.0578 | 0.0628 |
| 3 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 3 | 2 | 0.0052 | 0.0049 | 0.0051 |
| 3 | 7 | 0.0072 | 0.0075 | 0.0073 |
| 3 | 14 | 0.0077 | 0.0086 | 0.0082 |
| 3 | 28 | 0.0094 | 0.0057 | 0.0076 |
| 3 | 42 | 0.0118 | 0.0103 | 0.0111 |
| 3 | 56 | 0.0196 | 0.0189 | 0.0193 |
| 3 | 70 | 0.0226 | 0.0220 | 0.0223 |
| 3 | 98 | 0.0271 | 0.0270 | 0.0270 |
| 3 | 202 | 0.0521 | 0.0589 | 0.0555 |
| 5 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 5 | 2 | 0.0047 | 0.0044 | 0.0046 |
| 5 | 7 | 0.0047 | 0.0070 | 0.0059 |
| 5 | 14 | 0.0052 | 0.0072 | 0.0062 |
| 5 | 28 | 0.0063 | 0.0081 | 0.0072 |
| 5 | 42 | 0.0100 | 0.0099 | 0.0099 |
| 5 | 56 | 0.0101 | 0.0157 | 0.0129 |
| 5 | 70 | 0.0142 | 0.0182 | 0.0162 |
| 5 | 98 | 0.0145 | 0.0210 | 0.0177 |
| 5 | 202 | 0.0427 | 0.0358 | 0.0392 |
| 10 gal | 0 | 0.0000 | 0.0000 | 0.0000 |
| 10 | 2 | 0.0050 | 0.0040 | 0.0045 |
| 10 | 7 | 0.0052 | 0.0050 | 0.0051 |
| 10 | 14 | 0.0066 | 0.0062 | 0.0064 |
| 10 | 28 | 0.0055 | 0.0054 | 0.0055 |
| 10 | 42 | 0.0069 | 0.0059 | 0.0064 |
| 10 | 56 | 0.0087 | 0.0085 | 0.0086 |
| 10 | 70 | 0.0103 | 0.0130 | 0.0116 |
| 10 | 98 | 0.0164 | 0.0184 | 0.0174 |
| 10 | 202 | 0.0333 | 0.0260 | 0.0296 |

APPENDIX 5

VOLATILE CONGENER AND OAK EXTRACTION DATA FROM SPIRAL TRIALS

Table 26: Volatile congener tracking with light toasted spiral in grain whiskey over 600 hours

| Light toast | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time | Acetaldehyde | Acetone | Ethylacetate | Methanol | Propanol | Isobutanol | Isoamyl |
| 0 | | | 0.024 | 0.045 | 0.243 | 0.735 | 1.364 |
| 48 | | | 0.019 | 0.05 | 0.228 | 0.725 | 1.339 |
| 96 | | | 0.018 | 0.064 | 0.234 | 0.745 | 1.369 |
| 168 | | | 0.018 | 0.056 | 0.234 | 0.71 | 1.32 |
| 288 | | | 0.02 | 0.061 | 0.232 | 0.744 | 1.453 |
| 600 | | | 0.023 | 0.054 | 0.239 | 0.737 | 1.355 |
| | | | | | | | |

Table 27: Volatile congener tracking with medium toasted spiral in grain whiskey over 600 hours

| Med toast | | | | | | | |
|---|---|---|---|---|---|---|---|
| Time | Acetaldehyde | Acetone | Ethylacetate | Methanol | Propanol | Isobutanol | Isoamyl |
| 0 | | | 0.024 | 0.045 | 0.243 | 0.735 | 1.364 |
| 48 | | | 0.02 | 0.053 | 0.229 | 0.727 | 1.343 |
| 96 | | | 0.028 | 0.052 | 0.248 | 0.714 | 1.334 |
| 168 | | | 0.024 | 0.051 | 0.235 | 0.702 | 1.297 |
| 288 | | | 0.025 | 0.055 | 0.24 | 0.748 | 1.379 |
| 600 | | | 0.02 | 0.06 | 0.231 | 0.745 | 1.476 |

Table 28: Volatile congener tracking with dark toasted spiral in grain whiskey over 600 hours

| Dark toast | | | | | | |
|---|---|---|---|---|---|---|
| Time | Acetaldehyde | Acetone | Ethylacetate | Methanol | Propanol | Isobutanol |
| 0 | | | | | | |
| 48 | | | 0.016 | 0.045 | 0.225 | 0.627 |
| 72 | | | 0.017 | 0.038 | 0.192 | 0.633 |
| 840 | | | 0.016 | 0.047 | 0.181 | 0.575 |
| 1008 | | | 0.01 | 0.045 | 0.174 | 0.555 |
| 1584 | | | 0.025 | 0.049 | 0.191 | 0.579 |
| | | | | | | |

Table 29: Volatile congener tracking with charred spiral in grain whiskey over 600 hours

| Char | | | | | | |
|---|---|---|---|---|---|---|
| Time | Acetaldehyde | Acetone | Ethylacetate | Methanol | Propanol | Isobutanol |
| 0 | | | 0.024 | 0.045 | 0.243 | 0.735 |
| 48 | | | 0.02 | 0.052 | 0.236 | 0.726 |
| 96 | | | 0.02 | 0.06 | 0.228 | 0.725 |
| 168 | | | 0.02 | 0.06 | 0.25 | 0.742 |
| 288 | | | 0.024 | 0.057 | 0.236 | 0.738 |
| 600 | | | 0.021 | 0.058 | 0.231 | 0.735 |
| | | | | | | |

Table 30: Oak extraction tracking for light toasted spiral in grain whiskey over 600 hours, from which Figure 20-24 is drawn

| Light | | | | | | |
|---|---|---|---|---|---|---|
| Time [wks] | Guaiacol | 2M4MPh | Eugenol | Vanillin | Acetovan | Syr-ald |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 48 | 0.0002 | 0.0002 | 0.0000 | 0.0007 | 0.0000 | 0.0060 |
| 168 | 0.0009 | 0.0002 | 0.0004 | 0.0010 | 0.0000 | 0.0071 |
| 600 | 0.0009 | 0.0002 | 0.0005 | 0.0010 | 0.0000 | 0.0078 |
| | | | | | | |

Table 31: Oak extraction tracking for medium toasted spiral in grain whiskey over 600 hours, from which Figures 20-24 is drawn

| Medium | | | | | | |
|---|---|---|---|---|---|---|
| Time [wks] | Guaiacol | 2M4MPh | Eugenol | Vanillin | Acetovan | Syr-ald |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 48 | 0.0012 | 0.0003 | 0.0000 | 0.0007 | 0.0006 | 0.0052 |
| 168 | 0.0008 | 0.0004 | 0.0003 | 0.0009 | 0.0004 | 0.0060 |
| 600 | 0.0006 | 0.0005 | 0.0003 | 0.0027 | 0.0004 | 0.0080 |

Table 32: Oak extraction tracking for dark toasted spiral in grain whiskey over 600 hours, from which Figures 20-24 is drawn

| Dark | | | | | | |
|---|---|---|---|---|---|---|
| Time [wks] | Guaiacol | 2M4MPh | Eugenol | Vanillin | Acetovan | Syr-ald |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 48 | 0.0009 | 0.0003 | 0.0000 | 0.0033 | 0.0005 | 0.0000 |
| 168 | 0.0010 | 0.0006 | 0.0004 | 0.0045 | 0.0005 | 0.0149 |
| 600 | 0.0012 | 0.0007 | 0.0006 | 0.0048 | 0.0005 | 0.0189 |

Table 33: Oak extraction tracking for charred spiral in grain whiskey over 600 hours, from which Figures 20-24 is drawn

| Char | | | | | | |
|---|---|---|---|---|---|---|
| Time [wks] | Guaiacol | 2M4MPh | Eugenol | Vanillin | Acetovan | Syr-ald |
| 0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 48 | 0.0006 | 0.0009 | 0.0000 | 0.0010 | 0.0003 | 0.0055 |
| 168 | 0.0007 | 0.0010 | 0.0000 | 0.0012 | 0.0004 | 0.0056 |
| 600 | 0.0008 | 0.0009 | 0.0000 | 0.0012 | 0.0003 | 0.0060 |

Table 34: Final extraction concentrations for spirals and barrels from which Figures 25-27 data is drawn

| Product | Guaiacol | 2M4MPh | Eugenol | Vanillin | Syr-aldehyde |
|---|---|---|---|---|---|
| 2gallon, 200Day | 0.0048 | 0.0065 | 0.0020 | 0.0094 | 0.0628 |
| 3gallon, 200Day | 0.0031 | 0.0027 | 0.0013 | 0.0083 | 0.0555 |
| 5gallon, 200Day | 0.0024 | 0.0015 | 0.0013 | 0.0049 | 0.0392 |
| 10gallon, 200Day | 0.0020 | 0.0016 | 0.0010 | 0.0031 | 0.0296 |
| Light spiral, 25Day | 0.0009 | 0.0009 | 0.0005 | 0.0047 | 0.0149 |
| Med spiral, 25Day | 0.0006 | 0.0005 | 0.0003 | 0.0027 | 0.0080 |
| Dark spiral, 25Day | 0.0012 | 0.0007 | 0.0006 | 0.0048 | 0.0189 |
| Char spiral, 25Day | 0.0008 | 0.0009 | 0.0000 | 0.0012 | 0.0060 |

Table 35: Extraction calculations from which Figure 27 data is drawn

| Column1 | Guaiacol | 2M4MPh | Eugenol | Vanillin | Syr-aldehyde |
|---|---|---|---|---|---|
| 2gallon | 0.0048 | 0.0065 | 0.002 | 0.0094 | 0.0628 |
| 10gallon, 200 Day | 0.0020 | 0.0016 | 0.0010 | 0.0031 | 0.0296 |
| Combined spirals | 0.0036 | 0.0030 | 0.0014 | 0.0133 | 0.0478 |
| Spiral sectioned | 0.0009 | 0.0008 | 0.0004 | 0.0033 | 0.0120 |
| Recommended Dark | 0.000027 | 0.000022 | 0.000013 | 0.000117 | 0.000349 |

## APPENDIX 6

BARREL VOLUME AND ANGEL'S SHARE DATA

Table 36: Pre and post fill data for barrel 2.1 at day 270

| 2.1 | | |
|---|---|---|
| | Prefill | Post |
| Vol [mL] | 6694.28 | 4600.00 |
| Vol [L] | 6.69 | 4.60 |
| Vol [gal] | 1.76 | 1.21 |
| Angel share [L] | | 2.09 |
| Angel share [%] | | 31.28% |
| %ABV | 62.13 | 60.94 |
| %ABV drop | | 1.19 |
| EtOH loss [L] | | 1.36 |
| H2O loss [L] | | 0.74 |

Table 37: Pre and post fill data for barrel 2.2 at day 270

| 2.2 | | |
|---|---|---|
| | Prefill | Post |
| Vol [mL] | 6805.85 | 4948.00 |
| Vol [L] | 6.81 | 4.95 |
| Vol [gal] | 1.79 | 1.30 |
| Angel share [L] | | 1.86 |
| Angel share [%] | | 27.30% |
| %ABV | 62.13 | 60.95 |
| %ABV drop | | 1.18 |
| EtOH loss [L] | | 1.21 |
| H2O loss [L] | | 0.65 |

Table 38: Pre and post fill data for barrel 3.1 at day 270

| 3.1 | | |
|---|---|---|
| | **Prefill** | **Post** |
| Vol [mL] | 10152.99 | 7720.00 |
| Vol [L] | 10.15 | 7.72 |
| Vol [gal] | 2.67 | 2.03 |
| Angel share [L] | | 2.43 |
| Angel share [%] | | 23.96% |
| %ABV | 62.13 | 61.83 |
| %ABV drop | | 0.3 |
| EtOH loss [L] | | 1.53 |
| H2O loss [L] | | 0.90 |

Table 39: Pre and post fill data for barrel 3.2 at day 270

| 3.2 | | |
|---|---|---|
| | **Prefill** | **Post** |
| Vol [mL] | 9706.70 | 7517.00 |
| Vol [L] | 9.71 | 7.52 |
| Vol [gal] | 2.55 | 1.98 |
| Angel share [L] | | 2.19 |
| Angel share [%] | | 22.56% |
| %ABV | 62.13 | 61.52 |
| %ABV drop | | 0.61 |
| EtOH loss [L] | | 1.41 |
| H2O loss [L] | | 0.78 |

Table 40: Pre and post fill data for barrel 5.1 at day 270

| 5.1 | | |
|---|---|---|
| | **Prefill** | **Post** |
| Vol [mL] | 19078.69 | 16600.00 |
| Vol [L] | 19.08 | 16.60 |
| Vol [gal] | 5.02 | 4.37 |
| Angel share [L] | | 2.48 |
| Angel share [%] | | 12.99% |
| %ABV | 62.13 | 59.48 |
| %ABV drop | | 2.65 |
| EtOH loss [L] | | 1.98 |
| H2O loss [L] | | 0.50 |

Table 41: Pre and post fill data for barrel 5.2 at day 270

| 5.2 | | |
|---|---|---|
| | **Prefill** | **Post** |
| Vol [mL] | 18967.12 | 16768.00 |
| Vol [L] | 18.97 | 16.77 |
| Vol [gal] | 4.99 | 4.41 |
| Angel share [L] | | 2.20 |
| Angel share [%] | | 11.59% |
| %ABV | 62.13 | 59.62 |
| %ABV drop | | 2.51 |
| EtOH loss [L] | | 1.79 |
| H2O loss [L] | | 0.41 |

Table 42: Pre and post fill data for barrel 10.1 at day 270

| 10.1 | | |
|---|---|---|
| | **Prefill** | **Post** |
| Vol [mL] | 33582.95 | 30550.00 |
| Vol [L] | 33.58 | 30.55 |
| Vol [gal] | 8.84 | 8.04 |
| Angel share [L] | | 3.03 |
| Angel share [%] | | 9.03% |
| %ABV | 62.13 | 59.43 |
| %ABV drop | | 2.7 |
| EtOH loss [L] | | 2.71 |
| H2O loss [L] | | 0.32 |

Table 43: Pre and post fill data for barrel 10.2 at day 270

| 10.2 | | |
|---|---|---|
| | **Prefill** | **Post** |
| Vol [mL] | 35144.95 | 31398.00 |
| Vol [L] | 35.14 | 31.40 |
| Vol [gal] | 9.25 | 8.26 |
| Angel share [L] | | 3.75 |
| Angel share [%] | | 10.66% |
| %ABV | 62.13 | 60.24 |
| %ABV drop | | 1.89 |
| EtOH loss [L] | | 2.92 |
| H2O loss [L] | | 0.83 |

Table 44: Angel's share as percent volume, ethanol, and water loss and percent of angel's share lost as water and ethanol

| | 2gallon | 3 gallon | 5 gallon | 10 gallon |
|---|---|---|---|---|
| AVG Angel share[%] | 29.29% | 23.26% | 12.29% | 9.85% |
| % EtOH loss | 19.03% | 14.81% | 9.90% | 8.19% |
| % H2O loss | 10.26% | 8.45% | 2.39% | 1.65% |
| EtOH % of angel share | 64.96% | 63.67% | 80.54% | 83.21% |
| H2O % of angel share | 35.04% | 36.33% | 19.46% | 16.79% |

Table 45: Other angel's share related calculations utilized in the calculation of above data

| | 2 gallon | 3 gallon | 5 gallon | 10 gallon |
|---|---|---|---|---|
| Volume loss EtOH[L] | 1.28 | 1.47 | 1.88 | 2.82 |
| Volume loss H2O[L] | 0.69 | 0.84 | 0.46 | 0.57 |
| Avg barrel capacity[L] | 6.75 | 9.93 | 19.02 | 34.36 |
| Avg angel share [L] | 1.98 | 2.31 | 2.34 | 3.39 |
| Loss/capacity | 2.93 | 2.33 | 1.23 | 0.99 |
| Loss/capacity EtOH | 1.90 | 1.48 | 0.99 | 0.82 |
| Loss/capacity H2O | 1.02 | 0.85 | 0.24 | 0.17 |

APPENDIX 7

STANDARD CURVES FOR OAK EXTRACTS

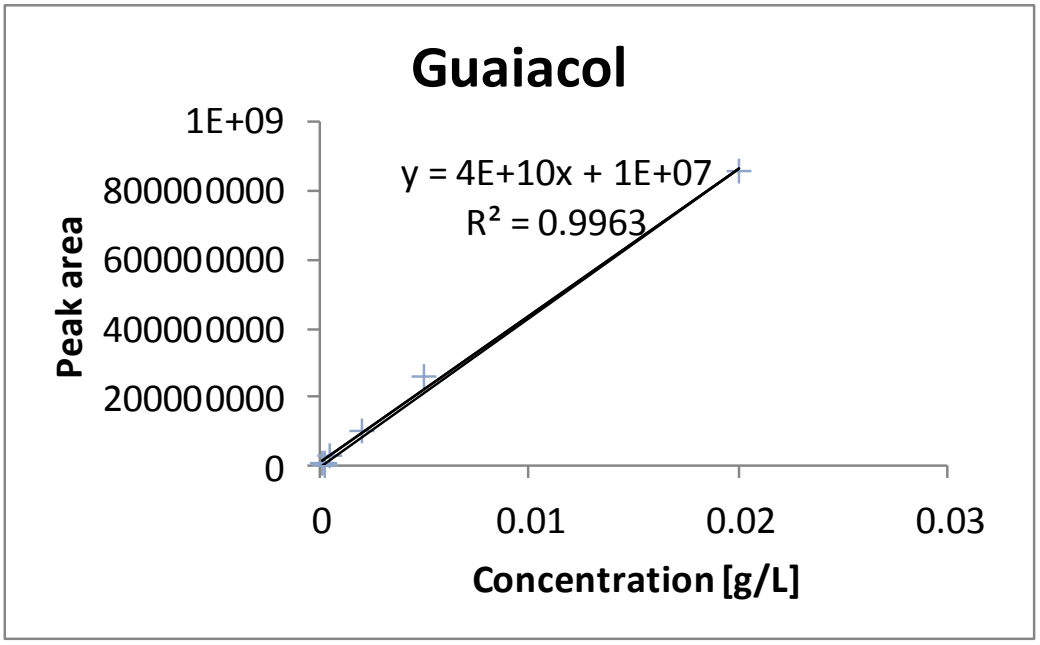


Figure 32: GCMS standard curve for guaiacol concentration

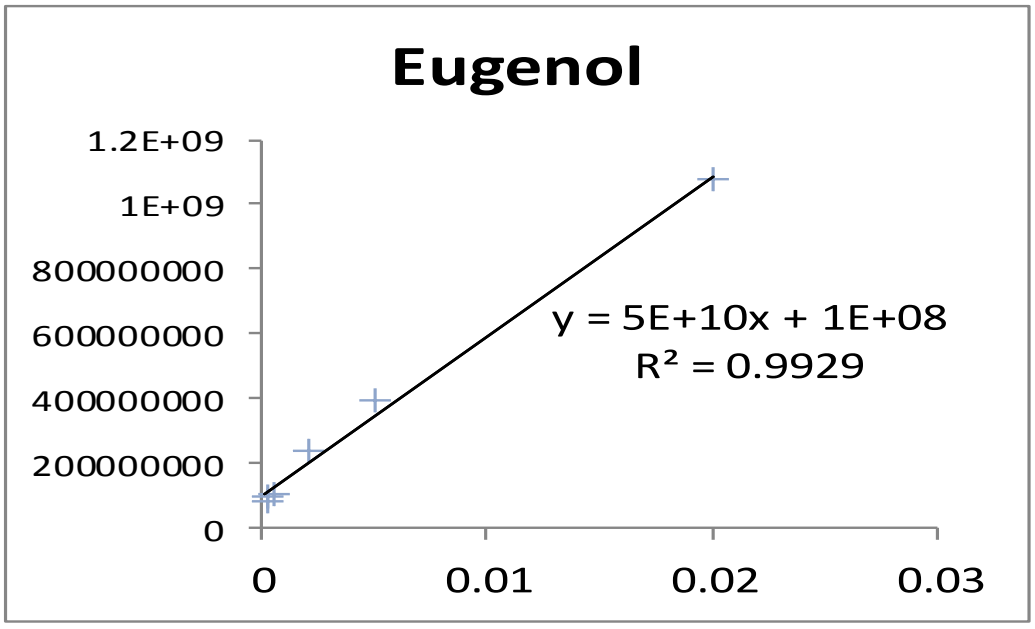


Figure 33: GCMS standard curve for eugenol concentration

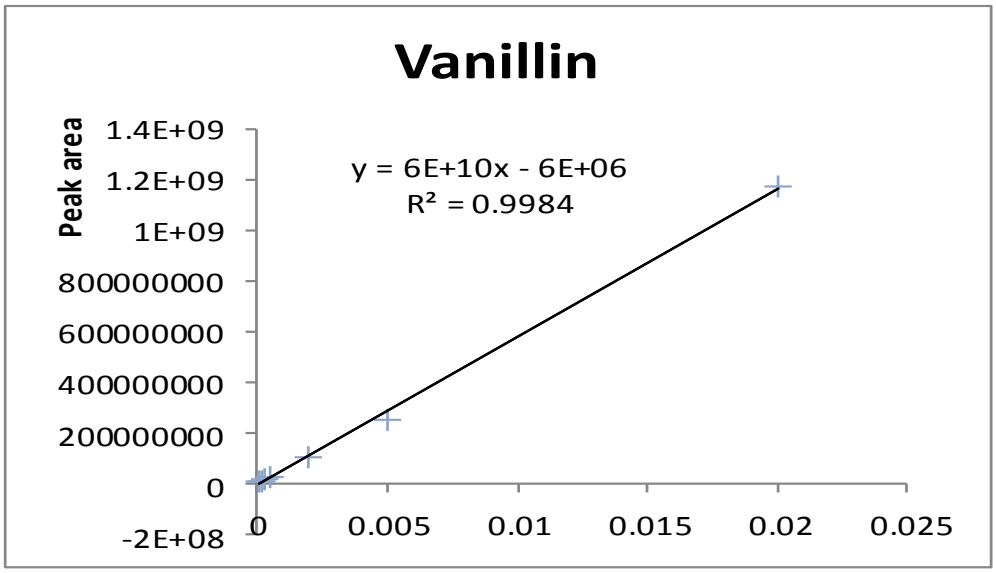


Figure 34: GCMS standard curve for vanillin concentration

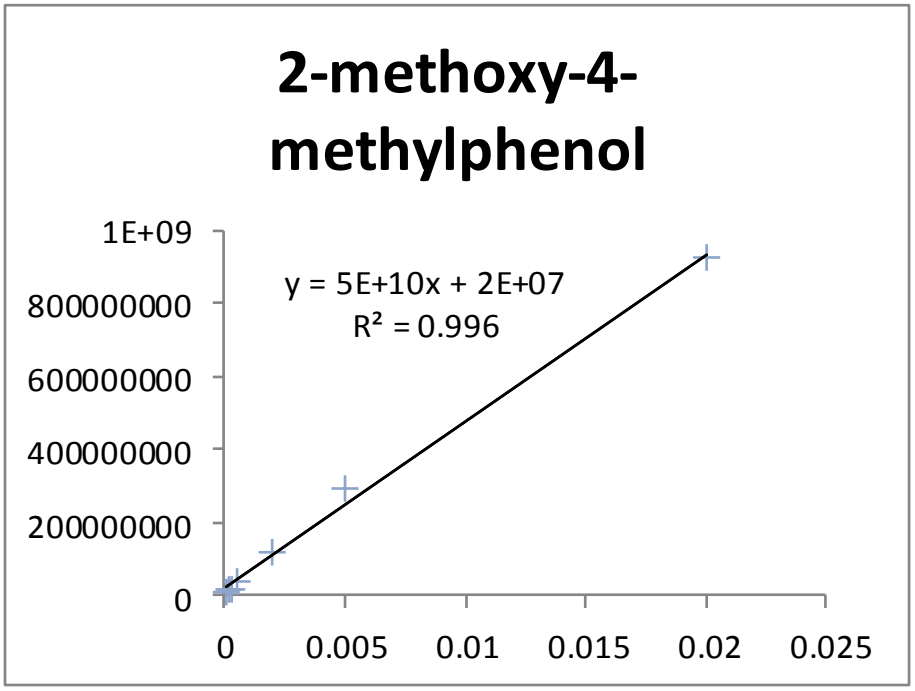


Figure 35: GCMS standard curve for 2-methoxy-4-methylphenol

APPENDIX 8

VOLATILE CONGENER CONCENTRATION IN WHISKEYS EXPOSED TO OAKING SPIRALS IN PYREX CONTAINERS OVER 25 DAYS

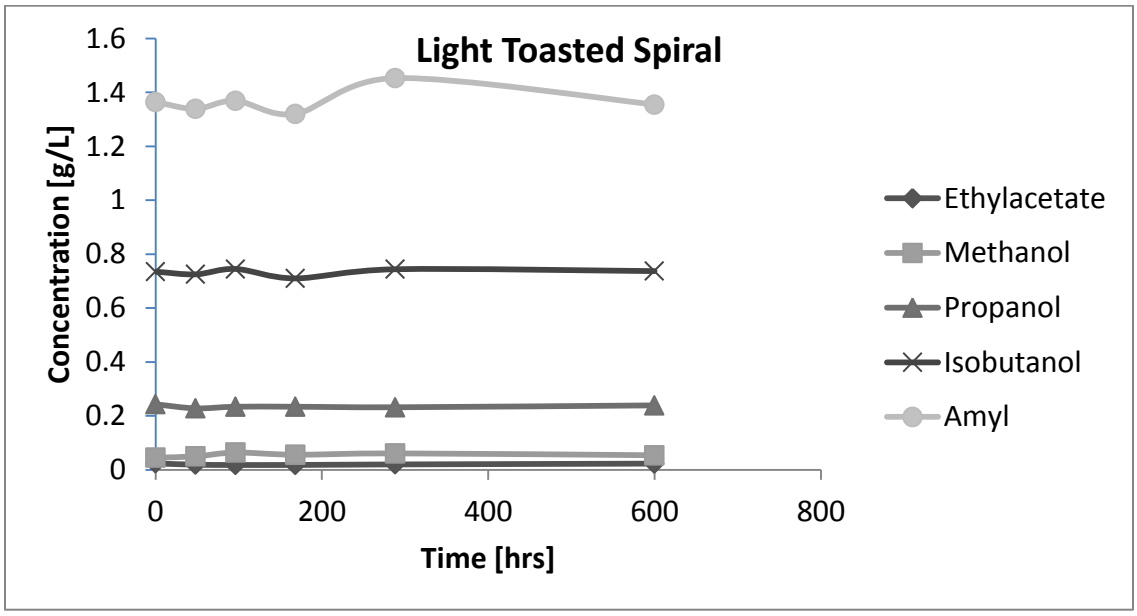


Figure 36: Volatile congener concentrations in Pyrex containers during exposure to light toasted oak spiral over 25 days

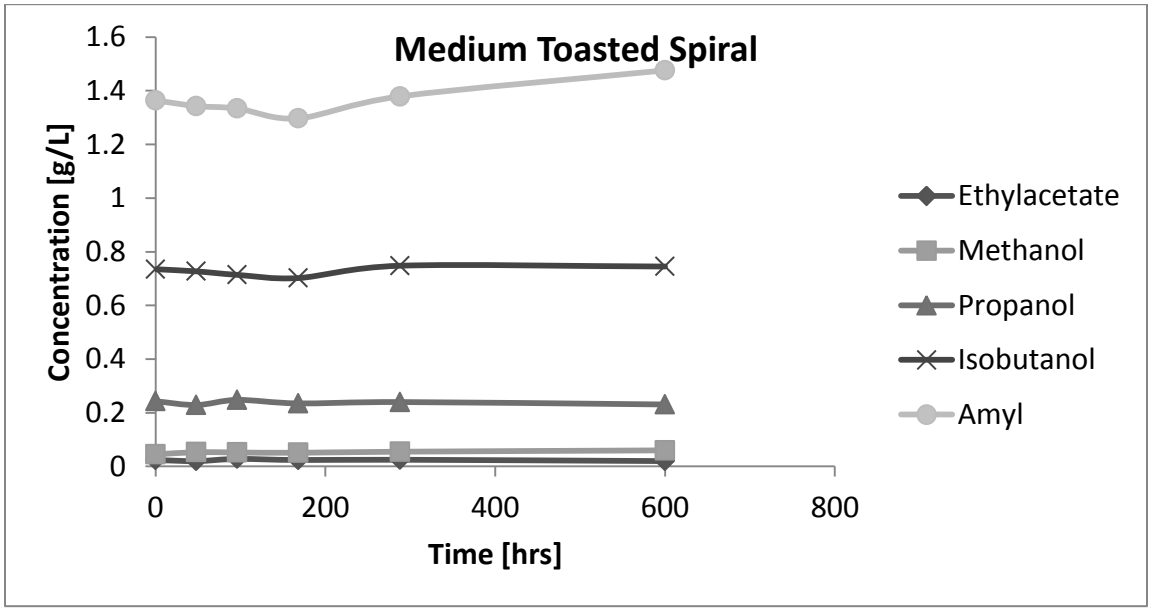


Figure 37: Volatile congener concentrations in Pyrex containers during exposure to medium toasted spiral over 25 days

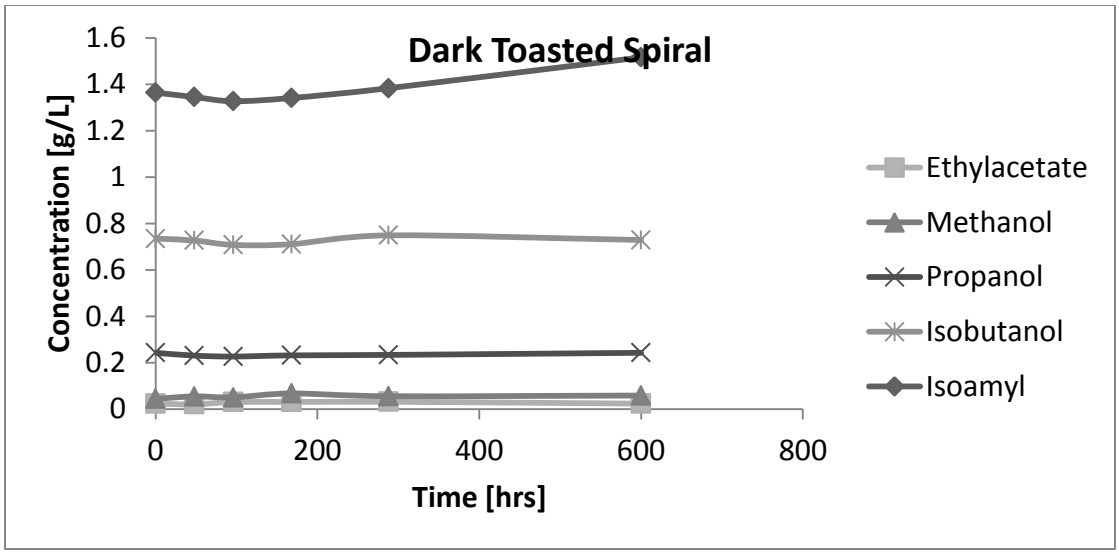


Figure 38: Volatile congener concentrations in Pyrex containers during exposure to dark toasted spiral over 25 days

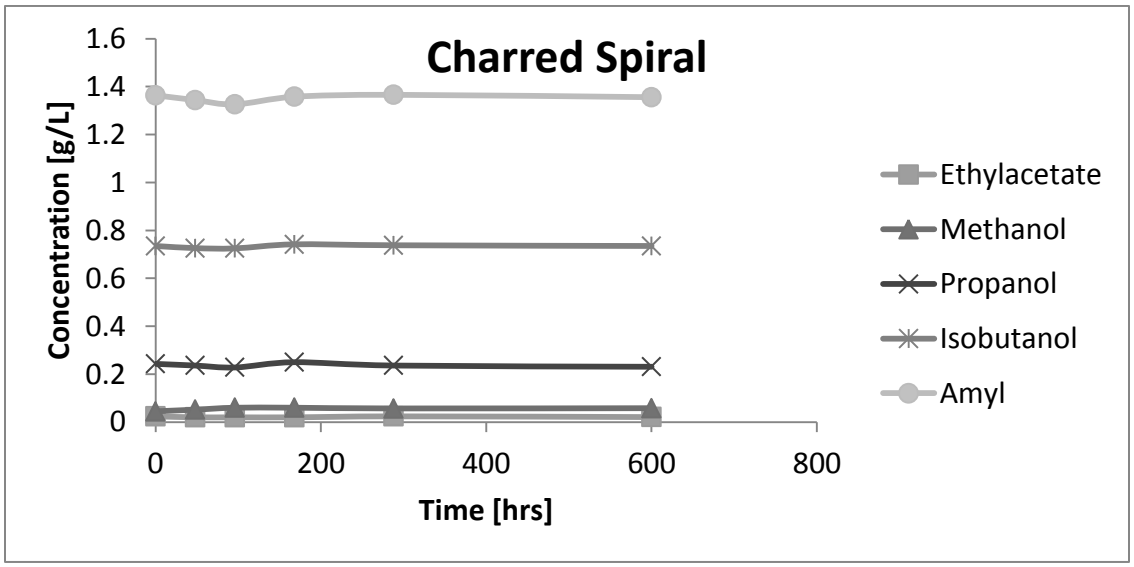


Figure 39: Volatile congener concentrations in Pyrex containers during exposure to charred spiral over 25 days

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