OPEN ACCESS

Journal of Brewing and Distilling

January-June 2023
ISSN 2141-2197
DOI: 10.5897/JBD
www.academicjournals.org

ACADEMIC JOURNALS
expand your knowledge

About JBD

The Journal of Brewing and Distilling (JBD) is a peer reviewed journal. The journal is published publishes articles relating to brewing such as fermentation technology and product analysis, filtration and packaging and malt induced premature yeast flocculation.

Indexing

The Journal of Brewing and Distilling is indexed in Chemical Abstracts (CAS Source Index)

Open Access Policy

Open Access is a publication model that enables the dissemination of research articles to the global community without restriction through the internet. All articles published under open access can be accessed by anyone with internet connection.

The Journal of Brewing and Distilling is an Open Access journal. Abstracts and full texts of all articles published in this journal are freely accessible to everyone immediately after publication without any form of restriction.

Article License

All articles published by Journal of Brewing and Distilling are licensed under the Creative Commons Attribution 4.0 International License. This permits anyone to copy, redistribute, remix, transmit and adapt the work provided the original work and source is appropriately cited. Citation should include the article DOI. The article license is displayed on the abstract page the following statement:

This article is published under the terms of the Creative Commons Attribution License 4.0
Please refer to https://creativecommons.org/licenses/by/4.0/legalcode for details about Creative Commons Attribution License 4.0

Article Copyright

When an article is published by in the Journal of Brewing and Distilling, the author(s) of the article retain the copyright of article. Author(s) may republish the article as part of a book or other materials. When reusing a published article, author(s) should;

Cite the original source of the publication when reusing the article. i.e. cite that the article was originally published in the Journal of Brewing and Distilling. Include the article DOI Accept that the article remains published by the Journal of Brewing and Distilling (except in occasion of a retraction of the article) The article is licensed under the Creative Commons Attribution 4.0 International License.

Self-Archiving Policy

The Journal of Brewing and Distilling is a RoMEO green journal. This permits authors to archive any version of their article they find most suitable, including the published version on their institutional repository and any other suitable website.
Please see http://www.sherpa.ac.uk/romeo/search.php?issn=1684-5315

Digital Archiving Policy

The Journal of Brewing and Distilling is committed to the long-term preservation of its content. All articles published by the journal are preserved by Portico. In addition, the journal encourages authors to archive the published version of their articles on their institutional repositories and as well as other appropriate websites.

https://www.portico.org/publishers/ajournals/

Metadata Harvesting

The Journal of Brewing and Distilling encourages metadata harvesting of all its content. The journal fully supports and implement the OAI version 2.0, which comes in a standard XML format. See Harvesting Parameter

Memberships and Standards

Academic Journals strongly supports the Open Access initiative. Abstracts and full texts of all articles published by Academic Journals are freely accessible to everyone immediately after publication.

Crossref is an association of scholarly publishers that developed Digital Object Identification (DOI) system for the unique identification published materials. Academic Journals is a member of Crossref and uses the DOI system. All articles published by Academic Journals are issued DOI.

Similarity Check powered by iThenticate is an initiative started by CrossRef to help its members actively engage in efforts to prevent scholarly and professional plagiarism. Academic Journals is a member of Similarity Check.

CrossRef Cited-by Linking (formerly Forward Linking) is a service that allows you to discover how your publications are being cited and to incorporate that information into your online publication platform. Academic Journals is a member of CrossRef Cited-by.

Academic Journals is a member of the International Digital Publishing Forum (IDPF).
The IDPF is the global trade and standards organization dedicated to the development and promotion of electronic publishing and content consumption.

Contact

Editorial Office: jbd@academicjournals.org

Help Desk: helpdesk@academicjournals.org

Website: http://www.academicjournals.org/journal/JBD

Submit manuscript online http://ms.academicjournals.org

Academic Journals
73023 Victoria Island, Lagos, Nigeria
ICEA Building, 17th Floor,
Kenyatta Avenue, Nairobi, Kenya.

Table of Content

Vol. 12(1), pp. 18-29, January-June 2023
DOI: 10.5897/JBD2022.0058
Article Number: 45C112B70727
ISSN 2141-2197

http://www.academicjournals.org/JBD

Journal of Brewing and Distilling

Full Length Research Paper

GC/MS analysis of traditional barrel aged whisky and whisky treated with accelerated aging techniques

Joe T. Elkins* and Heather A. Heinz

Department of Earth and Atmospheric Sciences, University of Northern Colorado, United States.

Received 09 August, 2022; Accepted 18 April, 2023

Accelerated aging techniques are an ongoing frontier in the production of whisky because they do not require traditional barrel aging methods to mature. Whisky samples from the Jack Daniels family as well as whisky from Elkins Distilling Co. that used accelerated aging techniques were tested by direct injection Gas Chromatography Mass Spectrometry. Chromatograms of samples were analyzed against NIST mass spectra to develop and compare sensory profiles of whisky. Results obtained from known commercial brands were used to build a baseline of sensory profiles, providing a framework for whiskies produced by the company using accelerated aging techniques and used to show comparable compounds between the barrel-aged whiskies and whiskies aged by accelerated aging techniques. This study provides qualitative data on sensory compounds present in whisky that underwent accelerated aging techniques, including treatment by ultrasonic waves, injection of atmospheric oxygen, and maceration on pieces of used whisky barrels from well-known brands that were also analyzed in this study. The data showed that injection of atmospheric oxygen had no result on the compounds detected, that ultrasonic waves have some effectiveness on the compounds present, and that maceration of wood chips showed the greatest effect on the compounds present.

Key words: Whisky, whiskey, barrel aged, accelerated aging, distilling.

INTRODUCTION

Craft spirit distilleries are looking for ways to decrease the time to market for whiskies produced in order to be competitive with long-established distilleries in Kentucky and Tennessee, who produce most of the whisky made in the United States (USA, 2021). As seen by Lennon and Shohfi (2021), bourbon prices have been increasing 9.1% or more per year.

Using accelerated aging techniques on distilled spirits is attractive for several reasons. Not all distilleries are financially able to have space conducive to barrel storage (Weber, 1974). If aging spirits can be achieved in less time by accelerated methods, the use of a barrel would be unnecessary (Chang, 2005). Also, faster aging methods would satisfy the increasing demand for whisky products worldwide (Rarick, 2015). As accelerated aging techniques can age whisky more quickly than a barrel, the demand for whisky products can be met more easily. During an interview with Bryan Davis of Lost Spirits Distillery regarding accelerated aging, Matt Pietrek of Cocktail Wonk (2015) quotes, “It can provide an invaluable tool to distillers to more confidently tailor the recipes and techniques they use to craft a target flavor

*Corresponding author. E-mail: joe.t.elkins@gmail.com.

profile," implying that accelerated aged whiskies could be a custom-made product, perhaps different and more targeted than some traditional barrel aged whiskies.

Many of the methods used to accelerate aging of newly distilled whisky were pioneered on other alcoholic beverages such as sake, rum, and brandy (Chang, 2005; Pugliese, 2017). In particular, ultrasonic treatment of alcoholic beverages has been very popular recently and its effects have been reported here and in popular media (Pugliese, 2017). It has also been the subject of successful patents (Terressentia, 2016; Knapp, 2013). Ultrasonic wave treatments have the potential to produce whisky products comparable to barrel aged products given the success of ultrasonic wave treatments on improving the flavor of other alcoholic beverages (Matsuura, 1994; Chang and Chen, 2002; Shyr and Yang, 2016). A study by Chang (2005) found that the ultrasonic wave process creates an environment in which elevated temperature and pressure generated from the waves causes chemical polymers to break into sub-particles and then recombine within the whisky. Chang accomplished this by comparing compounds of an alcoholic rice beverage aged one year in a barrel, and a comparable alcoholic rice beverage aged by ultrasonic wave treatments (an accelerated aging process). Samples were comparable as they were produced using as close to similar beverage-making techniques as possible. It was found that an alcoholic rice beverage aged by 16 treatments of 20 kHz ultrasonic waves was comparable in sensory profile to an alcoholic rice beverage aged 1 year in a barrel (Chang, 2005). Additional research has shown that ultrasonic wave treatments have been effective in changing the chemical and sensory profiles of coffee-liquors, sake, and rice and corn wine (Chang and Chen, 2002; Chang, 2005; Shyr and Yang, 2016). Terressentia Corporation is exploring accelerated aging with TerrePURE, a process involving the use of ultrasonic energy, oxygen, and heat to remove impurities from spirits that negatively affect the taste (Terressentia, 2016). However, distilleries using accelerated aging techniques publicize little to nothing about their methods as it is proprietary technology.

Analyzing compounds in alcoholic beverage is problematic because ethanol is volatile and can overwhelm the instrumentation used depending on the type of analysis being conducted. Several methods exist for analyzing compounds present in whiskey that either involve the use of a solvent to extract the desired compounds or non-solvent methodologies. Analytical methods involving the use of solvents include: Comparative Aroma Extract Dilution Analysis (AEDA), Stable Isotope Dilution Assays (SIDA), and Odor Activity Values (OAVs). These methods are problematic because the compounds extracted are solvent-dependent such that solvent choice also relies on the specific compounds being studied. Of these methods, SIDA is likely the best because it reduces bias in compounds analyzed resulting from extraction, but it is limited to the compounds that are extracted by the solvents. SIDA also reduces bias in compounds detected after extraction, but the method cannot be used to analyze compounds not extracted or compounds lost during extraction (Caldeira et al., 2007; Lahne, 2010; Kerley and Mufano, 2020).

Methodologies that do not include the use of solvents include: Phase Microextraction (SPME), Sample Dilution Analysis (SDA) and Gas Chromotogrpahy Mass Spectrometry (GC/MS) (MacNamara and Hoffmann, 1998; Plutowska and Wardencki, 2008; Lahne, 2010; Kerley and Mufano, 2020). Solid-Phase Microextraction (SPME) involves an adsorbent, coated, fiber which is submerged into the sample. The reproducibility of SPME along with being able to analyze a large number of samples are its main advantages. Its main disadvantage is that compounds of interest have varying absorption affinity depending on the coating used on the adsorption fiber. This can result in a failure to collect a representative sample of the compounds of interest. SPME is also costly thus being prohibitive for studies analyzing a wide range of compounds (Camara et al., 2007). Lahne (2010) showed Sample Dilution Analysis (SDA) to be a non-extractive, direct method of analyzing distilled spirits that provide equivalent results to AEDA while reducing analysis time and avoiding extraction bias.

This study uses GC/MS analysis of chemical compounds present in whisky to focus on a subset of compounds common in barrel-aged whisky (Table 1) and emphasizes comparison between the compounds present in traditional, barrel aged whiskies and whiskies that have been treated using accelerated aging techniques, including ultrasonic treatment. The compounds present in whiskey samples can be determined using Gas Chromatography Mass Spectrometry. Gas Chromatography Mass Spectrometry (GC/MS) separates and identifies components of complex chemical mixtures (Gates and Bull, 2008). Compound profiles are dependent on the type of whisky being tested (Piggott, 2016). Compound analysis for whiskey samples can be provided by GC/MS analysis and shows similarities among different whiskies for the major volatile congeners they contain as seen by Owens (2016), whose studies direct injection liquid chromatography along with Aylott (2010) who showed the utility of direct injection to analyze whisky. Russell and Stewart (2014) also found that of the spectrometric analysis methods available, chromatography offers advantages in speed, selectivity, and sensitivity. This research was conducted using GC/MS analysis of whisky samples aged by ultrasonic waves and wood chips at Elkins Distilling Co., a variety of Jack Daniel's Tennessee Whiskey products, and several whiskies from Elkins Distilling Co. that have not come into contact with wood.

While GC-MS analysis provides a framework for analyzing compounds present in whisky, little research has been published on products aged by accelerated aging techniques, especially whisky. For this research, we compared the compounds present between colorless,

Table 1. Main compounds of interest present in whisky samples from the study.[a]

Approximate retention time (min)	Common Name, Molecular Formula, Mass (g/mol)
5.5	Furfural, $C_5H_4O_2$, 96.08
5.7	Isoamyl acetate, $C_7H_{14}O_2$, 130.19
7.4	Ethyl hexanoate, $C_8H_{16}O_2$, 144.21
10.5	Phenylethyl alcohol, $C_8H_{10}O$, 122.16
11.1	Ethyl caprylate, $C_{10}H_{20}O_2$, 172.27
11.3	Diethyl succinate, $C_8H_{14}O_4$, 174.19
11.9	Octanoic acid, $C_8H_{16}O_2$, 144.2
13.0	2-Phenylethyl acetate, $C_{10}H_{12}O_2$, 164.02
15.1	cis-Whiskeylactone, $C_9H_{16}O_2$, 156.22
15.6	Ethyl caprate, $C_{12}H_{24}O_2$, 200.32
16.3	Decanoic acid, $C_{10}H_{20}O_2$, 172.27
17.6	Vanillin Lactoside, $C_{20}H_{28}O_{13}$, 476
17.7	Vanillin, $C_8H_8O_3$, 152.15
20.1	Ethyl laurate, $C_{14}H_{28}O_2$, 228.37
21.3	Isoamyl decanoate, $C_{15}H_{30}O_2$, 242.40
23.8	Syringaldehyde, $C_9H_{10}O_4$, 182.17
24.4	Ethyl myristate, $C_{16}H_{32}O_2$, 256.42
28.3	Ethyl palmitate, $C_{18}H_{36}O_2$, 284.48
31.5	Ethyl linoleate, $C_{20}H_{36}O_2$, 308.50
31.6	Ethyl oleate, $C_{20}H_{38}O_2$, 310.51

Source: Author

unaged whisky, whisky that has been treated with accelerated aging techniques, and whisky that has been traditionally aged by barrel method. It is suspected that whiskies having undergone barrel aged methods will yield a more chemically complex profile, which Mosedale and Puech (1998) found to be true as, “The extraction of compounds from the oak cask during barrel aging is a leading determinate of flavors representative of specific sensory-related compounds present.”

METHODOLOGY

Collection of raw materials

Jack Daniel’s Tennessee Whiskey has several products that have been treated differently: the original ‘Old No. 7’ which is their flagship, Gentleman Jack which has undergone ‘charcoal aging’ twice before bottling, and Single Barrel which is limited to less than four hundred 750 ml bottles per barreling. These products from Jack Daniel were also tested for their chemical compounds in this research. Jack Daniel is of particular interest because Elkins Distilling Co. uses chips of Jack Daniel’s barrels as part of their accelerated aging treatments as of this writing.

Production of whiskey by traditional and accelerated aging techniques

Each stage of the whisky production process plays a role in the final product’s character (Piggott, 2015). Understanding the whisky production process can help to explain which compounds are available for reactions when undergoing mellowing. In whisky production, the first step is the processing of grains to release starch, which is then converted into fermentable sugar with the addition of enzyme-rich malted barley (Russell and Stewart, 2014). Fermentation then begins and alcohol is created from the addition of yeast. After fermentation is complete, distillation of the alcohol produced occurs. By vaporizing the alcohols off the fermented mash, the alcohols undergo a phase change from liquid to vapor. The vapors rise, travelling into a column surrounded by cool water called a condenser, which forces the vapors to condense back into a liquid. Separation of distilled liquid components is based on differences in volatility, or vaporization ability (Russell and Stewart, 2014). The resulting distillate is colorless. The colorless whisky is most often put into oak barrels for storage and maturation to mellow until it is ready for bottling. When whisky is mellowed in a barrel chemical polymers originate from the barrel itself. The extraction of compounds from the oak cask during barrel-mellowing is a leading determinate of flavors representative of compounds present (Mosedale and Puech, 1998).

Each part of the production process can be seen as a variable, and variables such as yeast strain, fermentation specifications, distillation equipment and processes, blending techniques, and the type and duration of time the whisky spends in a barrel ultimately lead to sensory compounds that determine the whisky’s character (Russell and Stewart, 2014). It is therefore significant to study the chemical reactions and compounds produced in whisky mellowed by barrels in order to determine the desired compounds that need to be created through accelerated mellowing techniques to produce a comparable product.

Elkins Distilling Co. does not use traditional barrel methods to age some of the whisky they produce. Their whisky is aged using three accelerated aging treatments: injection of atmosphere, maceration on wood chips, and ultrasonic wave treatment (Figure 1). The injection of atmosphere is done using a VicTsing Ultra

Figure 1. Ultrasonic setup at Elkins Distilling Co. Shows wave generator, immersion bath with ultrasonic transducer, and stainless-steel reaction vessel containing whisky, wood chips, and air pump.
Source: Author

Table 2. Names of whisky samples analyzed during this study via GC/MS analysis.

Jack Daniel
Jack Daniel's Single Barrel Select
Gentleman Jack
Elkins Colorado Whisky
Elkins Unsonocated Colorado Whisky
Elkins "Hearts" tank
Elkins injected with Atmosphere

Source: Author

Silent High Out Energy Efficient Aquarium Air pump with 2 Air stone/2M Silicone Tube. Maceration on wood was done using 29.4 L of Jack Daniel's Tennessee Whiskey Barrel Smoking Chips, 2 L of toasted French oak 1 cm × 1 cm cubes, 2 L of 1 cm × 1 cm toasted American oak cubes, and 75.7 L of unaged white corn whisky at 75% ABV. The ultrasonic wave treatments were completed using a wave generator producing ultrasonic waves at 46 kHz at 1.8 Amps to an ultrasonic transducer. The process takes 10 days from mashing, fermentation, distillation, accelerated aging, to bottling. A sample of each step in their accelerated aging processes was collected and analyzed to determine what effect each step (variable) has on the chemical compounds present in the resulting whisky.

GC/MS analysis

Unopened, commercially-available, barrel aged whiskies by Jack Daniel's brand were purchased from retail settings in liquor stores in Colorado and can be found in Tables 2 and 3. Elkins Distilling Co.

Table 3. Compound presence in Jack Daniel's sample set. The values represent retention times and dashed lines mean the compound was not found.

Compound	Jack Daniel	Jack Daniel's Single Barrel	Gentleman Jack
Furfural	-	-	-
Isoamyl acetate	5.7	5.6	5.7
Ethyl hexanoate	7.4	7.4	7.4
Phenylethyl alcohol	-	10.5	10.2
Ethyl caprylate	11.1	11.1	11.1
Diethyl succinate	-	11.3	-
Octanoic acid	-	-	-
2-Phenylethyl acetate	13.0	13.0	13.0
cis-Whiskeylactone	15.1	-	15.1
Ethyl caprate	15.6	15.6	15.6
Decanoic acid	-	-	-
Vanillin Lactoside	17.7	17.6	17.7
Vanillin	-	17.7	-
Ethyl laurate	-	20.1	-
Isoamyl decanoate	-	-	-
Syringaldehyde	23.8	23.8	23.8
Ethyl myristate	-	24.4	-
Ethyl palmitate	-	28.3	-
Ethyl linoleate	-	-	-
Ethyl oleate	-	-	-

Source: Author

provided samples (at least 50 mL of each) of their corn whisky from various stages in the accelerated aging process and results for these can be found in Tables 3 and 4. During this research, all whisky samples were tested at the %ABV of the purchased product as bottled by the manufacturer.

Immediately prior to analysis, a subset of each whisky product was transferred to 50 ml vials, labeled. Upon analysis, a subset of each sample was transferred into a 3 mL capped glass vial and labeled. For each sample, 1 µL was collected in a Hamilton gastight 25 µL syringe with a cemented needle and sampled through the injection port of the gas chromatograph. The samples were then individually analyzed and separated through an Agilent 7890 GC column with a 5975a MSD using helium as a carrier gas (Buckeye Welding) at 0.5 mL/min, which can be seen in other spirit analysis done using GC-MS (Lynman and Zou, 2016). The Agilent column had wax specifications listed 30 m length, 0.25 mm internal diameters, and 0.25 µm film thickness. Tank pressure was 60 psi. The mass detector in the analyses used an electron impact ionization (EI) with a single hyperbolic quadrupole mass filter. The initial oven temperature was set at 60°C with a solvent delay of 3 min. After the solvent delay, the oven was ramped up to 100°C at a rate of 20°C/min. Once at 100°C, the oven was ramped to 240°C at 5°C/min and held for 10 min followed by cool down. Compounds eluting from the column were collected as a Total Ion Current Chromatogram (TIC). Peaks of interest were evaluated against the NIST library of compounds and recorded for comparisons. In between each sample, the Hamilton gastight syringe was rinsed thoroughly with deionized water. Effort was made to ensure the absence of air bubbles during sampling.

The TIC produced for each whisky sample and the included peaks of interest were labeled according to NIST library comparisons and percent probability. All TICs were saved to the computer in the University of Northern Colorado Analytical Chemistry Lab.

RESULTS

Although there are a vast number of compounds to be tested for, as seen by Gonzalez-Robles (2018), only a small portion of compounds were tested for here due to program and equipment limitations. The following compounds were chosen as a sample list and found among the whiskies listed in Table 1: furfural, isoamyl acetate, ethyl hexanoate, phenylethyl alcohol, ethyl caprylate, diethyl succinate, octanoic acid, 2-phenylethyl acetate, cis-whiskeylactone, ethyl caprate, decanoic acid, vanillin lactoside, vanillin, ethyl laurate, isoamyl decanoate, syringaldehyde, ethyl myristate, ethyl palmitate, ethyl linoleate, and ethyl oleate (Figures 2 to 8). All the compound names are listed in Table 1.

The Jack Daniel's sample set has a seven compound difference between phenylethyl alcohol, diethyl succinate, cis-whiskeylactone, vanillin, ethyl laurate, ethyl myristate, and ethyl palmitate (Table 3). The Jack Daniel's Single Barrel Tennessee whiskey has the greatest number of compounds present with a total of 13 compounds. The Jack Daniel's Tennessee Whiskey has the fewest number of compounds present with a total of eight compounds. The compounds exhibited by Jack Daniel's Single Barrel Tennessee whiskey but not by Jack Daniel's Tennessee whiskey are phenylethyl alcohol, diethyl

Table 4. Compound presence in Elkins Distilling Co. Whisky sample set.

Compound	Elkins Colorado Whisky[a]	Elkins Unsonicated Colorado Whisky[b]	Elkins Sonicated "Hearts"[c]	Elkins Atmosphere[d]	Elkins "Hearts" tank[e]
Furfural	5.6	-	-	-	-
Isoamyl acetate	-	-	-	-	-
Ethyl hexanoate	7.4	-	-	-	-
Phenylethyl alcohol	-	10.5	10.5	10.5	10.5
Ethyl caprylate	11.1	11.1	11.1	11.1	11.1
Diethyl succinate	-	-	-	-	-
Octanoic acid	-	-	-	-	-
2-Phenylethyl acetate	-	-	-	-	-
cis-Whiskeylactone	15.9	15.8	-	-	-
Ethyl caprate	15.6	15.6	15.6	15.6	15.6
Decanoic acid	-	-	-	-	-
Vanillin Lactoside	17.7	17.7	-	-	-
Vanillin	-	-	-	-	-
Ethyl laurate	20.1	20.1	20.1	20.1	20.1
Isoamyl decanoate	21.2	-	21.2	21.2	21.2
Syringaldehyde	23.8	23.8	-	-	-
Ethyl myristate	24.4	24.4	24.4	24.4	24.4
Ethyl palmitate	28.3	28.3	28.3	28.3	28.3
Ethyl linoleate	31.5	31.5	31.5	31.5	31.5
Ethyl oleate	-	-	-	-	-

The values represent retention times and dashed lines mean the compound was not found. [a]Elkins Colorado Whisky was steeped with Jack Daniel's barrel chip pieces while undergoing ultrasonic wave treatments for three days along with atmosphere. [b]The Elkins Unsonicated Colorado Whisky steeped with Jack Daniel's Tennessee whiskey barrel chips, but no ultrasonic treatment or atmosphere. [c]The Elkins Sonicated "Hearts" is undiluted whisky from the "hearts" tank mellowed with ultrasonic wave treatments for three days. [d]The Elkins Atmosphere whisky is "hearts" whisky that has been injected with atmosphere and steeped with barrel chips. [e]The Elkins "Hearts" tank is whisky produced from the final spirits run and is undiluted with no treatment of barrel chip.
Source: Author

succinate, vanillin, ethyl laurate, ethyl myristate, and ethyl palmitate.

The Elkins Distilling Co. sample set has an eight compound difference. The differing compounds include furfural, isoamyl acetate, ethyl hexanoate, phenylethyl alcohol, cis-whiskeylactone, vanillin lactoside, isoamyl decanoate, and syringaldehyde (Table 4). The Elkins Colorado Whisky has the greatest number of compounds present with a total of 12 compounds. The Elkins "Hearts" tank has the fewest number of compounds present totaling eight compounds. The compounds found in Elkins Colorado Whisky but not in Elkins "Hearts" tank are furfural, ethyl hexanoate, cis-whiskeylactone, vanillin lactoside, and syringaldehyde.

DISCUSSION

Barrel aging of whisky seems to be primarily an additive process through the spirit entering the wall of a cask and passing back to the bulk liquid while also carrying smaller compounds (Le Floch et al., 2015; Heinz and Elkins, 2019). Accelerated aging processes also appear additive but result in differing or additional compounds than those present in barrel aged whiskies, with some similarities. In general, barrel aged whiskies contain compounds with high retention times, which refers to the amount of time it takes from injection to detection of solute components, dependent upon parameters set within the GC-MS program. High retention times are typically an indication of longer chain compounds (Lynman and Zou, 2016). The unaged colorless whiskies mimic characteristics found in a barrel aged whisky, but are likely missing some longer chain compounds (Liebman and Scherl, 1949).

The complexity of whisky subjected either to accelerated aging or traditional barrel aging methods both have similarity as shown here. Accelerated aged whisky seems to be comparable to the complexity of barrel aged whiskies when looking at their compound breakdowns, and this could contribute to the fact that at times during the production process, accelerated aged whisky samples (as seen here) were treated with retired Jack Daniels whiskey barrels. In other words, the compounds present in Elkins accelerated aged whiskies

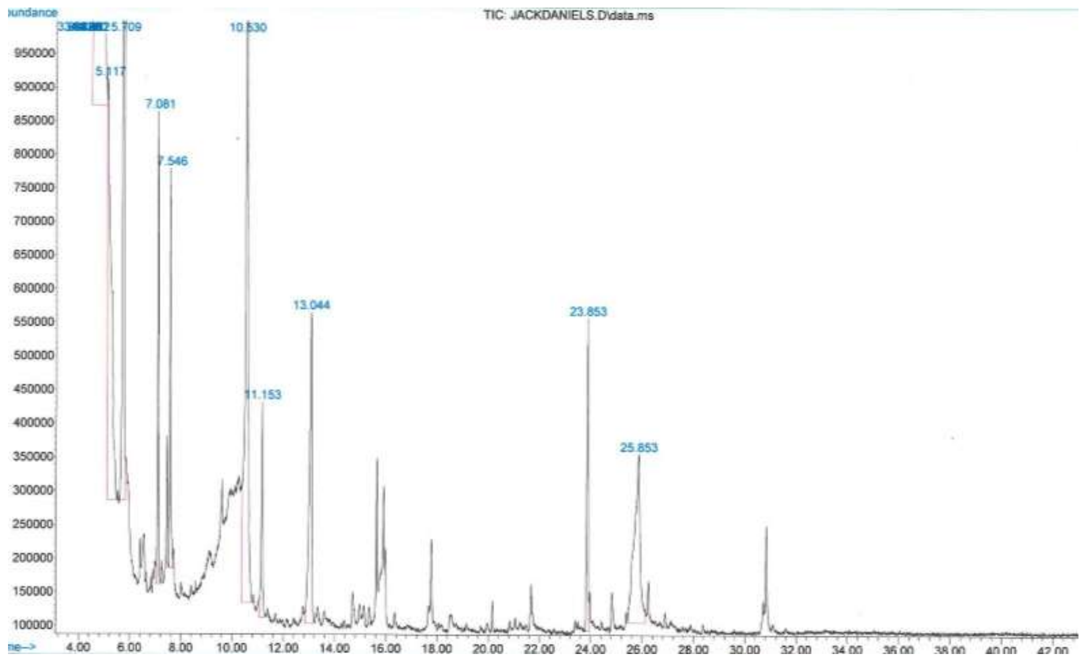

Figure 2. Total Ion Chromatogram (TIC) showing compounds present in Jack Daniels. Numbers in blue represent retention times.
Source: Author

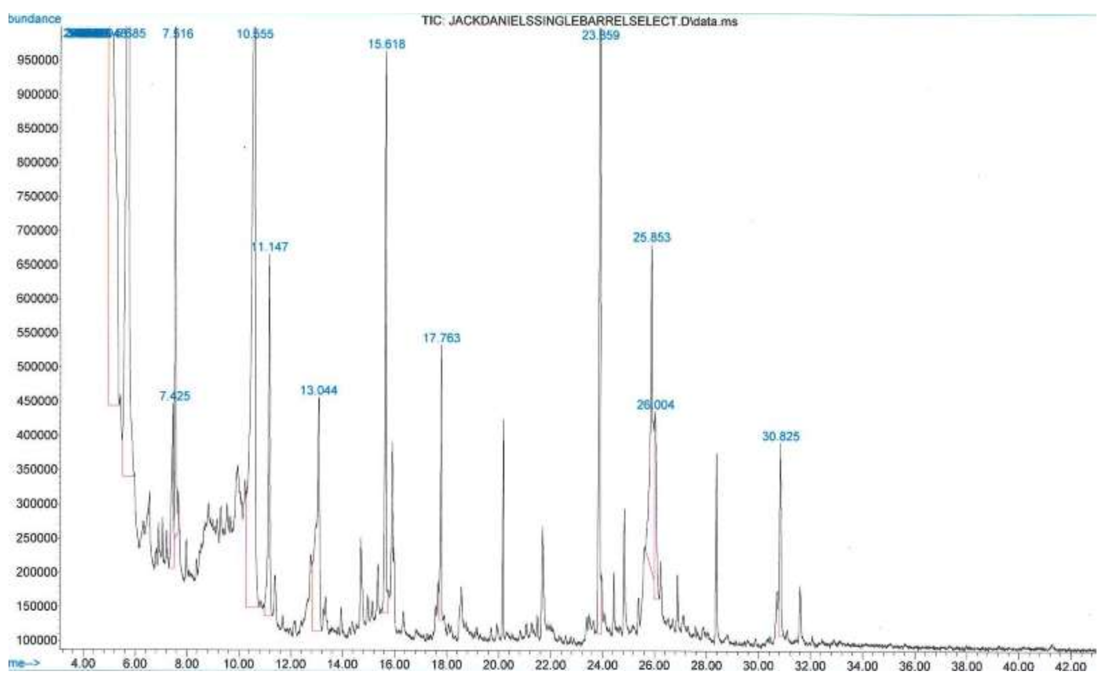

Figure 3. Total Ion Chromatogram (TIC) showing compounds present in Jack Daniels Single Barrel Select. Numbers in blue represent retention times.
Source: Author

are found mainly due to barrels (in the use of chips or cubes) used in their maturation process. These same compounds were found in the barrel-aged whisky whose barrel would eventually become part of the accelerated aging process. Specifically, Elkins Colorado Whisky uses Jack Daniel's Tennessee Whiskey barrel chips as part of

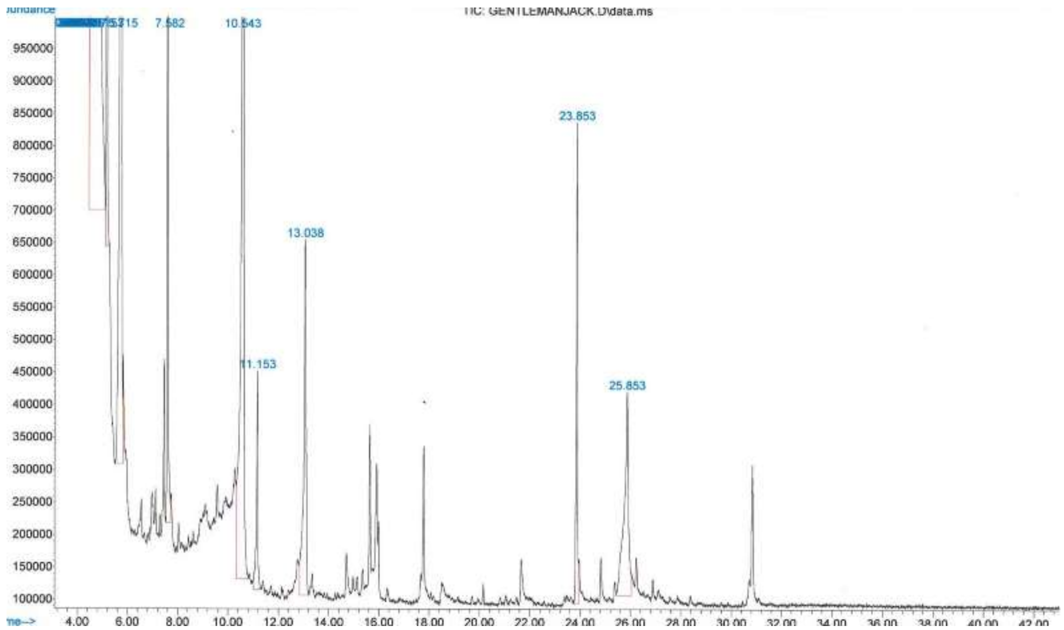

Figure 4. Total Ion Chromatogram (TIC) showing compounds present in Gentleman Jack. Numbers in blue represent retention times.
Source: Author

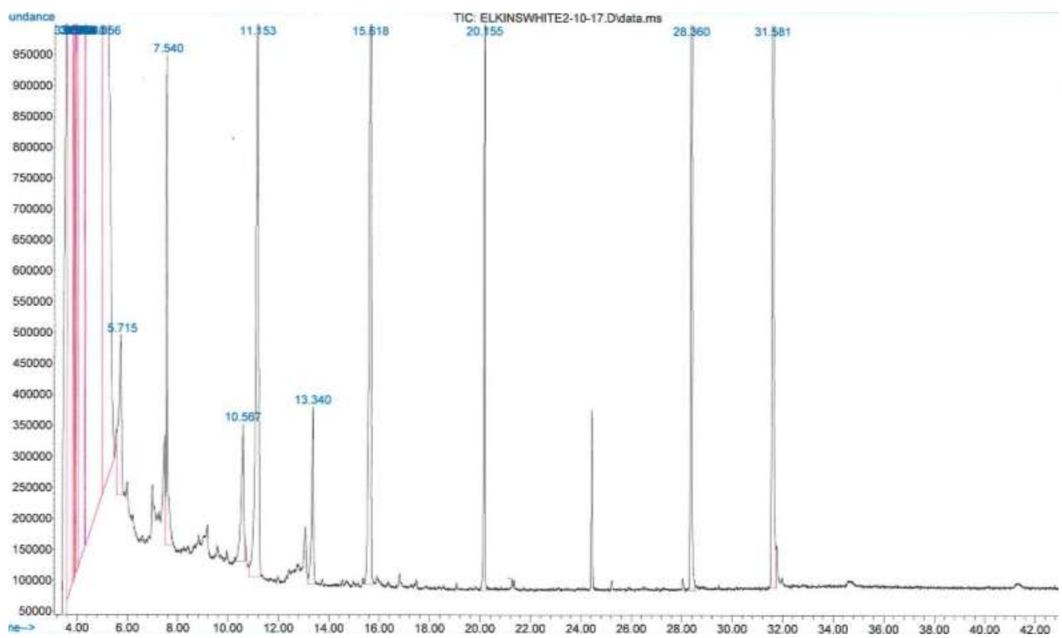

Figure 5. Total Ion Chromatogram (TIC) showing compounds present in Elkins White Corn Whisky. Numbers in blue represent retention times.
Source: Author

their accelerated aging process and the compound similarities between Elkins Colorado Whisky and Jack Daniel's Tennessee Whiskey are generally consistent. It was found that Jack Daniel's whiskey samples yield a more complex profile, which agrees with Reazin (1981) suggesting a marker for aging exists when increased compound concentration are found within an aging spirit inside a barrel.

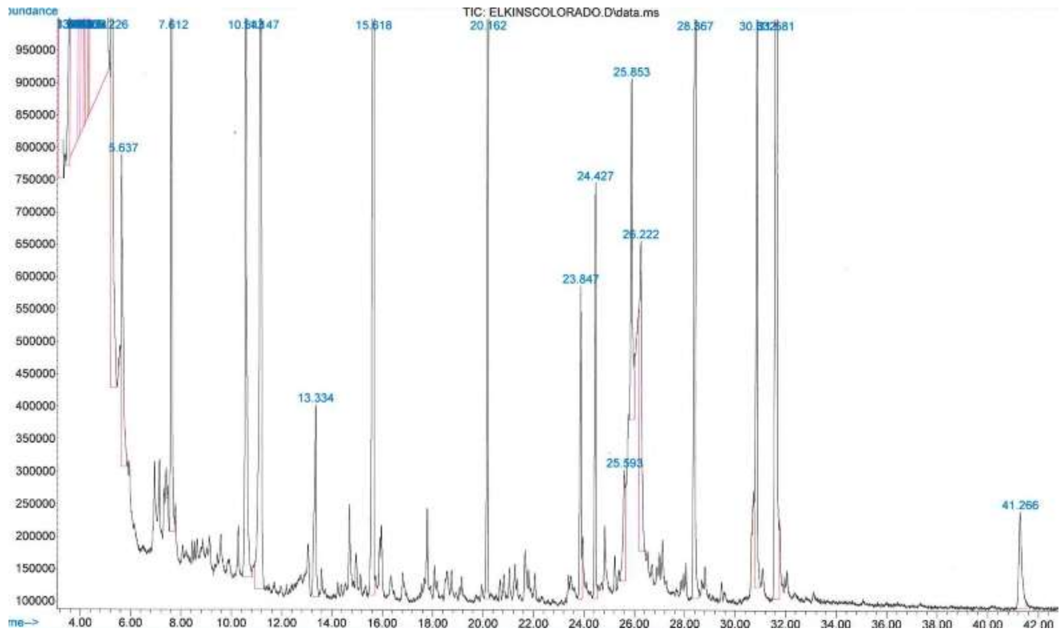

Figure 6. Total Ion Chromatogram (TIC) showing compounds present in Elkins Colorado Whisky. Numbers in blue represent retention times.
Source: Author

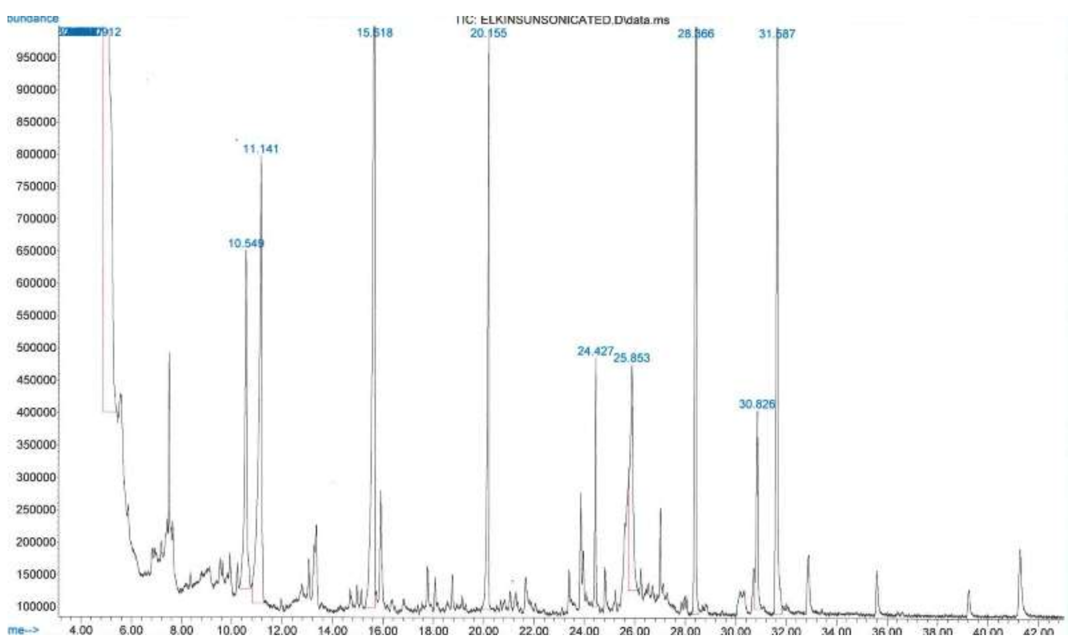

Figure 7. Total Ion Chromatogram (TIC) showing compounds present in Elkins Whisky Unsonicated. Numbers in blue represent retention times.
Source: Author

A trend among whisky samples with a barrel aged and unaged version is the increase in compounds within the barrel aged version. The presence of syringaldehyde and vanillin, for example, among the barrel aged versions and not their unaged versions was noticed across Elkins whisky samples (Table 4). Ethyl hexanoate was also only present in whiskies (studied here) that had an interaction with toasted or charred wood, and not present in any

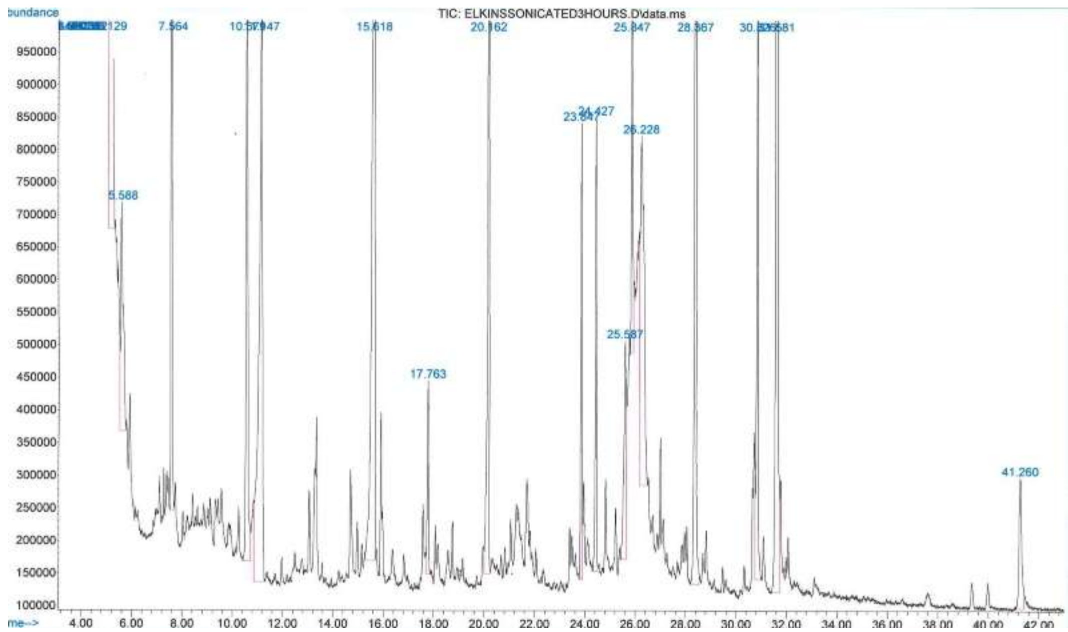

Figure 8. Total Ion Chromatogram (TIC) showing compounds present in Elkins Whisky Sonicated 3 Hours. Numbers in blue represent retention times.
Source: Author

unaged samples. Aldehydes and esters contribute to the flavor of barrel aged products and can be used as aging markers (Liebmann and Scherl, 1949). Thus, it is likely that the presence of these compounds and their sensory contributions is due to barrel aging or the interaction with retired barrels.

The following compounds were found among all whisky samples tested shown in Table 4: phenylethyl alcohol, ethyl caprylate, ethyl caprate, ethyl laurate, and ethyl palmitate. These compounds are likely to have been produced during the fermentation process and seem to have remained stable throughout distillation. There are several esters and fusel alcohols that will form during fermentation and remain throughout the maturation process (Sun, 2013).

cis-Whiskeylactone, vanillin lactoside, and syringaldehyde are types of ellagitannin compounds and are easily extracted from wood by water-alcohol mixtures (Viriot, 1993). cis-Whiskeylactone is found in all the barrel aged whiskies except for Jack Daniel's Single Barrel Tennessee Whiskey, which is either due to a literal compound difference or sensitivity issues regarding the method of GC/MS usage. Regardless, cis-Whiskeylactone is not found in any of the unaged whiskies implying it is a product of barrel aging.

Not all compounds have a predictable or intuitive presence among all the whisky samples. Isoamyl decanoate appears in unaged colorless Elkins corn whisky and Elkins Colorado Whisky. However, an important note is the milder temperature at which wood is toasted versus the temperature at which it is charred. A larger array of compounds are available within toasted products (Russell, 2014; Rogerson, 2016). It is likely that isoamyl decanoate is a product of the toasted cubes used during Elkins's accelerated aging process. Furfural gave inconclusive results as it was only found in the Elkins Colorado Whisky sample and none of the Jack Daniel's samples tested, which could be due to method error or sensitivity issues within the GC/MS. As stated by Spedding (2018), there is still much to understand about control within these systems.

Analysis of Elkins Colorado Whisky (accelerated aged) shows similarities to the compounds present within barrel aged whiskies. The following compounds are present in Elkins Colorado Whisky shown Table 4: ethyl hexanoate, cis-whiskeylactone, vanillin lactoside, and syringaldehyde. Steeping with Jack Daniel's Tennessee Whiskey barrel chips, but not ultrasonic wave treatment, yielded the same list of compounds just mentioned. Given that the Elkins whisky process involves toasted wood cubes and the Jack Daniels whiskey process does not, it is likely that the differences in compound extraction can be attributed to the depth and type of heat treatment used on the wood types. Rogerson (2016) states, "Toasted staves extracted more oak compounds than charred staves for specific oak compounds. However, for overall color, total soluble phenolics, and pH level, charred and toasted staves equally extracted more after 3 months than at time 0." As the whisky comes into contact with the wood, merely soaking without the use of sonication, reactions begin and compounds are exchanged, suggesting the use of ultrasonic waves alone have less of an impact than physical connection (and time) between whisky spirit and wood.

Generally, there is an increase in the number of compounds within Elkins' whiskies at each step of the accelerated aging process (Table 4). However, there are no compound differences between the Elkins "Hearts" tank and Elkins Atmosphere, suggesting that oxidation without wood present is either not occurring or undetectable using this GC/MS method. Oxygen and oxidation reactions play a valuable role in barrel aging as they allow for the production of acetaldehyde from ethanol, which then cascades into further reactions impacting flavor, aroma, and phenolic composition (Spedding 2017a, Spedding, 2017b, Spedding, 2018). Without the formation of acetaldehyde, it's likely the sensory profile of the finished whisky would be lacking in complexity or flavor.

The fact that no compound differences occur between the "Hearts" tank, the sample treated only with atmosphere, or the sample treated only with ultrasonic wave treatments indicate that those steps of the accelerated aging process are either ineffective at causing changes in the unaged whiskies, that they require wood as an organic material from which to exchange compounds and form esters, or that the GC/MS methodology used in this study is not sensitive enough to detect the compound differences that occur. As shown in Tables 3 and 4, the chemical complexity of samples grows as their production process involves the interaction of wood.

As previously mentioned, there are compounds present in Elkins Colorado Whisky that are also present in barrel aged whiskies. Chang (2005) shows that compounds resulting from traditional aging techniques (barrel aging) can also be replicated using ultrasonic wave treatments. Thus, it is possible that the compounds present in Elkins Colorado Whisky are the result of ultrasonic wave treatments. However, all the compounds present in Elkins Colorado Whisky are present in all Jack Daniel's products. Elkins Colorado Whisky is steeped on Jack Daniel's barrel chips. It is therefore reasonable to deduce that compounds found in Jack Daniel's that are found in Elkins Colorado Whisky are most likely the result of steeping Elkins Colorado Whisky on Jack Daniel's Barrel chips.

A consideration to be made related to the compounds present among whiskies sampled here are limitations of the GC/MS methodology and the methodology's ability to detect all compounds present.

Conclusion

Generally, compounds present in the unaged colorless whiskies are also present in the barrel aged and accelerated aged whisky samples. Those compounds are a product of mashing and fermentation and have the structural stability to withstand the distillation process. Compounds appearing in the barrel aged whiskies not present in the unaged colorless counterparts are most likely the product of barrel aging and suggest that the interaction with charred, toasted, or treated wood, plus the addition of time and a controlled environment, is the primary source. Therefore, barrel aging is an additive process and the most significant part of the whisky production process in terms of sensory compounds being formed.

From the results here, steeping unaged whisky with Jack Daniel's wood chips or toasted cubes seemed to have the most significant effect on increasing the compounds present of the finished product. Pumping atmosphere into the whisky, along with ultrasonic wave treatment, do not appear to influence the compounds present in the samples as detected by this GC/MS methodology. However, Elkins Colorado Whisky contains furfural, which is not present in any of the other whiskies sampled. This suggests that the presence of furfural is the result of the cumulative effects of the accelerated aging process or a sensitivity issue with the GC/MS instrument or methodology.

Isoamyl decanoate provided inconclusive results regarding the effects of aging as its presence was widely inconsistent across the sample sets suggesting the possibility of issues with GC/MS sensitivity or methods used.

Additional compounds of significant finding are cis-whiskeylactone, syringaldehyde, and vanillin in both the Elkins Colorado sample and Jack Daniel's traditional barrel aged samples. The presence of these suggests barrel aging, or the interaction with such retired barrels, as the primary additive process in the formation of potent and desirable compounds.

It is the opinion of these researchers, based on the data here, that ultrasonic wave treatments are effective in producing compound differences from unaged, colorless whisky to whisky aged by accelerated methods with the addition of wood. However, it is also the opinion of these researchers that accelerated aging techniques have more ground to cover in terms of their ability to produce a comparable whisky to traditional barrel aged products of similar mash bill. Whereas the data presented here suggests ultrasonic wave treatments have some effect on the compounds present in an accelerated aged whisky, the data still shows barrel aged whiskies to be of higher complexity in terms of their compounds available to experience.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

Aylott R, MacKenzie W (2010). Analytical strategies to confirm the generic authenticity of scotch whisky. Journal of the Institute of

Brewing 116(3):215-229.
Caldeira M, Rodrigues F, Perestrelo R, Marques JC, Camara JS (2007). Comparison of Two Extraction Methods for Evaluation of Volatile Constituents Patterns in Commercial Whiskeys Elucidation of the Main Odour-Active Compounds. Talanta 74(1):78-90.
Camara JS, Marques JC, Perestrelo RM, Rodrigues F, Oliveira L, Andrade P, Caldeira M (2007). Comparative Study of the Whisky Aroma Profile based on Headspace Solid Phase Microextraction using Different Fibre Coatings. Journal of Chromatography 1150(1-2):198-207.
Chang AC, Chen FC (2002). The application of 20 kHz ultrasonic waves to accelerate the mellowing of different wines. Food Chemistry 79(4):501-506.
Chang AC (2005). Study of ultrasonic wave treatments for accelerating the mellowing process in a rice alcoholic beverage. Food Chemistry 92(2):337-342.
Gates DP, Bull DI (2008). Gas chromatography mass spectrometry (GC/MS). Available at: http://www.bris.ac.uk/nerclsmsf/techniques/gcms.html
Gonzalez-Robles IW (2018). Flavour Interactions between the'estery'and'mature/woody'characters of whisky, bourbon & tequila (Doctoral dissertation, University of Nottingham).
Heinz H, Elkins J (2019). Comparison of unaged and barrel aged whiskies from the same Mash Bill using gas chromatography/mass spectrometry. Journal of Brewing and Distilling 8(1):1-6.
Kerley T, Munafo JP (2020). Changes in Tennessee Whiskey Odorants by the Lincoln County Process. Journal of Agriculture and Food Chemistry 68(36):9759-9767.
Knapp A (2013). Cleveland whiskey ages bourbon in one week. Available at http://www.forbes.com/sites/alexknapp/2013/05/29/cleveland-whiskey-ages-bourbon-in-one-week/#3ad6d66e72c3
Lahne J (2010). Aroma Characterization of American Rye Whisky by Chemical and Sensory Assay, Masters Thesis, University of Illinois at Urbana-Champaign, Urbana Illinois.
Le Floch A, Jourdes M, Teissedre PL (2015). Carbohydrate Research Mini Review Polysaccharides and lignin from oak wood used in cooperage: Composition, interest, assays: A review 417:94-102.
Lennon C, Shohfi T (2021). Unbridled spirit: Illicit markets for bourbon whiskey. Journal of Economic Behavior & Organization 191:1025-1045.
Liebmann AJ, Scherl B (1949). Changes in Whisky While Maturing. Industrial and Engineering Chemistry 41(3):534-543.
Lynman K, Zou Y (2016). Analysis of Distilled Spirits Using an Agilent J&W DB-WAX Ultra Inert Capillary GC Column. Available at https://www.agilent.com/cs/library/applications/5991-6638EN.pdf.
MacNamara K, Hoffmann A (1998). Gas Chromatographic Technology in Analysis of Distilled Spirits, In Instrumental Methods in Food and Beverage Analysis, Wetzel D, Charalambous G (eds) Elsevier Science pp. 303-346.
Matsuura K, Hirotsune M, Nunokawa Y, Satoh M, Honda K (1994). Acceleration of cell growth and ester formation by ultrasonic wave irradiation. Journal of Fermentation and Bioengineering 77(1):36-40.
Mosedale JR, Puech JL (1998). Wood maturation of distilled beverages. Trends in Food Science & Technology 9(3):95-101.
Owens J, Zimmerman L, Gardner M, Lowe L (2016). Analysis of whiskey by dispersive liquid microextraction coupled with gas Chromatography/Mass spectrometry: An upper division analytical chemistry experiment guided by green chemistry. Journal of Chemical Education 93(1):186-192.
Plutowska B, Wardencki W (2008) Application of Gas Chromatography–Olfactometry (GC–O) in Analysis and Quality Assessment of Alcoholic Beverages – A review. Food Chemistry 107(1):449-463.
Pietrek M (2015). From alchemy to science: Esters, aldehydes, mass spectrometers and hyper-accelerated mellowing. Available at http://cocktailwonk.com/2015/04/from-alchemy-to-science-esters-aldehydes-mass-spectrometers-and-hyper-accelerated-mellowing.html.
Piggott JR (2016). Whisky, whiskey and bourbon: Composition and analysis of whisky. In: B. Caballero PM, Finglas, F Toldrá (Eds), Encyclopedia of food and health Oxford: Academic Press pp. 514-518.
Pugliese J (2017). One Man's Quest to Make 20-Year-Old Rum in Just Six Days. Available at: https://www.wired.com/2017/05/brian-davis-lost-spirits-distillery-aging-rum-fast/.
Rarick CA, Mich CC (2015). The American whiskey renaissance: The rebirth of an American spirit. Journal of the International Academy for Case Studies 21(3):149.
Reazin GH (1981). Chemical Mechanisms of Whiskey Maturation. American Journal of Enology and Viticulture 32(4):283-289.
Rogerson LE (2016). Master's Thesis, University of Tennessee. Available at http://trace.tennessee.edu/utk_gradthes/3804/
Russell I, Stewart G (2014). Whisky: Technology, production and marketing (Second; 2; 2nd ed.). Amsterdam: Elsevier Academic Press.
Shyr J, Yang S (2016). Acceleration of the mellowing process in coffee liqueur by ultrasonic wave treatment: Acceleration of mellowing of coffee liqueur. Journal of Food Processing and Preservation 40(3):502-508.
Spedding G (2017a). 80 Years of Rapid Maturation Studies- Why Are We There Yet? Part 1 of 3. Distiller Magazine. Available at https://distilling.com/distillermagazine/80-years-of-rapid-maturation-studies-why-are-we-there-yet/.
Spedding G (2017b). Eighty Years of Rapid Maturation Studies: Why Are We There Yet? Part 2 of 3. Distiller Magazine. https://distilling.com/distillermagazine/eighty-years-of-rapid-maturation-studies-why-are-we-there-yet/
Spedding G (2018). Eighty Years of Rapid Maturation Studies: Why Are We There Yet? Part 3 of 3. Distiller Magazine. Available at https://distilling.com/distillermagazine/eighty-years-of-rapid-maturation-studies-why-are-we-there-yet/
Sun Z (2013). Accelerated Seasoning of Manuka and Oak Wood Chips Destined for Wine and Spirit Flavor. A thesis submitted in partial fulfilment of the requirements for the degree of Master of Applied Science. AUT University.
Terressentia Corporation (2016). Terrepure. Available at https://www.terressentia.com/about/terrepure/
USA Spirit Ratings (2021). A Brief Guide to the Top Whiskey regions in the USA. Available at https://usaspiritsratings.com/en/blog/insights-1/a-brief-guide-to-the-top-whiskey-regions-in-the-usa-45.htm#:~:text=Of%20course%2C%20the%20search%20for,Tennessee%20as%20a%20close%20second
Viriot C, Scalbert A, Lapierre C, Moutounet M (1993). Ellagitannins and lignins in aging of spirits in oak barrels. Journal of Agricultural and Food Chemistry 41(11):1872-1879.
Weber GR (1974). Accelerated aging of alcoholic beverages. United States Patent Office US 3787587.

Related Journals: