Sources of variation in bourbon whiskey barrels: a review

Jarrad Gollihue,1,2 Victoria G. Pook1,2 and Seth DeBolt1,2*

Oak barrels serve two purposes in the production of distilled spirits: storage containers and reaction vessels. It is the latter function which bestows barrel aged spirits with their unique and highly sought after flavour profiles. However, achieving consistent flavour profiles between barrels is notoriously difficult as no two barrels are comprised of the same source of oak. Source variation is due to a range of factors, beginning with the genetic and topographical background of the oak tree from which the barrel staves originate, the spatial region of the tree from which the stave was taken and continuing through each step of the barrel production process. In this review, we detail each source of variation and highlight how this variation affects the reactants present in the barrel staves. The effect of pyrolysis on biomass is explored and how this knowledge relates to barrels that undergo the practices of toasting and charring is discussed. We also detail the significance of variation in the availability of reactants during the maturation process. The goal of writing this review is to identify areas of needed research, stimulate research and encourage investigation into the possibility of creating barrels with more consistent properties. © 2021 The Authors. Journal of the Institute of Brewing published by John Wiley & Sons Ltd on behalf of The Institute of Brewing & Distilling.

Keywords: Bourbon whiskey; cooperage; oak; stave; maturation

Introduction

According to Future Market Insights, the cooperage industry is projected to be a US$5.2 billion industry by 2027 (1). Growth in this sector of the wood products industry is in part driven by increasing demand for bourbon whiskey, which, by definition, requires aging in a new barrel constructed from American white oak (Quercus alba) (2). To highlight this boom, roughly 790,000 barrels of bourbon were filled in Kentucky in 2009 with 1,700,000 barrels filled in 2019 (3). The cost of these American white oak barrels varies depending upon many factors based on scale and specification of construction with a general range from $150 – $500 a barrel. The methods and processes (Fig. 1) employed by cooperers have remained largely unchanged across the centuries, with the addition of metal hoops constituting the only major modification. However, although these practices are carried out in a similar manner, cooperages often use custom made equipment and many of the specifics, such as the duration of toasting and charring and the temperatures applied to barrels during these procedures, are typically trade secrets. There is a dearth of academic research in this area and causal relationships among these variables are not yet established. With this review, we aim to compile the information that is available and provide guidance on which relationships warrant further study, with a focus on barrels destined for whiskey production.

Diversity at the source: oak trees

Ranging from the Mississippi River to the eastern coast of the United States (4–7), the first source of variation among barrels is the oak tree itself. American white oak trees are not clonally propagated like grapevines in vineyards, and they do not inbreed. Rather, these trees are monoecious with separate male and female flowers, resulting in outcrossing events between two parents. Therefore, while sibling level similarities are plausible, populations carry inherent genetic variance. Oak for stave production is also harvested from natural stands rather than plantations (8). Efforts to improve growth rate and stand uniformity by selective breeding have been reported, yet more work is needed (9). When harvested at the age of 70-100 years, an oak tree has experienced a unique set of biotic and abiotic stimuli. These differences combine to produce trees with unique extractable profiles, each capable of interacting with distillate in a different way (4, 7, 10–14). Though it has long been known that oak barrel staves impart flavours to bourbon whiskey, understanding how the volatile profiles of oak may be predicted or controlled presents an opportunity for premium barrel aged products. As the demand for barrels increases, the importance of the science of cooperage is becoming more pronounced with regard to improving the extracted flavour and also the traditional focus of efficiency in barrel production.

Barrel staves, like any other wood product, comprise a matrix of biopolymers (cellulose (15) and hemicellulose) and phenolic compounds (lignin) (16–18). Within this matrix, components reside such as hydrolysable tannins (5, 6, 10, 19–21), tyloses, lipids (22), whiskey lactone (23), and other trace compounds (24). While many of these components remain constant, regardless of the environment in which the oak tree has grown, ethanol or other solvent extractable compounds have been found to vary (6, 19, 20). The significance of this variation was investigated by Marco et al. (14),
who conducted a sensory evaluation of whiskey from barrels that had each been constructed from oak trees grown in a single stand. The study concluded that the sensory characteristics of the whiskey varied with the stand from which the barrel staves originated, leading to the idea that barrels, like grapevines, may have a terroir. However, Marco and others could not predict the major drivers (soil, humidity, rainfall, topography, etc.) for terroir in oak stands (14). The terroir for oak found by Marco was geographical and forest based for French oak, but such a relationship could not be found for American oak. Understanding these features could provide a rational basis for quality improvement. Furthermore, gene-environment (GxE) interactions are known to further complicate phenotypic responses and therefore would also need to be addressed. Perhaps, a study of the topography of forest regions in the United States could generate a similar understanding compared to the French forest districts or allow for a rational basis for quality improvement of American oak.

An additional variable is the genetic background of the tree (Table 1). The genus *Quercus* comprises of about 600 species and is divided into two subgenera, each with a number of sections. The sections *Quercus* (white oak) and *Mesobalanus* (Hungarian oak), both found in the subgenus *Quercus*, are important for barrel construction. Hybridisation commonly occurs among species from a given section or subgenus, particularly as they are wind pollinated and monoecious (25). There are several factors that may contribute to the prevalence of interspecific hybridisation including weak biological barriers to prevent hybridisation and an inability to discriminate against the pollen of species from a related subgenus (25). A deeper understanding of this may reveal some interesting effects. For example, shifts in morphological traits

---

**Figure 1.** Overview of barrel construction focusing on the how and when variation is introduced. Barrels are produced from oak trees that are cut into logs, processed into staves, then stacked, and weathered. Staves are then assembled into a barrel. Once assembled, barrels are charred with a torch, finished, filled with bourbon whiskey, and stored into a rickhouse to mature. [Colour figure can be viewed at wileyonlinelibrary.com]
create difficulties when attempting to identify white oak trees for harvest (5, 26–28).

In Mexican red oak, hybridisation resulted in shifts in leaf morphogenic traits within specific geographic locations (26). This shift occurs from introgression suggesting that the genetics underscoring a specific leaf trait within a particular species of red oak may vary across its range. Studies linking genetics to morphology have found evidence of hybridisation and introgression between oak species (25, 26, 29). It is plausible that a similar level of variation exists in white oak across its range and this may be an important, and as yet unexplored, factor in barrel variation (13). For example, genetic variation has the potential to impact on stave wood via differences in extractable compounds, biopolymer composition, grain, and tylose content. Studies on the hybridisation and shifts in morphogenic traits in Quercus petrea and Quercus robur have found no link between chemical and anatomical or morphological characteristics but rather the chemical composition and content found in the populations of both trees is an overlapping continuum. It would be interesting to see if the same is found in mixed stands of Quercus alba in the United States (5). These studies will certainly have value but a summation of previous work in Quercus populations indicates some degree of intergradation and hybridisation (5, 26, 30). This idea of an overlapping continuum in mixed stands is interesting but significant differences have also been reported between the various oak species (4, 7, 13) (Table 1).

### Variation in stave production

In addition to genetic variation in oak species and subspecies (9) and environmental factors that could lead to variation in the properties of stave wood (16), the way in which the wood is selected and processed can also play a significant role in creating variation in the resulting barrel aged distillate. The following subsections critically evaluate the cultural treatments during cooperage and how these could influence reactions during maturation.

#### Stave log selection

Stave logs are selected based on their size and the quality of their grain (31). In general, the white oak trees considered large enough to produce stave logs are more than 70 and up to 120 years old. As an oak tree grows, it lays down ‘earlywood’ and ‘latewood’, the sum of which produces the annual growth ring (16, 31). The pattern of these rings is known as the grain and is used as a metric for the quality of the wood. It may be described as tight (1-3 mm) or wide (3-10 mm) (31). The grain influences the porosity of the wood and determines the amount of dry matter that interacts with the liquid within the barrel. It also

### Table 1. Sources of variation in barrel production

| Step          | Source(s) of variation                                                                 | Possible effects                                      |
|---------------|----------------------------------------------------------------------------------------|------------------------------------------------------|
| Tree          | Genesitis (26, 27)<sup>26, 27</sup> Species (13)<sup>13</sup> Growth location (9, 14)<sup>9, 14</sup> Biomass composition (15)<sup>15</sup> Grain density<sup>15</sup> | Variation in soluble compounds (42) Variation in ring density: oxygen diffusion Variation in extractables and biomass |
| Cutting       | Variable amount of white wood (134)<sup>134</sup> Location of board in tree<sup>134</sup> Quarter sawn/split<sup>134</sup> | Variation in composition (19) Variation in extractable (19) Variation in wood structure |
| Weathering    | Stack location: Geographical and within stack locations (11)<sup>11</sup> Microbial population and community (47)<sup>47</sup> Duration (50)<sup>50</sup> Precipitation Exposure | Alters oak composition (138) Alters tannin content (44, 45) |
| Kiln drying   | Temperature and duration (21, 54)<sup>21, 54</sup> | Alters biomass composition Alters tannin content (51) |
| Raising       | Number of barrel staves<sup>31</sup> Thermolysis (53)<sup>53</sup> | Alters joins number: oxygen diffusion (39) Alters biomass composition Extractive compound loss (45) |
| Bending:      | Exeptive (water/bending) (45)<sup>45</sup> | Alters extractable compounds formation (45) Alters biomass composition (68) Alters oxygen diffusion (39) Alters tannin content (12) (45) |
| Fire          | Hydrothermolysis (45, 52)<sup>45, 52</sup> | | |
| Steam Water   | Ramp rate (85, 123)<sup>85, 123</sup> Duration (85, 118)<sup>85, 118</sup> | Alters extractable compounds formation (45) Alters biomass composition (68) Alters oxygen diffusion (39) Alters tannin content (12) (45) |
| Toasting      | Maximum temp (80)<sup>80</sup> Mineral content (74)<sup>74</sup> Acids (139)<sup>139</sup> Moisture content (71–73)<sup>71–73</sup> Biomass composition (68)<sup>68</sup> Oxygen content (68, 85, 119–123)<sup>68, 85, 119–123</sup> Quench (85, 123)<sup>85, 123</sup> | | |
| Repair        | Cattail addition<sup>Unknown: May alter oxygen diffusion</sup> | |

© 2021 The Authors. Journal of the Institute of Brewing published by John Wiley & Sons Ltd on behalf of The Institute of Brewing & Distilling.
affects the quantity and the rate at which oxygen diffuses through the wood (32, 33). Coopers prefer to use stave logs with tight grain but over the past 150 years, grain density has generally decreased while wood volume has increased due to human management (34). This preference for grain profiles may not be a necessity for maturation in bourbon as the oak used for cognac maturation is from fast growing Limousin oak (a forest in northwest France, which has a mixed species of Q. petraea, Q. pubescens and Q. robur) with a looser grain structure (27, 35). This highlights that various cultural elements of stave processing may be more important than grain with regard to oxidation, recovery and maturation. This is an area that would benefit from further exploration (personal communication, Andrew Wiehebrink). Accordingly, modern coopers do not always have the choice as grain is influenced by a variety of factors (31–33, 36, 37) including the oak species, genetic fitness, silviculture management and geographic location (31, 36).

Wood cutting/splitting

Logs selected for stave production are first debarked and cut into smaller pieces (Fig. 2A). These smaller pieces are then either cut into staves if using American white oak or split into staves if using French oak. Though cutting barrel staves generates less waste than splitting, the properties of French oak necessitate splitting, as barrels made of such wood will leak if the staves are cut (36, 38). When cutting American oak, a series of passes with a blade first divides the log in two, and then into four, to form quarter bolts (Fig. 2B). Each bolt is then sawn in a manner that ensures every

---

**Figure 2.** Barrel construction, anatomy, and nomenclature. Barrels are produced from oak logs (a) which are composed of bark, sapwood and heartwood. Logs are debarked and cut into quarter bolts (b) which are further cut into rough boards by sawing (c). As efficacy is important in American barrel production the maximum amount of boards are cut from each quarter bolt. This leads to variation in the width of in the rough cut boards and in the final barrel staves. The sapwood (c 5/v) is generally considered undesirable and is therefore discarded. Barrel heads (g) are created using staves with a tongue and groove cut, with a bevel placed into the head, or in some cases dowel and pin. The heads are then charred and attached to the barrel. Barrel heads can also be formed using dowel rods to connect staves together and subsequently cutting the head to shape. The completed barrel (f) has a bung hole drilled into the bilge stave and the barrel is pressure tested. (Colour figure can be viewed at wileyonlinelibrary.com)
Variation in bourbon whiskey barrels

piece of wood can be used either for staves or heading (Fig. 2C). The process of splitting follows the direction of the grain as disrupting this pattern compromises the capacity of the wood to be watertight. Similar to quarter sawing, the first split produces two half short bolts which are further split into quarters. The quarters are then split into triangular sections that are worked into staves. The difference in yield between the different methods is significant with quarter sawing producing double the quantity of staves (39). It can be hypothesised that the practice of cutting versus splitting affects the penetration of oxygen into the distillate and the penetration of distillate into wood, but this comparison has yet to be made.

Freshly cut barrel staves are composed of both heartwood and sapwood (also known as whitewood in the cooperage industry). Sapwood is the living tissue in the trunk and the ‘limbs’ that conduct water through the tree (36, 40). It is visibly lighter in appearance than the heartwood found in the centre of the tree (6), which is non-conductive and is regarded as non-living (31, 40). The chemical composition of whitewood and heartwood is very different and large amounts of sapwood in staves is generally thought to be responsible for decreased liquid recovery per barrel and undesirable flavours in the distillate (personal communication, Andrew Wiehebrink). However, it should be noted that there is no evidence of this hypothesis being either tested or published. Due to the preference for staves made from heartwood, the amount of whitewood present in each stave is low with the tolerance varying among producers.

Seasoning and drying

Before fresh staves are ready to be coopered, they are seasoned for up to five years (41) (Table 1). In addition to enabling staves to be successfully joined into barrels, the seasoning process leads to measurable changes in the volatile profiles of wood. Most significantly, the green aroma that is associated with fresh cut wood is lost (10–12, 42–44), with seasoned staves possessing milder aromas of coconut and celery (36, 45). The environmental conditions that the stave wood is subjected to during seasoning alters the amount of whiskey lactone (42), vanillin (46) and hydrolysable tannin (19) present in the wood. In addition, the geographical location in which the stave wood is seasoned also affects the volatiles present in the staves (11, 12). Finally, a plethora of microorganisms take up residence in stave wood during seasoning and they too influence its aroma and constituent biopolymers. Further, longer seasoning of stave wood has been reported to reduce whiskey lactone content (44, 47–50).

Though the abiotic factors influencing the properties of stave wood are beyond our control, there is an opportunity to further our understanding of the effects of microbial communities and geographic location. Communities of microorganisms growing on barrel wood have been shown to alter barrel flavour (11, 44, 47) and could be considered to be part of the terroir. These microbial communities can be manipulated by the simplest of changes, e.g. altering the pattern in which the stave wood is stacked (personal communication Andrew Wiehebrink). These communities could also be artificially modified through sterilisation and/or inoculation and the resulting effects on structural biopolymers and the generation of volatiles measured.

After stave wood is seasoned it is dried. Wood is hygroscopic and, therefore, most cooperages will kiln dry stave wood to achieve the desired moisture content of 14-18% (36, 47). In addition to sterilising the surface of the stave wood, kiln drying degrades ellagitannins and partially degrades the xylene and glucomannan fractions of hemicellulose (51). The degradation of these biopolymers leads to the production of reactants that play an important role during whiskey maturation.

Variation in barrel production

Raising and shaping

After the stave wood is kiln dried it is shaped into trapezoids which can be formed into a barrel in a process known as ‘raising’. This is carried out through the manual selection of staves to fill a head truss ring around a stand. Staves vary in width and therefore, barrels vary in the number of staves used in their formation (28–32). This variation is important to consider as stave joints constitute the major avenue through which oxygen enters the barrel during whiskey maturation (33). To date, studies of dissolved oxygen ingress into a barrel are not well defined. After the final stave is placed into the head truss, the staves are encircled with a cable that is drawn to the size of the hoop, keeping the wood in place, while it is bent into shape using the application of heat. This can be achieved via fire, water or steam and each method has the potential to alter the extractable compounds in the barrel staves.

Thermal forces are applied to facilitate bending of staves. In some cases, the raised staves are set over an open fire, causing the heat to be funnelled into the confined space of the barrel interior. Tannin is easily degraded by heat (51) and it is likely this process leads to increased conversion to gallic acid in the barrel staves. Bending staves using water entails soaking the entire barrel in water at a temperature of 82°C for 20 minutes. During the soaking period, it is likely that many of the water extractable compounds are removed from the wood penetrated by water. However, to date no quantitative assessment of the amount or rate of water soluble extraction has been performed. Steaming, the third alternative, varies among cooperages, with the temperature ranging from 160 to 180°C, for a period of 20 minutes. Exposure to steam at such temperatures for such a duration can lead to hydrothermolysis of the biopolymers in the staves as this has been shown to occur in other systems (45, 52). In addition, the thermal pressure applied during steaming may produce similar results as exposure to fire, in that tannin may be degraded, producing gallic acid. All three of these thermal applications are capable of altering the profile of volatile compounds present in the staves. There is a clear gap in the literature regarding which reactions take place and the rate at which they occur, in addition to which extractables are lost.

Thermal modification

After the staves are made pliable through the application of heat, they are shaped into a barrel using a windlass, and metal hoops are placed around the circumference. The interior surface area of the barrel is now ready for thermal modification. In the case of barrels destined for the production of bourbon whiskey, this is generally achieved through charring, a chemical process akin to fast pyrolysis.

The interior of the barrel is charred by the direct application of a natural gas flame for a minimum of 15 seconds (36). The exact time varies among cooperages and is adjusted according to the purpose of the barrel. Cooperages also experiment with, produce, and sell barrels subjected to a combination of toasting and
charring. Toasting, which is usually reserved for barrels destined for wine maturation, is achieved by setting the barrel around a fire of oak wood scraps. The heat produced by the fire is funnelled up into the barrel, which remains in place for the duration of the toast (53). Barrels which have been subjected to both thermal treatments have the physical appearance of a deeper char than those that only undergo charring (personal communication, Andrew Wiehebrink).

The temperature and duration used during thermal modification of barrel interiors vary with the producer and each cooperage has its own unique grading system (5, 45). For example, a barrel may be toasted at a temperature that ranges from 47 to 240°C, and this thermal treatment can last for many hours (21, 54). Each biopolymer within the stave wood can withstand a different intensity of heat, with hemicellulose (composed of mostly xylan and glucomannan (55)) breaking down first at around 225-325°C, followed by the β-1,4 linked glucan crystalline cellulose at 315-440°C. Lignin is the component that is the most recalcitrant to thermal degradation, with some motifs withstanding temperatures up to 900°C (56–58). However, lignin degradation begins at around 200-275°C, with the majority of the motifs degrading at around 400°C (59, 60).

The degradation of these biopolymers leads to the presence of extractable compounds that are incorporated into the distillate in the barrels, affecting the flavour profiles of matured spirits (7, 10–12, 43, 53, 54, 61–65). It is important to note, that the temperature at which biopolymers are known to break down is much higher than the temperature at which the barrel is toasted, but despite this degradation still takes place. This phenomenon could be due to atmospheric oxygen lowering the temperature at which pyrolysis reactions occur in the stave wood (66–68). An explanation of the physical mechanism behind this is explored later in this review.

Achieving consistency in thermal modification has proved to be a challenge, even when using industrial methods (53, 69, 70). Recent work demonstrates that the moisture content (71–73), ash content (74, 75) and variation in wood composition (76–78) of the starting material can affect the outcome of the thermal treatment. In addition, interactions between cell wall components (cellulose, hemicellulose and lignin) and the physical structures of the biomass (79) affects the generation of extractable compounds. Further, the thermal ramp rate, maximum temperature and oxygen content of the thermal treatment are all influential factors (80). It is important to note that an additional unknown factor is how the heat is transferred through the staves during the thermal treatment.

Cellulose and hemicellulose generate the compounds furfural, 5-(hydroxymethyl)furfural, cyclotene, maltol, acetic acid and methanol (65). These breakdown products are of interest as they are extracted or degraded and converted to further products during the maturation process along with the wood polymers themselves. The degradation of carbohydrates generates furans, whereas the degradation of lignin generates vanilla and various phenols (16, 43, 47, 53, 54, 65, 81).

Barrels destined for bourbon whiskey production must be charred. The sensory characteristics of distillate aged in a new charred oak barrel are influenced by the charring process. For example, the accumulation of vanillin and compounds that are produced when lignin is at a high oxidation state, make positive contributions to the volatile profile of whiskey (17, 62, 65, 82). The rich colour of bourbon, on the other hand, is due to the layer of toasted stave wood beneath the char (83, 84). Charring can be achieved by an intense toasting fire that ignites the barrel or, alternatively, by direct application of a natural gas flame, and each technique may yield different compounds. For example, charring by toasting fire could yield more combustion products, whereas charring via natural gas flame creates conditions closer to those found during fast pyrolysis (85). The charring process leads to the carbonisation of some of the biopolymers resulting in a layer of active charcoal on the inner surface of the barrel (65). This may help remove impurities that are present in the distillate aged in the barrel. It should be noted that this effect is minor and sulphur impurities present in unaged whiskey will still be found in the finished product resulting in greasy, soapy notes (86). A question that could be explored further is to what extent charring leads to carbonisation and how effective this carbon is at removing compounds in quantities that affect the sensory profile of whiskey. Such experiments could be expanded to include the physical and chemical properties that result from different levels of char.

An area that is currently receiving a lot of attention and undergoing significant development is the usage of infrared emitters in the toasting process, instead of traditional fire pots. This enables greater control and consistency than the traditional toasting method which suffers from significant fluctuations in temperature (53). These emitters have the potential to be consistent not only in temperature but also in the wavelength of energy being transmitted. Different wavelengths have the potential to alter barrel wood in different ways as longer wavelengths are reflected whereas shorter wavelengths are absorbed, transferring thermal energy.

### Thermolysis and pyrolysis: mechanisms on how cell walls contribute flavour

There are several types of reactions that occur when biomass is subjected to thermolysis, and though the focus is on pyrolysis, other reactions are likely to take place in white oak barrels coopered for the bourbon industry. The idea that carbonisation is the only outcome of pyrolysis is outdated – barrel staves are modified in a variety of ways as a result of this thermal treatment, an example of which is the production of desirable oils (83). Accordingly, here we explore the chemistry of the thermal degradation of cell walls as it pertains to flavour development in oak barrel aged whiskey. Though the products of these reactions are influenced by the variation described above, the mechanisms by which they occur remain constant. Much of our understanding in this area comes from research into the conversion of biomass to value added products, and these findings are adapted to the cooperage practice.

Oak is composed of a mixture of different biopolymers (cellulose, hemicellulose, and lignin) that each have their own kinetic characteristics and are affected differently by pyrolysis. Cross-reactions of primary pyrolysis products and between pyrolysis products and the original feedstock molecules also occur (68, 79, 80, 85, 87–91). Although, when a barrel is charred, the decomposition of these polymers occurs simultaneously and in some cases the products interact with each other (68, 79, 80, 85, 87–91), each polymer will be explored individually. Understanding the chemistry of these processes is crucial for research into flavour development and barrel variation and could lead to innovation. It should also be noted that the charring and toasting reactions are further complicated by the addition of an ethanolaqueous solvent typically varying from 107 to 125 proof (53.5-62.5% ABV). The polarity of the solvent changes with the proof of the distillate added...
to the barrel and this, in turn, may influence extraction and reaction chemistry.

Pyrolysis is the thermal decomposition of materials in the absence of oxygen or in the presence of a quantity of oxygen that is insufficient for complete combustion (79, 80, 85, 88, 89, 91). The process for the thermal upgrading of plant cell walls to hydrocarbons was described in Mohan et al. (85). Considering that many of the same plant cell wall biopolymers exist in both study systems this concept has been used as a proxy for barrel pyrolysis.

Firstly, heat is transferred from the source to the barrel stave and the temperature of the barrel stave increases. Primary pyrolysis reactions are initiated, volatiles are released, and char is formed. Heat is then transferred on a gradient from the hot volatiles to the cooler parts of the stave that have yet to be pyrolysed. Tar may be produced if these hot volatiles condense in cooler parts of the stave and secondary reactions occur. Simultaneous autocatalytic secondary pyrolysis reactions and primary pyrolytic reactions compete with each other. The residence time/temperature/pressure profile of the pyrolysis process influence the occurrence of further thermal decomposition, reforming, water gas shift reactions, recombination of radicals and dehydrations. Since the density and composition of the barrel wood is variable due to the factors described above, it can be envisioned that this pyrolysis reaction could yield different products even if taken as steady state reactions.

Pyrolysis degradation occurs through radical driven breakdown of cell wall components (68, 79, 80, 85, 87–89, 92). The polymers are sheared generating monomers along with other breakdown products. Other chemical processes occur during pyrolysis such as steam explosion and chemical dehydration, due to the vaporisation of trapped moisture and the presence of heat, respectively (85, 87, 90, 93–95). These two processes influence how cellulose breaks down during charring. Cellulose makes up about 35% of bourbon barrel wood (15). Chemically, cellulose is a linear polymer of B- (1-4)-D glucopyranose units in a $\beta$-C$_4$ conformation. The cellulose polymer is stabilised by the chair structure formation of 5,000-10,000 glucose units that form long chains stacked on top of each other in 180° orientation to the next chain (56, 95–97). This allows for both intramolecular and intrastrand hydrogen bonds to hold the strand flat, allowing the strands to stack effectively (98). This structure gives cellulose a crystallinity that is difficult to break down under most conditions (96).

Though the crystalline structure of cellulose provides resistance to thermal breakdown, the rapid heating of wood containing moisture (e.g. barrel staves), causes a steam explosion-like process that is capable of disrupting the cell wall structure. The main pathway by which cellulose is degraded during pyrolysis involves the production of a glucose radical. This radical is generated by thermal inputs via bridging oxygen from the preceding monomer unit (94, 99–101). Studies that have mapped the breakdown of cellulose in isolation indicate the first compounds to arise during breakdown are anhydro sugars, furans, and char. These products are formed as the carbohydrates released from cellulose are dehydrated (91). These reactions are the first to occur (at around 300°C) under controlled conditions. Secondary reactions then generate acetic acid and other compounds (91, 102–104). Direct formation of acetaldehyde, furans and 2 (H) furanone require temperatures of 400–500°C (91).

Hemicellulose is a complex carbohydrate polymer that consists of several different monosaccharide subunits that vary in their composition but overall make up about 33% of the wood used in the construction of bourbon barrels (15). Hemicellulose is composed of glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid and galacturonic acid residues that form a polymer of roughly 150 units – considerably fewer than cellulose (55, 89, 91, 105–108). These shorter chains have branching side chains that decorate the central xylan polymeric strand. These shorter chains are decorated with acetal groups which become acetic acid when liberated from the polymer.

Lacking the structural elements found in cellulose, hemicellulose degrades at lower temperatures (130-260°C) and generates more volatile compounds and less char (79, 90, 91, 107, 108). The pyrolysis of hemicellulose can occur at lower temperatures if the duration of thermal exposure is increased (79, 89–91, 108). The mechanism by which hemicellulose is degraded during pyrolysis is still far from understood, but significant progress has been made regarding the identity of the breakdown products and the conditions under which they are generated. Studies using xylan polymers as a model for hemicellulose indicate that breakdown occurs at an earlier stage of the pyrolysis process. The products generated require another carbon in addition to the 5-carbon starting monomer, which indicates the polymer is undergoing depolymerisation and rearrangement followed by dehydration to yield furans and phloroglucinal (91).

Lignin is a phenolic polymer that is amorphous with no exact structure. It binds to cellulose providing protection against biological degradation (18, 59, 91, 109–113). Cellulose and hemicellulose are carbohydrate based polymers, whereas lignin is a phenolic based polymer composed of three monomers (p-coumaryl, coniferyl, and sinapyl) that are polymerised in a different way through radical dimerisation. The polymer that results from this radical chemical assembly is highly branched and three dimensional in nature with a variety of irregularly combined bonded units (18, 89, 91, 109, 111). The number of specific subunits in lignin found in trees varies according to whether they are hardwoods or softwoods (79, 89, 91, 109). Oak is a hardwood and, therefore, is composed of guaiacyl-syringyl lignin along with a copolymer composed of coniferyl and sinapyl phenylpropane units (18, 59, 91, 109–113).

The radical assembly of lignin subunits results in many possible resonance hybrid structures and this heterogeneity is increased further through nonselective random condensation (79, 89, 91, 109). Lignin has other bonds that occur between linked subunits, most of which are ether linkages but carbon to carbon linkages can also be found. These covalent linkages allow for lignin to bind to the hemicellulose and cellulose polymers found in wood (79, 89, 91, 109). There are, as yet, no studies that compare lignin pyrolysis in the white wood and heart wood of white oak or across white oak wood of various ages. This could be a fruitful avenue of future research.

Aside from 2-dimensional nuclear magnetic resonance spectroscopy (2D-NMR), it is difficult to conduct studies on the pyrolysis of lignin in naive biomass because the polymer is damaged or altered during isolation and, therefore, its properties vary depending upon the method of isolation. The complexity and variation of the lignin polymer makes comparisons between the products of pyrolysis and thermal decomposition difficult as each sample will exhibit significant variation prior to any treatment taking place (91, 111). Lignin is degraded over a temperature range of 280-500°C and yields phenols via the cleaving of ether and carbon linkages. Compared to the carbohydrates found in cellulose and hemicellulose, which are easily chemically dehydrated, the components of lignin are resistant to such processes (111). When lignin is assembled many different linkages are formed, the thermal stability of which
varies significantly. The linkages observed are influenced by the method of isolation and can shift product from pyrolysis. While these studies are interesting, the results are unlikely to be directly applicable to barrels as the materials are dissimilar. Further studies in which more naive material is tested could help establish whether or not an association can be made here. Through the use of model dimers, understanding of how lignin reacts to thermal inputs has improved. Linkages found in lignin are β-ether, α-ether, β-aryl, β-β and biphenyl. During primary pyrolysis α- and β-ether bonds are readily cleaved, whereas condensed (C—C) type linkages remain stable (114–116). Lignin species also have various side chains that play roles in the chemical transformation that occurs during pyrolysis. These side chains are unsaturated alkyl, ethyl propyl, methyl and hydrogen groups (111). Such side chains can themselves react during pyrolysis and be converted to other substrates.

During the pyrolysis of lignin linkages various reactions occur, such as homolysis and heterolysis cleavage of C-O and C-C bonds, allowing for lignin with a β-ether suture to yield styrene and phenol (111). The cleavage of the ether linkage - the primary linkage in lignin - is critical for the depolymerisation of this polymer. The cleavage of each of these linkages generate different starting materials that are broken down during pyrolysis through a complex set of reactions (89, 90, 111). However, the products generated can be classified into three types: (i) those that are stable, (ii) those that are capable of repolymerisation and (iii) those that become char. Where barrel aroma is concerned, it is the stable products that are of the most interest as they can be extracted. The repolymerised portion of the lignin is more difficult to extract and as noted above several questions remain about char. If understanding of thermal reactions in lignin could be optimised, it may be feasible to adjust the yield of vanillin breaking down from the parent lignin model, but it will likely require detailed 2D-NMR studies combined with predicted heating regimes.

There are a variety of conditions under which pyrolysis chemistry occurs and a subset will be explored that are most likely found in bourbon barrels. Pyrolysis yields several different products from wood as breakdown occurs but broadly these compounds can be classified as char, bio-oil, and gas (85). The oil and char fractions are more likely to directly influence flavour development via extraction, whereas the gas fraction interacts throughout the process. Bio-oil is a combination of the following compounds: guaiacol, catechol, syringol, vanillin, furancarboxaldehyde, isoeugenol, pyrone, furan, acetic acid, formic acid, carboxylic acid hydroxylaldehyde, hydroxyketone, sugar, carboxylic acid, and phenolics (85, 117). Alteration of the pyrolysis method leads to the generation of different products and rapid quenching of the reaction can yield intermediate products. Traditional pyrolysis, as noted above, is carbonisation (85). In order to achieve carbonisation, the material is required to be heated for days at a low temperature, with a maximum of around 400°C resulting in charcoal (118). Conventional pyrolysis occurs over a period of 5-30 minutes, with material slowly being heated to 500°C (85, 118). This method is more akin to char-ring methods practiced in some cooperages that use a modified toasting fire to char the interior of the barrel over 30 minutes. During conventional pyrolysis, the gas produced does not escape and thus these gases react and form alongside the char and oil fractions.

Quick pyrolysis is the process of heating material very rapidly to pyrolysis temperature and generally this is performed in the absence (or minimal amounts) of oxygen (85, 119–122). Quick pyrolysis results in the production of vapours, a dark brown mobile liquid and some charcoal like char along with the biomass being decomposed (85). The conditions that separate quick pyrolysis from the other process is the very high ramp rate along with rapid quenching (85, 123). Although other conditions found in quick pyrolysis for fuel production studies such as fine particle size, short reaction duration and carefully controlled temperature range (<2 seconds) are not applicable to barrels (85, 124), the conditions overall are similar to those found when a barrel is charred with a natural gas torch. The products of the two processes are similar and the barrel is charred at a very high rate. In addition, when a barrel is charred, the temperature range is controlled, and the duration of charring tends to be less than 5 minutes, and is therefore less similar to conventional pyrolysis (85, 118).

Most studies examining pyrolysis are conducted under inert atmospheric conditions where material is placed in a chamber with oxygen displaced by nitrogen, helium or in a vacuum (66–68, 125, 126). The findings of such experiments can be difficult to apply to a cooperage setting. However, there are a small number of studies that investigate the interplay between oxygen and fast pyrolysis chemistry. Results of such studies indicate that the presence of oxygen lowers the active pyrolysis temperature and boosts the combustion of char at higher temperatures, in addition to increasing the decomposition of biomass (66–68, 125, 126). This results in an activation energy that is lower in the presence of oxygen and may explain how cell wall degradation occurs in oak products at temperatures below what would be expected. Fast pyrolysis occurs when wood is exposed to a high temperature with a very quick ramp rate in the absence of oxygen or in the presence of a low quantity of oxygen that is consumed very quickly (127–131). This process generates vapours, charcoal-like char and brown liquid condensate that has many compounds of interest to both whiskey and biofuel producers (65, 85, 132, 133). Quick pyrolysis most likely occurs during the barrel charring process, where a natural gas torch is directly applied to the interior of the barrel.

Another issue that needs to be considered while seeking to link pyrolysis studies to understanding barrel compound formation, is that many studies work on isolated cellulose, hemicellulose, and lignin. When these biopolymers are broken down simultaneously, they interact and alter the resulting products (134). It is also noteworthy that products formed during pyrolysis may interact with catalysts influencing subsequent reactions. Though many studies in this area examine exotic substances, a similar effect can be achieved with mineral elements such as calcium, potassium, and sodium found in wood. Each of these elements interact differently with each of the cell wall polymers (74, 76, 87, 89–91, 124, 135, 136).

The chemistry of pyrolysis is complex even in the most controlled experiments that use small uniform particles and uniformly heated reactors. The charring of an oak barrel cannot be carried out with this level of control, adding variables and uncertainty to an already complex process. Figure 3 provides a diagrammatic representation of the processes that occur when the interior of a barrel is charred with a torch. The heat from the torch is transferred through the staves resulting in a range of thermal conditions. Interestingly, the char that builds up on the surface of the staves insulates the interior, slowing the process of degradation - a concept that is applied to the development of ablative materials used on rocket nozzles (137). The process starts as heat enters the barrel through convection and radiation, raising the temperature of the surface of the staves, leading to the decomposition of the wood and the
release of pyrolysis gasses. The heat from the surface is then conducted into the interior of the stave. This pattern of thermal treatment results in barrel staves with two separate zones, namely a char zone, which is degraded via pyrolysis, and a thermally degraded zone (known as the ‘brown layer’), which is degraded indirectly. This thermally degraded zone is in need of study as the effect of thermal treatment occurs on a gradient throughout the barrel stave and has the potential to be critical for whiskey flavour development.

An additional factor to take into consideration when investigating the barrel charring process is the physical structure of the stave wood. For example, Figure 3 shows how the pores and the cell lumina can trap volatile organic compounds. Therefore, despite the fact that wood is technically a solid, thermal transfer through the staves is non-uniform, affecting the occurrence of liquid and gas phases and influencing the various reactions taking place.

Future work investigating new barrels would benefit from detailed documentation of the wood composition and mineral content of staves. As explored above, many factors influence pyrolysis chemistry and thus the formation of compounds that are extracted by whiskey during maturation. To understand how these processes might affect the whiskey that is produced, a detailed analysis of new barrel staves is required. The production process, history and handling of barrels should also be reported in as much detail as possible as much of the variation in compound formation is likely to occur as a result of minor changes in production processes.

**The effects of barrel variation on whiskey maturation**

The variation in volatile and extractable compounds found in barrel staves is well documented yet poorly understood. Lists of compounds found in whiskey were compiled by Lee et al. and Collins et al. and their tabulated summaries are an excellent resource. As described above, identifying where the variation in these compounds arises can be difficult. But if variation leads to shifts in the composition of cell wall biopolymers that are available to be degraded during maturation, then in turn, it is expected that measurable changes in the volatiles that
are formed will occur (65, 142). This is evidenced by changes in the volatile profile of whiskey that undergoes sequential maturation in different barrels (64). The combination of these factors means that homogeneity in the cooperage process is difficult to achieve. However, the situation does create opportunities for innovation.

Whiskey maturation within barrels is complex as extractable compounds are formed from biological factors and modified through thermal treatments. Cell wall compounds are hydrolysed and then undergo further reactions that generate volatile compounds (15–17, 65, 82, 140). There are two major chemical reactions that occur during maturation – transesterification (64, 65) and Fenton chemistry (143, 144). Transesterification is the reaction of alcohols and acids to form esters, many of which have fruity aromas. Ester formation occurs as a function of time during whiskey maturation, and it may occur independently of the barrel (36, 65). Whiskey functions as a solvent and therefore the oxidation reactions that occur during maturation include compounds extracted from the barrel. The oxidation state of wood derived compounds, specifically lignin compounds, increase as a result of charring (64).

Oxidation in food products is generally considered to be negative and is associated with spoilage. However, in whiskey, oxidation is critical to flavour development. Though Fenton chemistry is still yet to be understood completely, the signs of this chemical process have been documented as ethanol changes to acetic acid and acetaldehyde (36, 64, 65). Fenton chemistry in wine has been studied extensively and, while the mechanisms of this process are still being dissected (144, 145), there is consensus regarding the identity of particular products. Hydrogen peroxide, for example, is produced as a result of phenolic compounds reacting with oxygen and the charge state is regenerated from iron and copper ions (145, 146). The implications of these reactions are interesting and deserve investigation in barrel aged distilled spirits because many volatiles are likely to be the same as those produced in port (142), cheese or rancid cooking oil (147, 148). In whiskey, the rate of oxidation is influenced by the composition of polyphenols, the presence of transition metals, pH, temperature, dissolved oxygen content and ethanol content (144). Barrel wood after pyrolysis is biochar and has the capacity to adsorb and desorb various compounds and metals. The unravelling of these relationships could present a rewarding area of study particularly in barrels that are used for a second time (63,149).

It is likely that other chemical reactions are occurring during whiskey maturation. It is important that in our efforts to elucidate these chemical reactions we are also able to understand their impact on the sensory characteristics of the end products. Keeping this goal in sight will help to ensure that findings will be more easily adapted to the production and improvement of whiskey.

Whiskey aromas are highly complex and it is important to note that a change in the level of a single volatile can influence the entire sensory profile of the beverage (132, 150). In addition, volatile compounds can interact leading to alterations in the resulting aroma. For example, the high alcohol content of whiskey masks the fruity aroma of the esters formed during maturation (132), and the addition of furans alters the sensory characteristics of whiskey lactone (65). Whiskey is a complex mixture of alcohols, acids, esters, phenolics, and various other organic compounds and how these are balanced is influenced by the production process (151–154). Therefore, each product has a unique chemical ‘fingerprint’ which can be exploited in the development of anti-counterfeiting technology (155). Not to downplay the importance of such efforts, but exploration and attempts at understanding flavour development during maturation and possible interventions to change flavour have not been widely published and would be valuable to the industry.

Maturation studies offer crucial insight into a poorly understood process and more work in this area is needed. Such studies could provide insight into an important part of the production process and the lack of information in this area is a concern. Whiskey production is steeped in tradition and is conducted around the world under very different conditions. This variation in production has been enhanced further with the dramatic rise of the ‘craft’ sector of the industry. Though there may be some resistance from within the industry from those that would like to maintain tradition, it is clear that many distilleries value the impact that such studies could have. Unfortunately, there is a considerable amount of research by producers in the past that has either not been shared or lost due to employees retiring or leaving their positions. Publishing research findings in scientific journals not only benefits the industry as a whole but ensures that those carrying out research retain access to the results.

Conclusions and opportunities

The capacity for barrels to impact the flavour of distillate is fascinating and is of great value to the beverage alcohol industry. However, variation can be introduced by the natural environment in which an oak tree grows, at almost every step of the barrel production process, and during maturation. Continued studies into specific processes that take place within barrel staves are merited, particularly investigations into the chemistry and physics of these processes. Thermal modification of barrels, for example, significantly impacts the generation of volatile compounds, however this occurs in unpredictable ways (53, 54). Meanwhile, we are just beginning to understand the potential influence other cooperage processes, such as the weathering of barrel staves, may have. Other opportunities for study include careful evaluation of the influence of white wood on barrel quality and/or the flavour of the resulting distillate.

In conclusion, product variation comes from both biological sources and cooperage practices. Some factors, such as oak genetics, are beyond our control, but acknowledging their impact may help identify populations with common beneficial traits. There are some parts of the production process that lend themselves to research and this is where studies on barrel derived sensory characteristics should be focused. Examples include examination of wood flaws and taints, various thermal events, heat transfer through stave wood, and the exploration of wood polymer decomposition and how weathering conditions affect microbial communities.

Author contributions

Jarrad Gollihue - wrote the original draft of the manuscript
Victoria G Pook - reviewing, editing and figure building.
Seth DeBolt - supervision, reviewing and editing.
All authors have read and agreed to the published version of the manuscript.

Acknowledgements

We wish to thank the assistance of Andrew Wiehebrink and the independent stave company for relevant industrial production information. The authors declare no conflict of interest.
Variation in bourbon whiskey barrels

References

1. Analysis and review of wine barrel market by oak type - French oak, American oak, and Eastern European oak for 2019-2029. 2019. https://www.futuremarketinsights.com/reports/wine-barrel-market, (last accessed February 2021).

2. Labelling and Advertising of Distilled Spirits 1969 (US) s.5.22 (l) (1) https://www.ecfr.gov/cgi-bin/text-idx?SID=c7b5694734f535251e7126b2f0833bb8&mc=true&node=se27.1.122&rgn=div8

3. The economic and fiscal impacts of the distilling industry in Kentucky. 2019. https://kybourbon.wp.com/wp-content/uploads/2019/02/2019-Economic-Impact-Report_FINAL.pdf, (last accessed 10 February 2021).

4. Mosedale JR, Savill PS. 1996. Variation of heartwood phenolics and oak lactones between the species and phenological types of Quercus petrea and Quercus robur. Int J For Res 22: 47-55. https://doi.org/10.1093/forestry/69.1.47

5. Mosedale JR, Feuillat F, Baumes R, Dupouey JL, Puech JL. 1998. Variability of wood extractives among Quercus robur and Quercus petreae trees from mixed stands and their relation to wood anatomy and leaf morphology. Can J For Res 28: 994-1006. https://doi.org/10.1139/f97-7-994

6. Mosedale JR, Charrier B, Janin G. 1996. Genetic control of wood colour, density and heartwood ellagitannin concentration in European oak (Quercus petreae and Quercus robur). Forestry 69: 111-124. https://doi.org/10.1093/forestry/69.2.111

7. Prida A, Puech J-L. 2006. Influence of geographical origin and botanical species on the content of extractives in American, French, and East European oak oak woods. J Agric Food Chem 54: 8115-8126. https://doi.org/10.1021/jf0616098

8. Grossman BC, Gold MA, Dey DC. 2003. Restoration of hard mast species for wildlife in Missouri using precocious flowering oak in the Missouri River floodplain, USA. Agrar Syraf Syst 9: 3-10. https://doi.org/10.1023/A:1026147710797

9. Huang Y-N, Zhang H, Rogers S, Coggeshall M, Woeste K. 2015. White oak growth after 23 years in a three-site provenance/progeny trial on a latitudinal gradient in Indiana. For Sci 62: 99-106. https://doi.org/10.5849/forsci.15-013

10. Cadahia E, Munoz L, de Simon BF, Garcia-Vallejo MC. 2001. Changes in low molecular weight phenolic compounds in Spanish, French, and American oak woods during natural seasoning and toasting. J Agric Food Chem 49: 1790-1798. https://doi.org/10.1021/jf0006168

11. Spillman PJ, Sefton MA, Gawel R. 2004. The effect of oak wood source, and fumigation on the development of wine matured in oak barrel. Eur Food Res Technol 220: 533-547. https://doi.org/10.1007/ s00217-004-1252-3

12. Doussot F, Pardon P, Dedier J, De Jeso B. 2000. Individual, species and geographic origin influence on cooperage oak extractible content and its impact on wine quality. PLoS One 13: e0197135. https://doi.org/10.1371/journal.pone.0197135

13. Campbell JI, Sykes M, Sefton MA, Pollnitz AP. 2005. The effects of size, temperature and air contact on the outcome of heating oak fragments. Aust J Grape Wine Res 11: 348-354. https://doi.org/10.1111/ j.1755-0283.2005.tb00034.x

14. Rowell RM. 2012. Handbook of Wood Chemistry and Wood Composites, In Rowell R M (ed), CRC press, Boca Raton

15. Williams JH, Boecklen WJ, Howard DJ. 2001. Reproductive processes in two oak (Quercus) contact zones with different levels of hybridisation. Heredity 87: 690-690. https://doi.org/10.1046/j.1365-2540.2001.00968.x

16. Gonzalez-Rodriguez A, Arias DM, Valencia S, Oyama K. 2004. Leaf morphometric variation in Quercus affinis and Quercus laurina (Fagaceae), two hybridizing Mexican red oaks. Bot J Linn Soc 147: 427-435. https://doi.org/10.1111/j.1095-8399.2004.00394.x

17. Feuillat F, Dupouey J-L, Badeau V. 1993. Morphological variability of oaks (Quercus robur L., Quercus petreae, and Quercus pubescens Willd) in northeastern France: preliminary results. Ann For Sci 50: 35s-40s. https://doi.org/10.1051/forest:19930702

18. Feuillat F, Dupouey J-L, Sciama D, Keller R. 1997. A new attempt at discrimination between Quercus petrea and Quercus robur based on wood anatomy. Can J For Res 27: 343-351

19. Conte L, Cotti C, Cristofolini G. 2007. Molecular evidence for hybrid origin of Quercus crenata Lam. (Fagaceae) from Q. cerris L. and Q. suber L. Plant Biosystems 141: 181-193. https://doi.org/10.1080/11263500701401463

20. Gonzalez-Rodriguez A, Arias DM, Valencia S, Oyama K. 2004. Morphological and RAPD analysis of hybridisation between Quercus affinis and Quercus laurina (Fagaceae), two Mexican red oaks. Am J Bot 91: 401-409. https://doi.org/10.3732/ajb.91.3.401

21. Chuteira CA, Grão AB. 2012. Oak: Ecology, Types and Management, Nova Science Publisher’s, Incorporated, New York

22. Sanza MdA, Neaves Dominguez I. 2015. Oxygen transfer rate in oak barrels: annual evaluation for dynamic oxygen intake and entry. Wines & Vines.

23. del Alamo-Sanza M, Neaves I. 2014. Recent advances in the evaluation of the oxygen transfer rate in oak barrels. J Agric Food Chem 62: 8892-8899. https://doi.org/10.1021/jf502333d

24. Pretzsch H, Biber P, Schütte G, Kemmerer J, Uhl E. 2018. Wood density reduced while wood volume growth accelerated in Central European forests since 1870. For Ecol Manag 429: 589-616. https://doi.org/10.1016/j.foreco.2018.07.045

25. Diaz-Maroto IJ, Tahir S. 2018. Testing of wood physical properties in oak species (Quercus robur L., Q. petraea (L.) Mattie and Q. pyrenaica (Willd.) For cooperage. Part ii: wood grain. Wood Res 63: 959-969. http://www.woodresearch.sk/wr/201806/04.pdf

26. Mosedale JR, Puech JL. 1998. Wood maturation of distilled beverages. Trends Food Sci Technol 9: 95-101. https://doi.org/10.1016/S0924-2244(98)00024-7

27. del Alamo-Sanza M, Neaves I, Mayr T, Baro JA, Martinez-Martinez V, Ehgartner J. 2016. Analysis of the role of wood anatomy on oxygen diffusivity in barrel staves using luminescent imaging. Sens Actuators B Chem 237: 1035-1043. https://doi.org/10.1016/j.snb.2016.08.075

28. Chatonnet P, Dubourdieu D. 1998. Comparative study of the characteristics of American white oak (Quercus alba and European Oak (Quercus petreae and Q. robur) for production of barrels used in barrel aging of wines. Am J Enol Vitic 49: 79-85.

29. del Alamo-Sanza M, Neaves I. 2017. Oak wine barrel as an active vessel: A critical review of past and current knowledge. Curr Rev Food Sci Nutr 58: 2711-2726. https://doi.org/10.1080/140408398.2017.1330250

30. Pallardy SG. 2010. Plant Physiology of Woody Plants, 3rd ed, Elsevier Science, Amsterdam

31. Bureau Veritas Group. 2019. Attestation of recognition attributed to Canton wood products.

32. Chateigner S, Vasseur A, Morel A, Carette O, Auderset D, Kien R, Lemoine E, Charrier B, Janin G. 2013. Genetic constitution of oak wood used in cooperage: Composition, interest, assays: A review. Carbohydr Polym 97: 1-12. https://doi.org/10.1016/j.carbpol.2013.07.003

33. Conner JM, Paterson A, Piggott JR. 1992. Analysis of lignin from oak casks used for the maturation of Scotch whisky. J Sci Food Agric 60: 349-353. https://doi.org/10.1002/jsfa.2740600312

34. Santos RB, Capanema EA, Balakshin MY, Chang HM, Jameel H. 2012. Lignin structural variation in hardwood species. J Agric Food Chem 60: 4393-4390. https://doi.org/10.1021/jf301276a

35. Masson G, Moutoumet M, Puech JL. 1995. Ellagitannin content of oak wood as a function of species and of sampling position in the tree. Am J Enol Vitic 46: 262-268.
Variation in bourbon whiskey barrels

88. Mettler MS, Vlachos DG, Dauenhauer PJ. 2012. Top ten fundamental challenges of biomass pyrolysis for biofuels. Energy Environ Sci 5: 7797-7809. https://doi.org/10.1039/C2EE21679E

89. Collard F-X, Blin J. 2014. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. Renew Sust Energ Rev 38: 594-608. https://doi.org/10.1016/j.rser.2014.06.013

90. Stefanidis SD, Kalganioglu KK, Ilipouollo EF, Michailof CM, Pilavachi PA, Lappas AA. 2014. A study of lignocellosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. J Anal Appl Pyrolysis 105: 143-150. https://doi.org/10.1016/j.jaap.2013.10.013

91. Froelich KB, Andrews JS, Chew JW, Dauenhauer PJ, Mushriikh SH. 2019. Fast pyrolysis of cellulose, hemicellulose, and lignin: effect of operating temperature on bio-oil yield and composition and insights into the intrinsic pyrolysis chemistry. Ind Eng Chem Res 58: 15388-15852. https://doi.org/10.1021/acs.iecr.9b00920

92. Morf P, Hasler P, Nussbaumer T. 2002. Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. Fuel 81: 843-853. https://doi.org/10.1016/S0016-2361(01)00216-2

93. Banyasz JL, Li S, Lyons-Hart J, Shafer KH. 2001. Gas evolution and the mechanism of cellulose pyrolysis. Fuel 80: 1757-1763. https://doi.org/10.1016/S0016-2361(01)00060-6

94. Mamleev V, Bourbigot S, Le Bras M, Yvon J. 2009. The facts and hypotethical relations relating the phenomenological model of cellulose pyrolysis: Interdependence of the steps. J Anal Appl Pyrolysis 84: 1-17. https://doi.org/10.1016/j.jaap.2008.10.014

95. Scheirs J, Camino G, Tumiatti W. 2001. Overview of temperature during the thermal degradation of cellulose. Eur Polym J 37: 933-942. https://doi.org/10.1016/S0014-3057(00)00211-1

96. Sturcova A, Hes I, Appenley DC, Sugiyama J, Jarvis MC. 2004. Structural details of crystalline cellulose from higher plants. Biomacromolecules 5: https://doi.org/10.1021/bm034517p

97. Driemeier C, Santos WD, Buckridge MS. 2012. Cellulose crystals in fibrovacular bundles of sugarcane culms: orientation, size, distortion, and variability. Cellulose (Lond) 19: 1507-1515 https://doi.org/10.1007/s10570-012-9743-z

98. Nishiyama Y, Langan P, Chanzy H. 2002. Crystal structure and variability of cellulose, hemicelluloses and lignin. Biomass Bioenergy 19: S1385-8947(02)00142-0

99. Scheirs J, Camino G, Tumiatti W. 2001. Overview of temperature during the thermal degradation of cellulose. Eur Polym J 37: 933-942. https://doi.org/10.1016/S0014-3057(00)00211-1

100. Chen H, Liu N, Fan W. 2006. Two-step consecutive reaction model and calculation of kinetic parameters relevant to the decomposition of Chinese forest biomass. Energy Fuels 20: 1810-1817. https://doi.org/10.1021/acs.energyfuels.8b03226
130. Yang Y, Chen J, Zhang L, Tan M, Lin J, Wang S, Wang Y, Wang Y. 2018. Enhanced antioxidation stability of iron-based catalysts via surface decoration with ppm platinum. ACS Sustain Chem Eng 6: 14010-14016. https://doi.org/10.1021/acssuschemeng.8b02505

131. Sun K, Xu Q, Shao Y, Zhang L, Liu Q, Zhang S, Wang Y, Hu X. 2019. Cross-polymerization between the typical sugars and phenolic monomers in bio-oil: a model compounds study. Energy Fuels 33: 7480-7490. https://doi.org/10.1021/acs.energyfuels.9b01856

132. Poisson L, Schieberle P. 2008. Characterization of the most odor-active compounds in an American bourbon whisky by application of the aroma extract dilution analysis. J Agric Food Chem 56: 5813-5819. https://doi.org/10.1021/jf800382m

133. Lee KYM, Paterson A, Birkyrne L, Piggott JR. 2001. Headspace congruence of blended Scotch whiskies of different product categories from SPME analysis. J Inst Brew 107: 315-332. https://doi.org/10.1002/j.2050-0416.2001.tb00100.x

134. Jia L, Buendia-Kandia F, Dumarcay S, Poirot H, Mauviel G, Gérardin P, Dufour A. 2017. Fast pyrolysis of heartwood, sapwood, and bark: a complementary application of online photoionization mass spectrometry and conventional pyrolysis gas chromatography/mass spectrometry. Energy Fuels https://doi.org/10.1021/acs.energyfuels.7b00110

135. Pan W-P, Richards GN. 1989. Influence of metal ions on volatile products of pyrolysis of wood. J Anal Appl Pyrolysis 16: 117-126. https://doi.org/10.1016/0165-2370(89)85011-9

136. Leijenhorst EJ, Wolters W, van de Beld L, Prins W. 2016. Inorganic elements transfer from biomass to fast pyrolysis oil: review and experiments. Fuel Process Technol 149: 96-111. https://doi.org/10.1016/j.fuproc.2016.03.026

137. Favaloro M. 2000. Ablative Materials, In Kirk-Othmer Encyclopedia of Chemical Technology (ed), Wiley Blackwell, Hoboken. https://doi.org/10.1002/0471238961.010212016012201.a01

138. Lionetto F, Del Sole R, Canoletta D, Vasapollo G, Maffezzoli A. 2012. Monitoring wood degradation during weathering by cellulose crystallinity. Materials 5: 1910-1922. http://www.mdpi.com/1996-1944/5/10/1910

139. Long Y, Yu Y, Chua YW, Wu H. 2017. Acid-catalysed cellulose pyrolysis at low temperatures. Fuel 193: 460-466. https://doi.org/10.1016/j.fuel.2016.12.067

140. Anjos O, Carmona C, Caldeira I, Canas S. 2013. Variation of extractable compounds and lignin contents in wood fragments used in the aging of wine brands. BioRes 8: 4484-4496.

141. Towey JP, Waterhouse AL. 1996. Barrel-to-barrel variation of volatile oak extracts in barrel-fermented chardonnay. Am J Enol Vitic 47: 17-20.

142. Cutzach I, Chatonnet P, Dubourdieu D. 1999. Study of the formation mechanisms of some volatile compounds during the aging of sweet fortified wines. J Agric Food Chem 47: 2837-2846. https://doi.org/10.1021/jf981224s

143. Oliveira CM, Ferreira ACS, De Freitas V, Silva AMS. 2011. Oxidation mechanisms occurring in wines. Food Res Int 44: 1115-1126. https://doi.org/10.1016/j.foodres.2011.03.050

144. Elias RJ, Waterhouse AL. 2010. Controlling the Fenton reaction in wine. J Agric Food Chem 58: 1699-1707. https://doi.org/10.1021/jf903127r

145. Danilewicz JC. 2016. Fe (II)/Fe (III) ratio and redox status of white wines. Am J Enol Vitic 67: 146-152. https://doi.org/10.5344/ajev.2015.15088

146. Singleton VL, Trousdale E, Zaya J. 1979. Oxidation of wines. I. young white wines periodically exposed to air. Am J Enol Vitic 30: 49-54.

147. Choe E, Min DB. 2006. Mechanisms and factors for edible oil oxidation. Compr Rev Food Sci Food Saf. 5: 169-186. https://doi.org/10.1111/j.1541-4337.2006.00009.x

148. Frankel EN. 1991. Review. Recent advances in lipid oxidation. J Sci Food Agric 54: 495-511. https://doi.org/10.1002/jsfa.2740540402

149. Yu B, Zhang Y, Shukla A, Shukla SS, Dorris KL. 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption — removal of copper. J Hazard Mater 80: 33-42. https://doi.org/10.1016/S0304-3894(00)00278-8

150. Poisson L, Schieberle P. 2008. Characterization of the key aroma compounds in an american bourbon whisky by quantitative measurements, aroma recombination, and omission studies. J Agric Food Chem 56: 5820-6. https://doi.org/10.1021/jf800383v

151. Collins TS, Zweigenbaum J, Ebeler SE. 2014. Profiling of nonvolatiles in whiskeys using ultra high liquid high performance liquid chromatography quadrupole time-of-flight mass spectrometry (UHPLC–QTOF MS). Food Chem 163: 186-196. https://doi.org/10.1016/j.foodchem.2014.04.095

152. Martins AR, Talhavini M, Vieira ML, Zaccia J, Braga JWB. 2017. Discrimination of whisky brands and counterfeit identification by UV-Vis spectrosopy and multivariate data analysis. Food Chem 229: 142-151. https://doi.org/10.1016/j.foodchem.2017.02.024

153. Stupak M, Goodall I, Tomaniova M, Pulkrabova J, Hajsova J. 2018. A novel approach to assess the quality and authenticity of Scotch Whisky based on gas chromatography coupled to high resolution mass spectrometry. Anal Chim Acta 1042: 60-70. https://doi.org/10.1016/j.aca.2018.09.017

154. Roullier-Gall C, Signoret J, Hemmler D, Witting MA, Kanawati B, Schäfer B, Gougeon RD, Schmitt-Kopplin P. 2018. Usage of FT-ICR-MS metabolomics for characterizing the chemical signatures of barrel aged whisky. Front Chem 6: https://doi.org/10.3389/fchem.2018.00029

155. Yang K, Somogyi A, Thomas C, Zhang H, Cheng Z, Xu S, Miller C, Spivey D, Blake C, Smith C, Dafoe D, Danielson ND, Crowder MW. 2020. Analysis of barrel-aged Kentucky bourbon whiskey by ultra high resolution mass spectrometry. Food Anal Methods 13: 2301-2311. https://doi.org/10.1007/s12161-020-01850-z