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Oak Wine Barrel as an Active Vessel: A Critical Review of Past and Current Knowledge

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Abstract

We review the role of the oak barrel as an active vessel for wine maturation. We present a historical background to highlight that previously established aspects of processes occurring with wine inside the oak barrel are still without confirmation. We argue that recently published new findings on the topic are determining factors in defining the manner in which the oak barrel works with wine. Several studies have been published reviewing how the wine barrel functions as an active vessel that releases chemical compounds into the wine, improving its physical, chemical, and sensory properties. Nevertheless, there are hardly any studies that describe how a wine barrel functions as an active vessel. The present review details the main factors affecting the gas exchange capacity of the barrel, such as the pressure drop generated within the barrel, the formation of a headspace, the effect of wood anatomy, the different oxygen entry routes, the role of wood moisture content and soluble ellagitannins, and the effect of barrel toasting on cooperage. Finally, a hypothesis is proposed regarding the function of the barrel as an active

vessel, which determines the manner in which it interacts with the wine that it contains during aging.

Introduction

Wine conservation and aging is a practice that has been used since antiquity (Kilby, 1971; Schahinger and Rankine, 2005; Taransaud, 1982; Vivas, 2005). According to the evidence found in shipwrecks, oak and chestnut barrels were the most frequently used in the 16th century (Cazenave de la Roche, 2004)—mainly oak because it is resilient, flexible, and relatively impermeable to liquids—which are properties strongly influenced by wood anatomy (Feuillat and Keller, 1997). The wood used in the manufacture of barrels should have a straight grain in its pieces and be free of defects that may cause leaks, and it must not contribute unpleasant flavors. In addition, it should be thermoplastic, allowing wood bending using heat, which is an essential operation in the manufacture of the barrel. In his 1974 study, Singleton details the use of wood of white oak, red oak, chestnut oak, red or sweet gum, sugar maple, yellow or sweet birch, white ash, Douglas fir, beech, black cherry, sycamore, redwood, spruce, bald cypress, elm, and basswood in the cooperages of the United States. In Europe, cooperage for wine or brandy has been made from oak, chestnut, fir, spruce, pine, larch, ash, mulberry, and a number of additional species imported from Africa, South America, and Australia (Vivas, 2005; Wagner, 1910). Therefore, very different types of wood have been used for the manufacture of casks and barrels due to having the necessary physical and structural properties. In addition to being impermeable to liquids, the barrel is an active vessel because the wood used in its manufacture releases compounds that characterize the final product within the barrel, as is the case with wines aged in oak barrels, and due to a mild oxygenation that improves the integration between the compounds of the wine and those released by wood (Ribereau-Gayon, 1933). Due to the high cost of oak barrels and the current lower availability of French oak wood and, recently, American oak wood,

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other woods are being considered as an alternatives to oak wood from America and Europe (Tao et al. 2013), although their capacity to supply the cooperage industry with barrels in the long term still remains to be seen. Several recent studies describe the effects of using wood of acacia (De Rossoet al., 2009; Fernández de Simón et al., 2009, 2014a, 2014b; Sanz et al., 2012), cherry (De Rosso et al., 2009; Fernández de Simón et al., 2009, 2014a, 2014b; Sanz et al., 2012; Soares, et al., 2012), chestnut (Arfelli et al., 2007; Caldeira et al., 2010; Canas et al., 2002, 2007; De Rosso et al., 2009; Fernández de Simón et al., 2009, 2014a; Gambuti et al., 2010; Sanz et al., 2010, 2012; Soares et al., 2012; Vivas et al., 1996), mulberry (De Rosso et al., 2009), pyrenaica oak (Alañón et al., 2011; Cadahía et al., 2007; Canas et al., 2000, 2008; De Coninck et al., 2006; del Álamo et al., 2010; Fernández de Simón et al., 1998, 2003, 2008, 2006, 2010; Gallego et al., 2012; Goncalves and Jordao, 2009; Jordão et al., 2005, 2006, 2007; Rodríguez-Bencomo et al., 2009) and Colombian oak (Martínez-Gil et al., 2017) for wine and/or brandy aging.

From the anatomical perspective, the oak is characterized by its rays, which run radially across the trunk from the pith to the bark, acting as a diffusion channel in growing wood. When planks are obtained from the trunk, from which the staves will be longitudinally obtained, the rays remain parallel to the inner side of the staves that will be in contact with the wine, forming a barrier to the diffusion of the liquid (Singleton, 1974) (Figure 1). In this manner, in a stave that is 25-20 mm thick, there will be no conducting vessels that communicate both sides of the stave, avoiding the leaking of wine contained in the barrel (Vivas, 2005). To achieve this arrangement, it is necessary to split the logs lengthwise, which means a poor utilization of the trunk, although essential in the management of European oaks (*Quercus petraea* Matt L, *Quercus robur* L ...), because they do not have abundant thyloses. The American oak most commonly used in cooperage belongs to the species *Quercus alba* L and has abundant thyloses. Thyloses are an outgrowth from an adjoining ray or vertical parenchyma cell through a pit-pair into the lumen of a vessel (Kollmann and Coté, 1968; Tsoumis, 1968). In this manner, the wood of *Quercus alba* is worked without strictly following the medullary rays, which does not ensure that the vessels will be parallel to the inner side of the barrel stave. In this case, the possible passage of liquid from the inside to the outside of the barrel will be obstructed by the thyloses completely occluding the conducting vessels and making the barrel impermeable to liquids (Siau, 1984; Singleton, 1995, 2000). American oak has thyllae membranes up to 10 times as thick as European oak. This specific structural aspect and, possibly, the composition of the thyllae would seem to provide a better explanation for the water tightness of sawn white oak stave wood rather than the differences in wood texture or density (Chatonnet and Dubourdieu, 1998). Owing to the generalized presence of thyloses, the staves can be obtained by sawing rather than splitting, which means a better use of the trunk, which goes from 20% with riving to 40-50% with quarter sawing (Vivas, 2005). This fact explains why 2 to 2.2 barrels are manufactured with each m^3 of split wood whereas 3.7 and 4 barrels are manufactured with each m^3 of sawn wood (Chatonnet and Dubourdieu, 1998; Zamora, 2003). Due to the above, the oak wood barrel is the cask chosen by the oenologist for wine aging because it allows the wine to evolve and express its full potential. For this reason, it is essential to understand how the oak wood barrel functions and to know the factors that condition it.

Oak wood as a porous solid

In cooperage, permeability is the ability of the wood to allow fluid flow to pass through it without altering its internal structure. In general, fluid flow through wood can occur in two ways,

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as in a porous solid following Darcy's law as the bulk flow of fluids through the interconnected voids of the wood structure under the influence of a static or capillary pressure gradient. Permeability in this manner is only possible if the voids are interconnected with the openings. If these openings are occluded or have incrustations, or if the pits are aspirated, then the wood works as a closed cell structure, and its permeability may be close to zero (Siau, 1995). The second way is permeability due to diffusion (Siau, 1984), also known as permeation, and the SI unit is mol·/m·s·Pa, whereas the SI unit for permeability in fluid mechanics is m^2. In turn, diffusion may occur as intergas diffusion, which includes the transfer of water vapor through the air in the cell lumen, and bound water diffusion, which occurs inside the cell walls of the wood (Siau, 1984).

In the complex case of an oak wood barrel stave during wine aging, both phenomena occur simultaneously. Wine as bulk flow penetrates into the wood, which is a porous solid, due to the hydrostatic pressure of the liquid, causing the water vapor and ethanol from the wine inside and the oxygen from the air outside to diffuse through the wood due to the concentration difference between the inside and outside of the barrel. Thus, we should differentiate between permeability to fluids and permeation to gases as the main phenomena that make the barrel impermeable to liquids (Vivas, 1995) and, in an apparent contradiction, permeable to gases (del Alamo-Sanza and Nevares, 2015a, 2015b; Moutounet et al., 1998; Ruiz de Adana, et al., 2005; Vivas, et al., 2003; Vivas and Glories, 1997).

Influence of oak anatomy on permeability to fluids

Oak is a ring porous species that involves a variation between spring wood (earlywood) and summer wood (latewood), with a very clear structural differentiation resulting in the differentiation of physical properties and chemical composition. Spring wood is composed of several rows (two or three) of large conducting vessels that involve large pores of up to 320 μm in diameter (Vivas, 2000), resulting in its lower density. Summer wood, on the other hand, is composed of much smaller vessels, being less porous and therefore denser, which explains the higher density of fast growing wood, that is, medium or coarse grain wood, compared to the lower density of fine- or very fine-grained slow growing wood.

One of the specific structural elements of the genus *Quercus* that provides an advantage for the manufacture of barrels is the presence of rays. As described above, the rays represent a barrier to fluids, making the wood amenable to bending in the manufacture of barrels and ensuring high dimensional stability, which is the reason why radial shrinkage is less than 4% (Lindsay and Chalk, 1954; Santos et al., 2013; Skaar, 1988).

Quercus wood has both multiseriate and uniseriate rays. However, what makes this wood special is that multiseriate rays are particularly abundant (Santos et al., 2013) and wide and have even been considered a special type called compound or disuse rays (Carlquist, 2015), which are larger in height (reaching up to 5 cm) along the grain than uniseriate rays. In *Quercus alba* L., they represent up to 28% of wood volume, which is much more than in other hardwoods, and their number is so high that if a stave is split, then a water molecule will have to pass through more than five rays to cross it perpendicularly (Singleton, 1974) from the inside to the outside of the barrel.

Oak gas permeability

There is a great amount of published data regarding the permeability of wood to gases (Bao et al. 1999; Choong et al., 1974; Comstock, 1967, 1970; Hansmann et al., 2002; Jinman et al., 1991, 1994; Kininmonth, 1971; Tesoro et al., 1974), although little is known about the transverse permeability of wood to gases and the influence that wood moisture has on this gas flow. Thus, Comstock (1975, Unpublished results) (Siau et al., 1995) found that transverse permeability is much lower than longitudinal permeability in hardwoods, with ratios ranging between $3{\cdot}10^4$:1 and $4{\cdot}10^8$:1, with the highest ratio being in the ring-porous red oak. Therefore, longitudinal permeability is of much greater importance than in transverse direction (Perré and Keey, 2015; Prak, 1970; Siau, 1971, 1984).

In a recent study conducted to update measurements performed on the apparent gaseous permeability of porous media in transversal directions in wood, a device was developed to measure permeability in porous solids such as wood (Ai et al., 2017). Based on high resolution pressure measurement systems, permeability due to a pressure gradient was determined according to Darcy's law in the three anatomical directions of Norway spruce (*Picea abies* L.) and European beech (*Fagus sylvatica* L.). The results confirm the existing measurements and the relationships between longitudinal and transverse permeabilities. Therefore, the available gas permeability values for dry wood are considered to be more reliable indicators for determining the relationships between longitudinal and transverse permeabilities. Since Comstock (Comstock, 1967) has shown that permeability values measured with gases and liquids are closely related, the relationships can be considered generally applicable (Comstock, 1970). Although the permeability difference between radial and tangential directions is not significant for most hard wood species, the mean values are generally higher for radial than for tangential permeability in oak species (Choong et al., 1974). Sebastian *et al*. (1973) observed that small vessels of ring-porous summer wood may be relatively impermeable to gas, in contrast to large

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vessels of spring wood. In ring-porous wood, the permeability of summer wood vessels is most likely between that of large vessels and that of fibers. Therefore, the proportion of latewood in a specimen is important for its overall permeability to gas, and the same may be true for diffusivity. For diffusion, the combined path of vapor movement through the cell lumens in series with bound water movement in the cross walls is of primary importance for both transverse and longitudinal movement (Choong, 1965; Perré and Keey, 2015).

Although most studies have measured the permeability of wood, Sorz and Hietz (2006) measured gas permeation or permeability due to diffusion in different types of wood by analyzing the influence of moisture content (MC). They measured the diffusion of oxygen against nitrogen gas in wood of *Quercus robur L.* trees, among other species, at different water and gas contents in the laboratory. They developed a device with luminescent technology to monitor how the oxygen of the air inside a chamber decreases because it crosses the wood by diffusion to another chamber with pure N_2 gas, both in tangential and radial direction and at different water content. They found that in *Quercus robur L.*, the diffusion coefficient strongly increased with the volume of air in the xylem. The difference between radial and tangential diffusion was low at low gas content, but diffusion in the tangential direction was 21 times higher than in the radial direction, contrary to what has been described by other authors for liquid flow (Choong et al., 1974). This concept of wood as a porous solid with a determined volume of gas that is displaced by the imbibed fluid has led to interesting studies, described below (del Alamo-Sanza et al., 2016; Nevares et al., 2014, 2016; Nevares and de Alamo-Sanza, 2014, 2015), focusing on barrel staves and on the effect of the heat treatment of wood in cooperage, toasting, and bending.

Oxygen transfer rate from the air to wine in the barrel

The annual rate of oxygen entry into barrels is the amount of oxygen that enters the barrel full of wine in one year, typically expressed as mg/L.year. The first mention of this entry of atmospheric oxygen into the barrel was reported by Ribereau-Gayon in 1933. In his doctoral thesis, this author confirmed that oxygen entered into barrels full of wine—therefore with wood that was wet — and hermetically sealed (Ribereau-Gayon, 1933) at rates of between 15 and 45 mg/L per year. Subsequently, Amerine and Joslyn (1970) described the studies that Frolov-Bagreev and Agabal'iants conducted in 1951 when they quantified the amount of oxygen absorbed by wine aged in 250 L barrels. Their results were 40 mL of oxygen in the first year and 30 mL of oxygen in the second, and in 1965, Prillinger (1965) measured between 2.8 and 7 mL/L. In his early studies conducted in 1974, Singleton (1974) admitted that barrel walls are permeable to oxygen. However, due to the studies that Peterson published in 1976 on the extent of the pressure drop occurring inside the barrels, he argued that air does not reach the body of the barrel by diffusing through the wetted portions of the barrel sides (Singleton, 1982). In 1995, Singleton proposed that oxygen and nitrogen could not diffuse through the wet stave and "fill" the headspace (Singleton, 1982, 1995) because if this were the case, then the vacuum that Peterson (1976) had measured inside the barrel would not occur. He also established one of the most widespread ideas regarding this subject, stating that oxygen enters into the barrel through the dry wood near the top, where it is in contact with the headspace. That is, in a hermetically sealed barrel that is not being filled during the aging process, over time, the headspace time become so large that the wine will not completely wet the inside of the barrel. The wood at the top of the barrel will then dry, and oxygen entry will increase, causing wine spoilage (Singleton, 1995). This hypothesis has been the most widely accepted in regard to how the barrel functions in wine aging. Almost simultaneously, Vivas and Glories (1997) measured oxygen entry into barrels full of wine and, therefore, wet wood barrels, built with French oak from Limousin and Centro. They found that the annual oxygen entry varied between 20 and 45 mg/L for new barrels and that the oxygen entry was 10 mg/L for five-year-old barrels from Centro, establishing these values as the OTR (oxygen transfer rate) values for French oak barrels during the last 20 years (Table 1). In the same study, they evaluate the effect of the barrel bung and whether hermetic sealing is achieved, obtaining annual oxygen transfer rates of 45 mg/L with a silicone bung and 28 mg/L when the barrel was tightly sealed. These results show that oxygen passes through wet wood and confirm what was published by Semenenko *et al*. (1979) in a study evaluating the permeability to oxygen of the staves of barrels used to age cognac. When the staves are wet, there are sudden changes in dissolved oxygen content (DO) throughout the maturation process. These changes could possibly be the result of the loss of depressurization generated inside the barrel, which would cause the entry of outside air. Therefore, they designed a device to measure the rate of oxygen entry through wood staves of different thicknesses (15, 20, and 26 mm) by subjecting the wood to different oxygen pressures. As a result, they obtained oxygen transfer rates through the wood that were directly proportional to the oxygen partial pressure exerted and the heat treatment of the wood.

Thus, whereas some authors (Moutounet et al., 1998; Singleton, 1995) had argued that oxygen does not enter the barrel full of wine because the wood is wet (Vivas and Glories, 1997), other studies showed that, even by sealing the joints between the staves of full barrels for six months, oxygen did in fact enter through the wood into the barrels. It was not until 2014 that a paper published the actual annual OTR in barrels (del Alamo-Sanza and Nevares, 2014). Specifically, the results reported were systematic measurements taken over one year of the OTR in four barrels of the same lot made with French oak *Quercus petraea* (Matt.) Liebl, under aging conditions full of model wine. The study presents 15 OTR measurements of each one of the same four barrels over a year, measuring the accumulation of dissolved oxygen inside the barrel using submersible photoluminescent oxygen probes and hermetically sealing the barrels with silicone bungs afterwards. The study used model wine, renewing and degassing it every time the oxygen entry in the barrels was measured. This process is essential to simulate the oxygen concentration gradient inside and outside of the barrel during aging. The results showed that the OTR decreased with the length of time that the barrels were filled and indicated that increases in wood moisture were responsible for the decreasing permeability of wood to oxygen because atmospheric oxygen diffuses better through dry wood. In summary, they analyzed the kinetics of oak barrel oxygen permeability for one year to establish the kinetics of the annual OTR of a barrel. In addition, they also studied 12 new barrels made of *Quercus alba* L. and *Quercus petraea* (Matt.) Liebl. These results confirmed the role of wood MC in the decrease of oxygen permeation through the wood. It should be noted that this study revealed that all of the values published hitherto overestimated the annual OTR of the barrels, given that the OTR of the barrels was dynamic. As a result, the data published by Vivas and Glories (1997) overestimated the OTR values of the barrels by extrapolating the rate of oxygen entry in two barrels for six months to an entire year to establish the annual rate.

The oxygen entering the barrel can do so through the wood, the joints between the staves, or the bung. In this regard, in the 1997 study by Vivas and Glories noted above, the main oxygen entry routes were measured in two French oak barrels, finding that of all the oxygen that the wine would receive in one year, 21% entered through the bung, 63% through the joints between the different staves, and only 16% through the wood of the staves. Subsequent studies (del Alamo-Sanza and Nevares, 2015; Nevares and Alamo-Sanza, 2014) evaluated lots of barrels from the same cooperage, consisting of four barrels of American oak (*Quercus alba*) and four of French oak (*Quercus petraea* (Matt.) Liebl.), establishing that oxygen entered through the wood and the joints between the staves. By analyzing only the oxygen entering through wood, it was confirmed that French wood permeates more oxygen than American wood. The assembly of the staves is essential when studying the OTR of oak barrels. In the case of barrels made with American oak, the amount of oxygen that entered through the joints between the staves and bung was 50% of the total, being almost the same as what entered through the wood (del Alamo-Sanza and Nevares, 2015). In the case of French oak barrels, it was found that 75% of all the oxygen entering the wine originated from the wood. This study confirmed the importance of the oxygen entry paths through the wood and the joints of the staves in the OTR_{global} of the barrels.

Finally, the estimation by Kelly and Wollan (2003) should be noted. These authors explained oxygen entry into the barrel, focusing on the wood and relating the behavior of an oak wood stave with that of a semipermeable membrane. To do this, they applied Fick's law of diffusion, in which the gas flow through a solid depends on the thickness of the solid, the difference in concentration of that gas on both sides of the solid, and the permeability of the solid to that gas. In this manner, they determined the maximum oxygen flow that could pass through an oak barrel stave. Quantifying the permeability of the wood at 20 Barrer (10^{-10} $cm^3 \cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cm\text{-}Hg^{-1}$), they determined that an oak stave that is 27 mm thick would allow a maximum oxygen diffusion flow of 2.2 mL/L.month, which implies an OTR of 26 mL/L.year (Table 1).

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Therefore, oxygen in fact enters the barrel during aging, and the understanding of this process can be very important for the cooper and the oenologist. In a study published by Nevares and del Alamo-Sanza (2015) showed that it is possible to manufacture high- and low-OTR barrels. They classified rough-staves by their OTR after measuring oxygen permeation and subsequently assembled two barrels using the staves obtained from those classified planks. In this manner, they were able to build a high-OTR barrel with raw wood of higher oxygen permeation and another low-OTR barrel with raw wood of lower oxygen permeation. Once the barrels were made, the role of the joints between the wood barrel staves was measured by OTR_{global}, finding that OTR_{joints} was 28% and 54% of OTR_{global} for high- and low-OTR barrels, respectively. Therefore, OTR_{wood} was ultimately 72% and 46% for high- and low-OTR barrels, respectively. Another research study from that year (Qiu, 2015) quantified the importance of the pressure exerted between the staves in the rate of oxygen entry through that route. The author determined that oxygen entry is not uniform throughout the joint between two staves, with greater oxygen entry in the middle of the staves where the joints support a pressure between 0 and 3 bar, whereas at the end of the staves, pressures reach higher values, between 25 and 30 bar. In addition, the authors made it clear that when the joints are of good quality, the oxygen entry exerting low pressure is similar to that found in joints of poor quality, in which more pressure is exerted. It should also be noted that the third route of oxygen entry into the barrel, quantified by Vivas and Glories (1997), is the bung, which seems to lose prominence with the widespread use of food-grade silicone bungs that allow a tight seal. These authors (Qiu, 2015) did not describe whether this route refers to the bung itself, to the joint with the bung hole, or to its use in the opening and closing during barrel topping.

In this regard, the process of topping the wine barrel suggests an undeniable source of air entry and, consequently, wine oxygenation. Several authors quantify that each topping up of a barrel adds approximately 4 mg/L to the wine (Tiquet-Lavandier and Mirabel, 2014). When a barrel with reduced internal pressure is opened for topping, the loss of the pressure difference can cause the barrel to recover its original shape with the corresponding volume increase. This effect sucks air from the outside and therefore causes oxygen entry, which has been quantified in four barrels filled with model wine in which the DO of the fluid was being measured a few cm from the surface (del Alamo-Sanza and Nevares, 2015c). When the barrel was opened, depressurization was lost, which caused the air to enter, but when the barrel was immediately filled with deoxygenated wine, it was verified that the DO level of model wine in the barrel did not vary significantly in all cases and, in some cases, even decreased slightly. Therefore, good management of the barrel topping process does not necessarily involve an increase in wine oxygenation.

Considering the previously published studies, it can be said that oxygen entry into the barrel occurs throughout aging in a dynamic manner and that there are several factors determining this entry that are all directly related. Of these, it is necessary to emphasize wood impregnation, the formation of reduced pressure inside the barrel, the type of seal, the wood, and the toasting performed in cooperage.

Factors that determine oxygen entry into the barrel

Wood impregnation and wine evaporation

Wine aging begins with barrel filling. The barrel is closed after having been completely filled with wine, which can be done by simply inserting the bung in the bung hole. To ensure tightness, the barrels can be turned 45º so that there is no air entry through the top of the barrel and the bung remains wet. The widespread option is the use of synthetic bungs made of food grade rubber or silicone that generate good tightness.

During the period in which the barrel full of wine is not being manipulated, a phenomenon of decrease or loss of wine occurs that has been studied by several authors to explain how it happens. Feuillat *et al*. (1994) studied the variation of fluid volume in contact with one of the sides of a piece of wood and proposed that this loss was due to two phenomena: wood impregnation with the fluid and evaporation of the latter through the wood. First, wood impregnation occurs quickly, a phenomenon that becomes stable after 40 days. Next, there is a latency phase called "retard à l'evaporation", followed by mass flow from the inside to the outside of the wood, which tends to become a linear function of time. In this manner, Feuillat determined that fluid loss in contact with a piece of wood occurred in two phases: an initial phase or transition state in which wood is impregnated until a steady state is achieved and a second phase or steady state in which the impregnation flow or entry of fluid into the wood has the same magnitude as the evaporation outflow to the exterior.

For his part, Singleton (1995) proposed a mechanism to explain how wood impregnation occurs, considering that both the water and the ethanol from wine are able to impregnate the wood due to their low molecular weights. The inner side of the wood staves in contact with the wine will be imbibed, their cells saturated, and the vessels filled with fluid. As the outside of the stave is reached, free fluid decreases in the wood, and the gas space between the lumens increases. Therefore, at the point at which there is no more free fluid and evaporation is the main phenomenon, the wood fiber saturation point (FSP) is reached. This point coincides with an approximate wood MC of 29-30% (Glass and Zelinka, 2010; Kollmann and Coté, 1968), and if the temperature is high, then it becomes difficult to maintain this MC on the external side of the wood, which will be affected by the relative humidity of the environment. Therefore, this wood over FSP will vary in the stave, depending on the season and changes in the environmental conditions of the barrel room. In the interior of the wood of the 27 mm staves, we find that there are no dimensional changes in the wood from the FSP to the exterior. However, toward the interior, in which the wood is above the FSP, the joined staves are pressed against each other, preventing the exit of wine toward the outside through the joints between the staves (Figure 2).

Ruiz de Adana (2002) proposed a mathematical model that replicates the process of mass transfer in the wood of an oak barrel, that is, to explain the phenomena of impregnation and evaporation described by Feuillat (Figure 3a). These two phenomena can be characterized by two mass transfer coefficients: the internal transfer coefficient, i.e., the diffusion coefficient, and the external transfer coefficient, i.e., the surface emission coefficient. Ruiz de Adana adjusted the diffusion models to a semi-infinite plate with Dirichlet and Robbins boundary conditions and used it to fit the internal and external mass transfer coefficients, respectively, to the experimental data of Feuillat (1996). From this fit (Figure 3b), the results obtained were $1.05 \cdot 10^{-11}$ m^2/s for the internal coefficient and $1.33 \cdot 10^{-8}$ m/s for the external coefficient. The results of the experiment validation, in which the RSS (root sum square parameter) is 0.0201, make it possible to conclude that the accuracy of the model is sufficient to simulate the moisture profile of an oak barrel stave (Figure 3c-d) (Ruiz de Adana et al., 2005).

In 2003, Vivas *et al.* (2003) performed measurements on oak wood pieces to evaluate, for the first time, the rate of oxygen entry through dry wood and under different MCs. For this purpose, they developed a device based on standard procedures for gas permeability measurement in membranes (ISO, 2007; ASTM, 2005, 2009), using a donor and carrier gas, and an electrochemical system to measure DO. The measurement technology used has two important limitations. On the one hand, the measure must be taken in a fluid flow (Nevares et al., 2008), and on the other hand, the measurement of very small quantities of DO in the carrier gas is not possible. This was the reason why measures could not be taken in woods of thickness similar to the staves of a barrel (20-27 mm), and they measured only woods that were 2, 4, 8, and 16 mm thick. These authors verified the dependence of OTR_{wood} on the thickness and water state of the wood on one side and the wood grain on the other, with the OTR being much lower when the wood was wet.

This condition of the wood had already been considered by Singleton (1995) on the basis that the diffusivity of oxygen in dry wood, which is 80% of the diffusivity of oxygen in the air, turns out to be much higher than that of oxygen in water. In fact, the oxygen diffusion coefficient in saturated air is 10820, i.e., 10.82·1000, times greater than that in water at 15°C (Denny, 1993). In addition to measuring for the first time the dependence of the OTR in wood on moisture, Vivas *et al*. concluded that the larger the wood grain is, the smaller its OTR, corroborating the result by testing three different thicknesses. Years later, Nevares *et al*. (2014) observed the diffusion movement of oxygen through a 27 mm oak stave in different water states. They applied a similar approximation of Fick's law and took advantage of the already consolidated photoluminescent technology to observe the movement of diffusing oxygen through the dry wood of a newly filled barrel, comparing it with that of a wine barrel stave after 40 days of wetting. To that end, they developed a device (del Alamo and Nevares, 2012) in which they fixed a stave section that was 27 mm thick (Figure 4). To that section, they attached a flat sensor, exciting it with light, and mapped the DO distribution both in the interior section of the stave and on both sides of it. To reproduce the condition of a full barrel, they exposed one side of the stave to the air and the other to the model wine, and to avoid the interference of oxygen from the air trapped in the porosity of the wood, they degassed the wood from the side that the interior of the barrel reproduced. In this manner, they were able to demonstrate that oxygen is able to pass through a wet stave for 40 days, avoiding outgassing and showing that the measurements performed by Vivas *et al*. years earlier in much thinner wood staves were reproduced in staves with normal thickness. In this same paper, they formulated the role of free water in wood as the cause of a determinant decrease in oxygen permeability and related the thickness of the wood stave as a multilayer system differentiated by its MC. In a subsequent study (Nevares et al., 2016), they were able to demonstrate in a complex experiment the high correlation between the free water trapped in the flooded layer on the side of the oak stave in contact with the wine and the diffusivity of oxygen in the stave and concluded that because the impact of moisture on the diffusion coefficient is so dramatic, moisture seems to be the key factor leading to the very low OTR conditions in wine barrels just two months after filling. In this regard, del Alamo-Sanza *et al.* (2017) have shown that when the water balance is reached in the wooden staves described by Feuillat (1996) and Ruiz de Adana (2002, 2005) after 82 days, the staves of both *Quercus petraea* (Matt.) Liebl. and *Quercus alba* L. allow the passage of perfectly quantifiable amounts of oxygen (Table 1). It is important to note that this test was performed with pieces of staves from built barrels that were disassembled for analysis, that is, after blending and toasting in cooperage, which ensures reproducibility in the actual barrels.

Recently, a study by Del Alamo-Sanza *et al.* (2017) has evaluated for the first time the OTR of American oak woods, also including French oak woods with different grains, and simultaneously measured the moisture profiles using the blade laminate technique described elsewhere (Gorvud and Arganbrigh, 1980). Figure 3c shows the wetting profile measured by these authors, which corresponds to the model defended by previous studies (Feuillat, 1996; Ruiz de Adana et al., 2005; Singleton, 1995) on wood staves in contact with wine on one side and atmospheric air on the other. The results have shown for the first time that the rate of oxygen entry through American oak wood is greater the smaller the grain of the wood is, and the same has been found to be true of French oak wood, agreeing with the results obtained by Vivas *et al.* in 2003. On the other hand, it has been verified that the OTR is defined by the degree of wood impregnation, decreasing the greater the moisture front is, in both French oak staves, already described in 2014 (Nevares et al., 2014), and American oak staves.

Modification of the interior pressure and formation of the headspace

Evidently, the process of evaporation of the water and ethanol from wine depends on the environmental conditions of the barrel room. In his model, Ruiz de Adana established the dependence of wine losses per annum on temperature, relative humidity, and air velocity (Ruiz de Adana, 2002), but there are other factors that, under equal conditions, cause wine losses to differ (closure, bung, reduced pressure, etc.). The evaporation of part of the wine during its long stay in barrels causes different situations, depending on the capacity of the barrel to adapt or not to the new reduced volume. When a full vessel is hermetically sealed and loses part of its volume, there are two possibilities. The first option for the vessel is to adapt, by deforming to the new volume, whereas the other would be a minimal initial deformation of the vessel in an attempt to adapt to the new volume of fluid. The deformation will reach its limit, followed by a decrease in the internal pressure that will generate a gas space at the top of the barrel, a space that significantly affects the operating conditions of a barrel. Peterson (1976) found that wine losses in barrels caused a drop in internal pressure below atmospheric pressure, generating an internal vacuum that began one month after filling the barrels without any type of topping. In some barrels, depressurization reached values of up to 240 hPa, whereas in other cases, the vacuum was lost when small leaks of wine appeared on the surface of the barrel, but the vacuum was recovered over time in most cases. He hypothesized that there would most likely be hardly any oxygen entry through the wood and that the differences found for the same aged wine in six equal barrels depended on the oxygen added during pumping, filling, and emptying. He concluded his study by stating that oxygen entry can vary widely from barrel to barrel during aging, even though the entire lot had been treated the same: the barrels were cleaned, filled, and stored simultaneously. Therefore, it was noted that wines obtained after long aging in similar and contiguous barrels can often have very different properties.

Moutounet et al. (1998) established the effect of the type of barrel seal on wine losses. Thus, in barrels that remain open or closed with a simple glass bung, it was found that volume losses are produced in a linear manner, representing annually by extrapolation between 4 and 5%. However, in barrels that were hermetically sealed, it was observed that there was no decrease in volume during the first week. After that time, the volume begins to decrease between 1.3 and 1.6% per year, which is much less pronounced than in the case of open barrels. Moutounet also observes that when opening hermetically sealed barrels, the wine level falls rapidly, with this loss of volume corresponding to the consumption or loss of wine that occurs during aging. In this regard, Vivas and Glories (1997), in their study on the supply of oxygen during winemaking, reported different rates of oxygen entry into the barrel as a function of bung placement, finding rates of 45 mg/L.year using a silicone bung to ensure an airtight seal, 28 mg/L for an unsealed barrel, or 36 mg/L.year for a sealed barrel with bunghole on the side. The studies by Moutounet et al. (1994) described that the phenomena of depressurization, due to the different rates of evaporation observed, depend on the degree of tightness of the barrel seal. Thus, it was observed that the silicone bung at the top of the barrel favors oxygen penetration, and the increase in the OTR was quantified as between 30% with the barrel turned and sealed with a wooden bung and 60% with a silicone bung and the barrel in the upright position.

When the barrel is hermetically sealed, depressurization can cause deformation of the wood from the heads, which is most evident in the case of French oak barrels. This deformation reduces the volume of the barrel and continues until there is no more deformation, which is the time when the headspace is formed, and increases in volume due to the wine losses. This gas volume has a gaseous composition that is modified during aging (Moutounet et al., 1998). A recent study describes the results obtained during the monitoring of the entry of dissolved oxygen and the depressurization generated in the interior of eight barrels (Nevares and del Alamo-Sanza, 2017), with four being composed of *Quercus alba L.* and four of *Quercus petraea (Matt.) Liebl.* (Figure 5 a-b). This study reports that French oak barrels have a tendency to deform more than American oak barrels, which explains why *Q. alba* oak barrels reach greater internal depressurization (60 hPa) than *Q. petraea* (10 hPa), which are values similar to those measured by Moutounet *et al*. (1998)

The studies cited so far indicate that the internal depressurization achieved by hermetically sealing the barrel favors the entry of a greater amount of oxygen and a greater amount in the case of silicone bungs when a headspace is formed with the bung being vertical. This headspace is caused by wine losses due to wood impregnation and by the evaporation of water and alcohol from wine through these same walls, which is quantified as being between 2 and 5 mL per liter of wine and year (Ribereau-Gayon, 1933), approximately 1125 mL per barrel and year, although unpublished personal experiences suggest higher losses, of 4 or 5 liters per year, depending on the barrel and the environmental storage conditions.

The barrel function hypothesis proposed by Moutounet *et al*. (1998) focused on the study of the headspace, performing measurements of gas composition (5-9% O_2 and 20% CO_2) and finding a composition that was very different from that of atmospheric air (20.946% O_2 and 0.035% CO_2). Moutounet *et al*. proposed that the oxygen consumption of the gas space by wine is faster than the diffusion of atmospheric air through the wood to that gas space. They also proposed that oxygen penetrating through the wood should be partially consumed by the wood's compounds because if oxygen diffused freely through wet wood, then it would quickly occupy the headspace, oxidizing the wine (Singleton, 1995). Ribereau-Gayón *et al*. (1976) had already indicated the possibility that oxygen would enter only through the top of the barrel, where the wood of the gas space would be dry due to not being in contact with the wine. The belief that the wood in contact with the gas surface of the headspace would have a low MC has been used to explain the entry of oxygen through that dry wood of the upper part of the barrel (Moutounet et al., 1994; Singleton, 1995). Recently, the wood MC of different barrel staves has been measured at 5 mm distance from the wine, showing that the moisture of the staves in contact with this gas space is at levels similar to the rest of the staves located in other positions of the barrel with continuous contact with the wine (Figure 6). One possible explanation for the high MC in the headspace may be that it is saturated with water vapor (del Alamo-Sanza and Nevares, 2015c; Nevares and del Alamo-Sanza, 2016). With these measurements, it was shown that the wood of the staves at the top of the barrel (position 1, Figure 6) is not dry, a result that does not corroborate the theory that favors the preferential entry of oxygen through the dry wood of the staves of the top of the barrel in contact with the gas space.

Moutounet *et al.* (1998) measured the composition of the headspace gas at the top of the barrels of aging wine that had generated depressurization, finding that the gas did not have the same composition as the air, presenting much lower oxygen levels and much higher CO_2 levels. Although low oxygen levels could be explained by the oxygen consumption of wine, it was not easy to explain the high levels of CO_2, which were almost 600 times higher than in the air (Moutounet et al., 1998). The origin of CO_2 was attributed to the degassing of carbon dioxide dissolved in the wine because it was verified that these levels were higher in wine barrels that underwent malolactic fermentation in the barrel. This theory could not be defended with the dissolved oxygen concentration reported by Vivas and Glories (1993), who measured a dissolved oxygen gradient from the top of the fluid in contact with the headspace that decreased toward the bottom of the barrel, although it is unknown whether depressurization had been generated inside the barrel because they did not report this issue in their study (Figure 5c).

The results recently published by our group (Nevares and del Alamo-Sanza, 2016, 2017) have corroborated the hypothesis of the degassing of wine in contact with the headspace (Figures 5c-d). The tests were performed with new American oak barrels filled with a deoxygenated solution (synthetic wine, 15%, pH 3.5) and in which the accumulated dissolved oxygen was measured with two submersible photoluminescent probes located at 15.6 cm (top probe) and 46.8 cm (bottom probe) from the bung.

Figure 5e shows the dissolved oxygen measurements reported by each of the probes when the barrel is not hermetically sealed, indicating that the closer to the bung, the more dissolved oxygen is being measured, which coincides with the data already reported (Vivas and Glories, 1993). However, when the seal is airtight, a headspace is formed, and the generation of a reduced pressure occurs, resulting in the consequent degassing of the wine, which is reflected in a higher dissolved oxygen content the farther away from the bung being measured (Figures 5d and f). A higher OD level is observed in the probe located at the bottom of the barrel, contrary to what might be expected according to what has been reported by other authors (Figure 5f). Based on these results, it can be argued that wine degassing exerts a significant influence on the entry and consumption balance of O_2, determining the composition of the headspace.

The role of ellagitannins as oxygen scavengers

The reactivity of ellagitannins to molecular oxygen has been highlighted in a model wine (Vivas and Glories, 1996). For a long period of time, there has been speculation on the role of oak ellagitannins as oxygen blockers because as oxygen diffuses into the free-liquid part of the staves against the "wind" of water and ethanol vapor, it would encounter and react with wine or oxidizable wood components such as gallic acid before reaching the beverage itself (Singleton, 1995). The products of phenolic oxidation polymerize and become brown. These larger products would have more difficulty diffusing back to the contents, and one might expect to observe a brown interface develop within the wood. Examples of this phenomenon have been observed in wood from old wine casks.

Feuillat (1996) also proposed that there would be an oxidation of the ellagitannins at the liquid-gas interface inside the impregnated wood (Figure 7a). The inner face of the fluid impregnated stave, loaded with dissolved phenolic substances extracted from the wood, would constitute an effective “barrier” to oxygen. In a study on barrel function according to the number of wines that the barrel has contained, Vivas *et al.* (1998, 1999) offered data that seemed to confirm this theory. In the non-impregnated layers of the stave, which are farther away from the wine, a greater number of insoluble ellagitannins can be found, which are produced by the oxidation of the soluble fraction of wood ellagitannins. To explain this finding, they used the model proposed by Feuillat (1996) and justified that the presence of wood moisture (MC≥30%) partially explains this oxidation that is catalyzed by transition metals present in the wood (Figure 7a).

Thus, in the first few millimeters of thickness of the stave in contact with wine (used barrels), the obstruction of the wood by tartrate salts and coloring matter from the wine makes the absorbance at 420 nm lower than in the inner wood layers (Figure 7b). In these deeper layers, the presence of oxidized insoluble ellagitannins from the wine of previous years causes an increase in absorbance at 420 nm. The lack of description of the methodology used by Vivas and his team to build these profiles does not allow these measures to be reproduced. Therefore, all interpretations seem to fit each other and apparently explain the predominant role of soluble ellagitannins of the flooded layer of the stave as an active barrier against oxygen, preventing it from reaching the

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wine. To explain this phenomenon, it would be necessary to demonstrate that the oxygen level is practically zero at the liquid-gas interface described by Feuillat (1996).

A recent study (Nevares et al., 2016) has measured the partial pressure of oxygen (pO_2) and the MC inside a stave under conditions similar to those of a stave of a barrel full of wine, simultaneously quantifying oxygen permeation. The results demonstrate that the gas-liquid interface (free water → MC>30%) acts as a “stopper” to obstruct the entry of atmospheric oxygen through the stave (Figure 8). In that interface, oxygen is accumulated, increasing the pO_2 from an initial situation in which the wood is deoxygenated, which clearly indicates that the role of ellagitannins as a buffer against oxygen, although it is very likely to exist, does not appear to be the key factor that determines the low permeation of a wet stave. The combined action of low oxygen diffusivity in a fluid medium compared to the air and the existence of wood compounds dissolved in this fluid, which are highly oxidizable, can be a good explanation of the phenomena that occur at the interface. In this study, a clear relationship between the free water content of the wood and oxygen accumulation inside the wood, far from the ideal OD profile proposed by Feuillat, was observed. The following studies corroborate these results, in the diffusion of oxygen in both French oak and American oak (del Alamo-Sanza et al., 2016, 2017), demonstrating that the key phenomenon in the reduction of the diffusion of atmospheric oxygen through the wood of the barrel staves toward the wine is mainly governed by the level of flooding of the stave, not by the capture of oxygen by ellagitannins.

In this line, it is important to note a recently published study in which it becomes clear that the ellagitannins, once extracted to the hydroalcoholic medium typical of model wine, undergo degradation and oxidation processes in both the presence of oxygen and the absence of oxygen

(García-Estévez et al., 2016). This finding indicates that solubilized wood ellagitannins decrease without an intervention by oxygen, thus confirming the unstable nature of these compounds in solution. In addition, this study demonstrates that the degradation of ellagitannins, released by the wood to a hydroalcoholic medium, can be attributed only to the presence of oxygen during the first few days of wine-wood contact, in both an air-saturated medium and a medium that has only the oxygen released by the wood. The results show that after the first 25 days of contact, the content of ellagitannins decreases in the same manner in the presence and absence of oxygen and that only 20% of the decrease in ellagitannins can be attributed to oxygen. These results corroborate the hypothesis described above, in which it is argued that the decrease in oxygen entry through the wood during aging is mainly governed by the level of flooding of the stave.

Finally, although the most recent studies on pieces of wood have been performed with the wood of staves of newly manufactured barrels disassembled for their study, many others have been performed using raw wood, and it is necessary to consider the effect that cooperage has on oxygen permeation. The importance of the processes of the bending and toasting of oak wood planks in cooperage is demonstrated in the study by Nevares and Alamo-Sanza (2015), in which in the case of high-OTR wood, these change from dosing 1.68 mg/L in rough staves to 0.37 mg/L in toasted staves, which represents a 4.5-fold decrease in the OTR. In the case of low-OTR wood, they went from 0.64 mg/L in rough staves to 0.21 mg/L in toasted staves. Therefore, wood loses up to three times its OTR during the toasting process.

Barrel function

With all that has been described above, it is possible to propose a barrel function that is somewhat different from what is generally accepted. In a barrel full of wine, the volume of liquid decreases because part of the wine impregnates the dry wood (with a MC of 14%) and another part is evaporated through the wood, causing wine losses. This loss of fluid volume can cause the barrel to deform, but if it cannot be deformed, either because the wood has reached its deformation limit or because the necessary depressurization to deform it is not reached, then a vacuum is generated, which must be filled with gas. This vacuum is the headspace, which is typically formed during wine aging in barrels and located at the top of the barrel. Most authors propose that the gas of this headspace comes from the outside because it enters through the dry wood of the top of the barrel. The wine's avidity for oxygen consumption would justify the low concentration of oxygen in the gas space, although it is difficult to explain the different composition of the gas in this space compared to the atmospheric air. In addition, the high MC found in the wood of the staves located at the top of the barrel does not justify a large entry of oxygen through the wood of these staves (up to two pieces) because they have a limited permeability to oxygen, similar to that in the remaining staves. With the data from the most recent studies, it can be proposed that wine degassing is the main cause of the composition of the gas in the headspace.

When the pressure in the headspace is lower than atmospheric pressure, the solubility of oxygen and carbon dioxide is lowered, which causes its degassing, given that it tends to equilibrate according to Henry's law, with the gas of the headspace with which it is in contact. Typically, the wine consumes oxygen rapidly, maintaining levels close to 0.05 mg/L or 0.57% O_2. If the internal barrel pressure drops from 980 to 880 hPa at 15°C, then the partial oxygen pressure will be 1.04 hPa. According to Henry's law, the oxygen concentration in the 225 L of wine tends to equilibrate with that of the headspace gas showing very similar partial oxygen pressures for both phases. Applying the ideal gas law, to reach the 5% oxygen reported by Moutounet *et al.* (1998) in a headspace of 400 mL, it would be necessary to degas approximately 125 liters of wine, 60% of the volume of the barrel. As a consequence of this degassing, a gradient of the dissolved oxygen levels should be observed, showing a lower concentration at the wine surface in contact with the headspace and a greater concentration toward the bottom of the barrel, a phenomenon that coincides with what has been reported in recent studies (Nevares and del Alamo-Sanza, 2016) and seems to be what actually occurs inside the barrel filled with wine.

Conclusions

Therefore, based on the results obtained to date, it can be said that the barrel behaves as an interactive vessel with wine because, on the one hand, it allows the transfer of substances from the wood to the wine and, on the other hand, the dynamic transfer of oxygen from the air to the wine during one year of aging.

Oak wood is a porous material permeable to oxygen which is flooded by the wine during aging and, as a result, the OTR of a wine barrel decreases until it is full of wine. It has been proved that the decrease in the OTR is governed mainly by the advance of the moisture front in the wood (wood impregnation), in contrast to the hypothesis which attributes it to the oxygen consumption by the soluble elagitannins of the wood.

The formation and composition of the gas space at the top of the barrel depends primarily on the vacuum generated inside due to wine evaporation together with barrel tightness, and by the degassing of the wine itself.

As regards the origin of the wood, all the research coincides in evaluating European wood (*Quercus petraea*) as being more permeable to oxygen as compared with American oak

(*Quercus alba*) and it has been found that the finer the grain, the greater the oxygen permeation in the wood of both species.

The oxygen reaching the wine contained in a barrel does so both via the wood and via the joints between staves, so the OTR of the barrel depends both on the wood it is made from and on the construction process, an area which has been studied very little.

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Table 1: Barrel OTR values published by different authors and the measurement conditions of each.

Oxygen Transfer Rate	Trial conditions	Oxygen measurement technique	Authors
2-5 mg/L.year	Oxygen through the wood	Assessing the formation of SO_4^{-2} after filling a barrel with an aqueous SO_2 solution.	(Ribereau-Gayon, 1933)
15 to 45 mg/L per year	hermetically sealed barrels		
0.7 to 3.3 mg/L	Unsealed barrels		
1st year 40 mL/year 2nd year 20 mL/year	Wine stored in 250 L barrels		(Frolov-Bagreev and Agabal'iants, 1951)
2.8-7 mg/L year	Wine stored in 50 gallon barrels (≈190 L)		(Prillinger, 1965)
1.25 mg/L.h	OTR through 26 mm thickness oak stave in cognac; trials carried out with pure oxygen	Gas chromatography	(Semenenko, et al., 1979)
28 mg/L.year	Unsealed barrel	Assessing the formation of SO_4^{-2} after filling a barrel with an aqueous SO_2 solution during 6 months	(Vivas & Glories, 1997)
36 mg/L.year	Sealed barrel, bunghole on the side		
45 mg/L.year	silicone bung to ensure an airtight seal		
19.5±1.5 mg/L.year	New barrels Limousin (wild grain)		
28±1 mg/L.year	New barrels Centre (tight grain)		
10±1.4 mg/L.year	5 year used barrels Centre (tight grain)		
Maximum 26 mL/L.year	permeability of oak to be no more than 20 Barrer (10^{-10} $cm^3.cm.cm^{-2}.s^{-1}.cmHg^{-1}$)	Barrel as a semipermeable membrane to gases → Fick's Law	(Kelly & Wollan, 2003)
60 mg/L.h	2, 4, 8 and 16 mm thickness wood pieces, and pure O_2	Electrochemical sensor	(Vivas, et al., 2003)
5.4 mg/L.h	8 mm thickness Allier (tight grain) 8 mm thickness Vosges (wild grain)		
Barrel:32±5.6 mg/L.year	4 new barrels American Oak (*Q. alba*)	2 Optoluminiscent dipping probes per barrel	(Nevares and del Alamo-Sanza, 2014)
Oak wood: 21±2.5 mg/L.year	4 new barrels French Oak (*Q. petraea*)		
Barrel:27±2.3 mg/L.year			
Oak wood: 16±2.8 mg/L.year			
11.3±0.9 mg/L.year	Dynamic barrel OTR; one year measurement 4 new medium-grain American Oak barrels	2 Optoluminiscent dipping probes per barrel	(del Alamo-Sanza and Nevares, 2014)
11.7±1.5 mg/L.year	4 new tight-grain		

	American Oak barrels		
8.2±0.5 mg/L.year	4 new tight-grain French Oak barrels		
High 265 µg/L·day	OTR through 27 mm thickness French Oak rough staves (quarter sawn)	Optoluminiscent dots	(Nevares and del Alamo-Sanza, 2015)
Low 140 µg/L·day			
High 8.3 (11.5) mg/L·year	Wood-OTR (barrel-OTR) in constructed barrels	Optoluminiscent dipping probes	
Low 4.1 (9) mg/L·year			
9.51±1.45 mg/L.year	Dynamic OTR through 27 mm thickness American Oak toasted staves	Optoluminiscent dots	(del Alamo-Sanza et al., 2017)
12.34±1.98 mg/L.year	Dynamic OTR through 27 mm thickness French Oak toasted staves		

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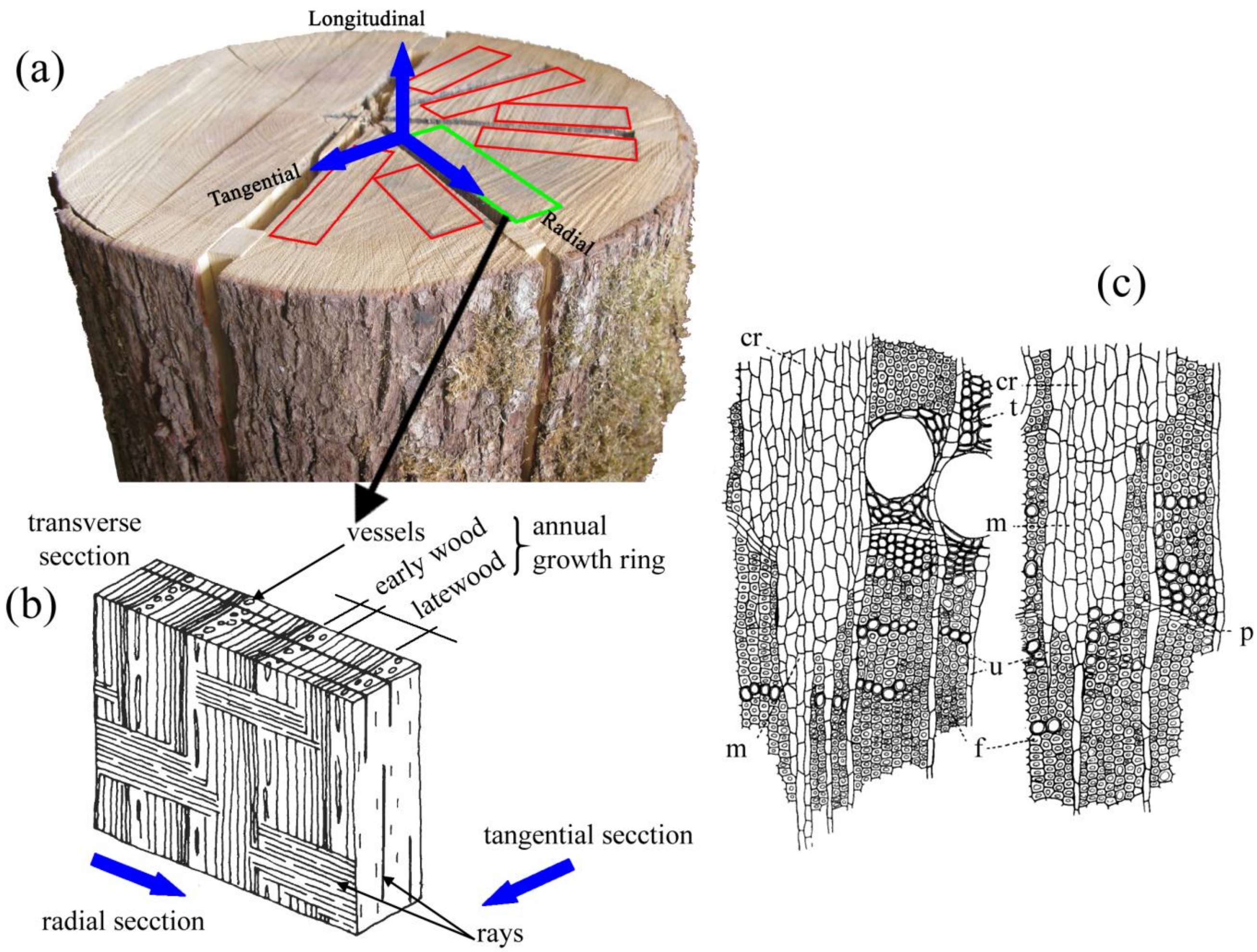

Figure 1.- a) Directions of the wood in a trunk of *Quercus petraea*. Schematic of the anatomical macrostructure of the wood in which it differentiates latewood, earlywood, and medullary rays. b) Transverse sections of portions of compound rays showing an abrupt mode of origin of compound rays: uniseriate (u), multiseriate (m), and compound (cr) rays; f, wood fibers; t, tracheids; p, thin-walled parenchyma marking boundary between rings of growth; X 200 (Langdon, 1918).

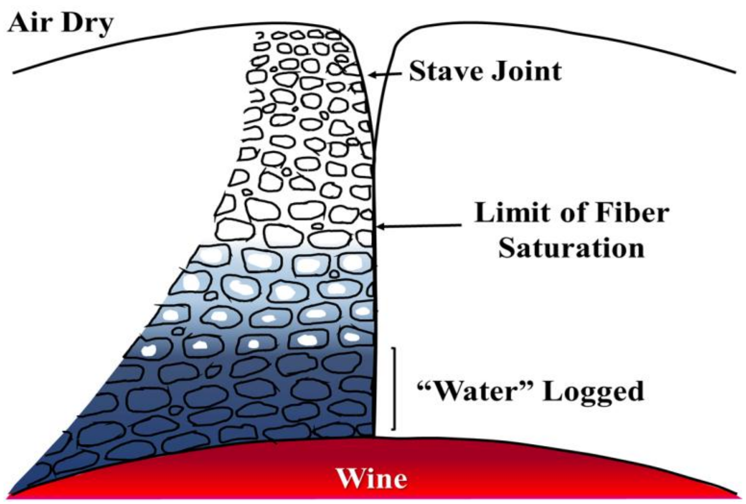

Figure 2.- Moisture relationships through a stave of a barrel in use for wine maturation (Singleton, 1995)

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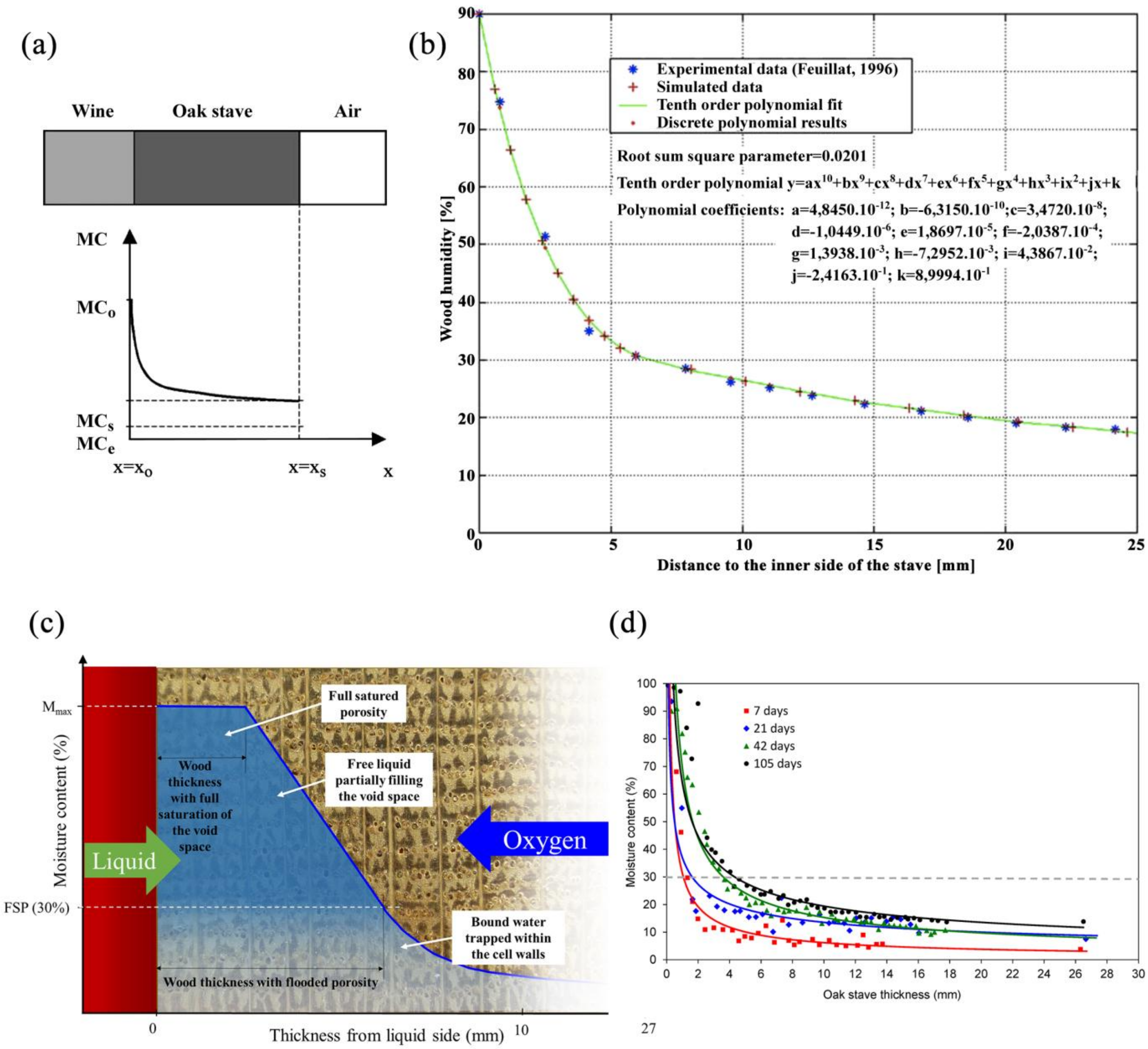

Figure 3.- a) Boundary conditions for a stave in a cask. b) Moisture profile in the staves of an oak cask (Ruiz de Adana et al., 2005). c) Moisture profiles of Allier 1.4 French oak wood at different moments of aging. d) Impregnation model of a stave under barrel conditions. (del Alamo-Sanza et al., 2017)

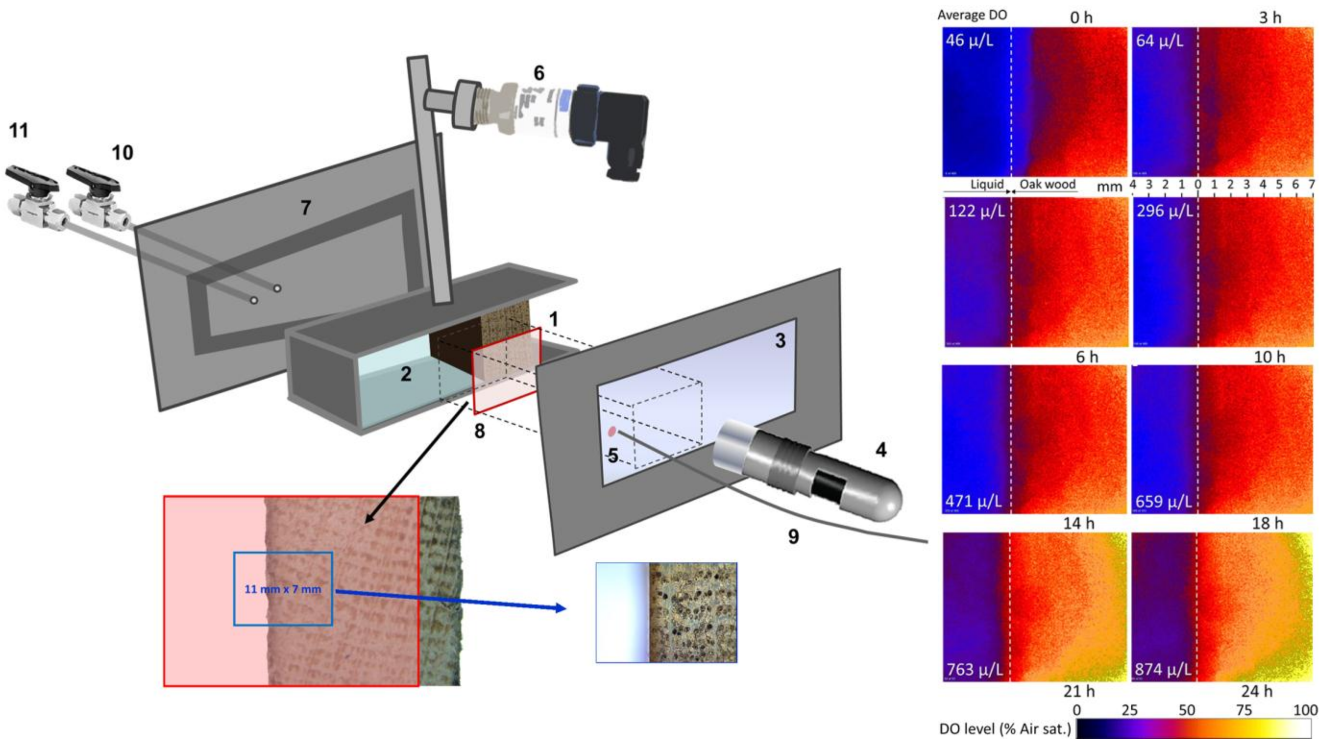

Figure 4. Schematic of equipment to measure the oxygen transmission rate across wood from the exterior to the interior of the stave under conditions similar to those operating in a barrel, considering the wood water saturation. (1) piece of barrel oak stave, 27 mm thick; (2) liquid chamber; (3) glass; (4) USB microscope; (5) spot Pst6; (6) pressure transmitter; (7) stainless steel side; (8) planar optode; (9) optical fiber and (10, 11) gas valves. (Nevares et al., 2014)

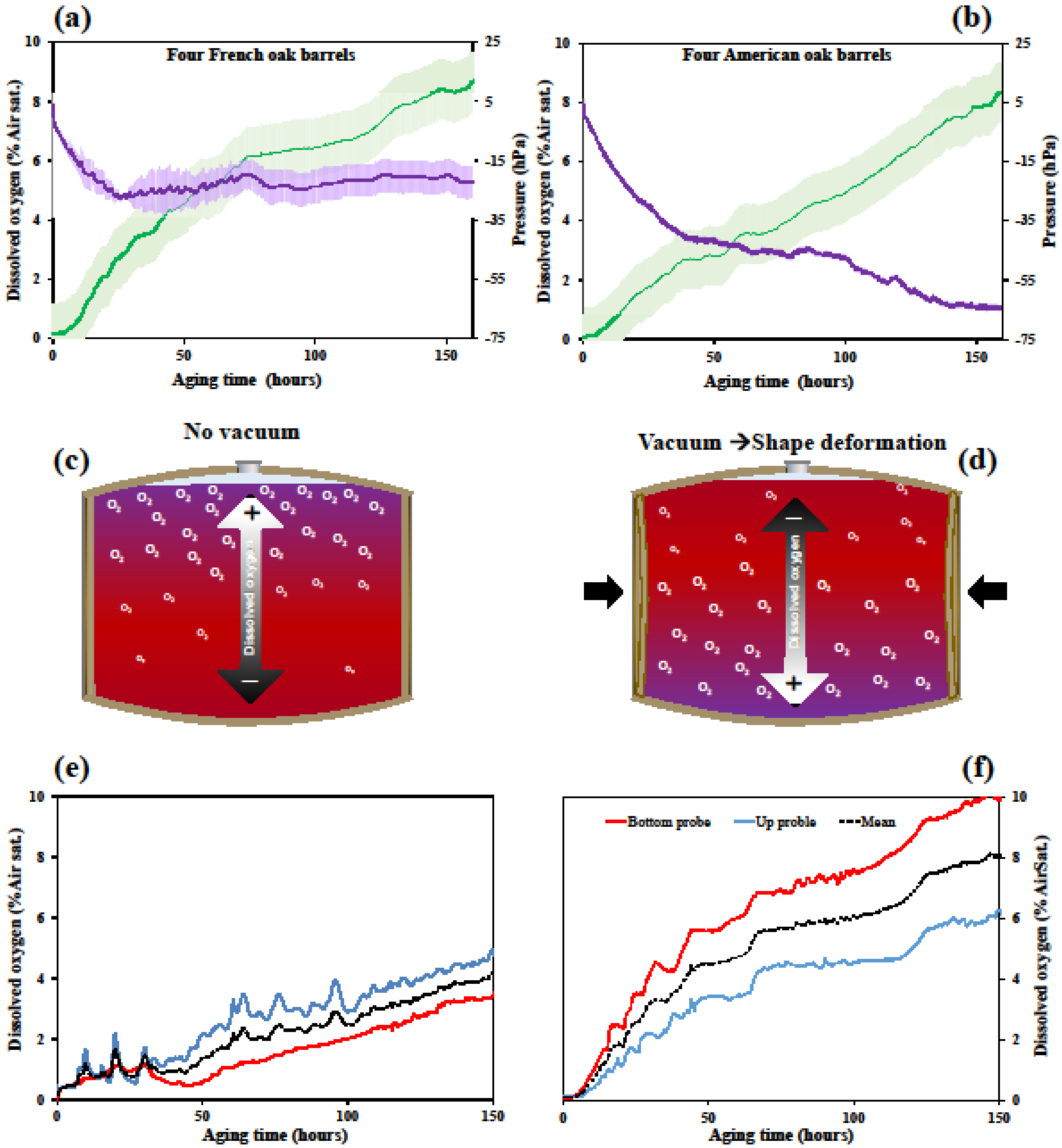

Figure 5: Pressure variation inside the barrel and vacuum generation (purple line) together with the dissolved oxygen evolution (green line). The shadow expresses the standard deviation of the measurements. a) 4 French oak barrels, b) 4 American oak barrels (Nevares and Del Alamo-Sanza, 2017). c) Dissolved oxygen gradients in wine stored in an oak barrel in no airtight

conditions with air entering the barrel (mainly through the bung) and, d) when it is airtight, vacuum creation and headspace formation after shape deformation. e) Evolution of oxygen accumulated inside the barrel without generating a vacuum. f) Evolution of the oxygen accumulated inside the barrel when a vacuum is generated (Nevares and del Alamo-Sanza, 2016).

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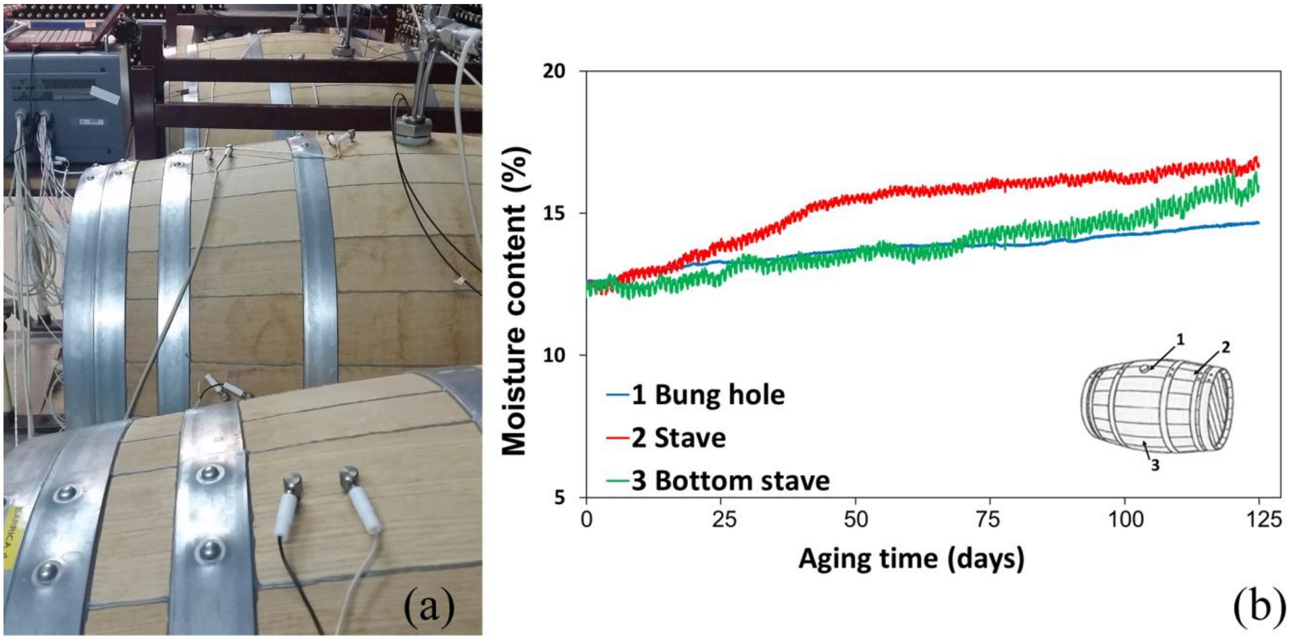

Figure 6. Moisture content (MC%) variation of the interior of the oak wood at 5 mm distance from the wine in different staves of a French oak barrel (del Alamo-Sanza and Nevares, 2015; Nevares and del Alamo-Sanza, 2016).

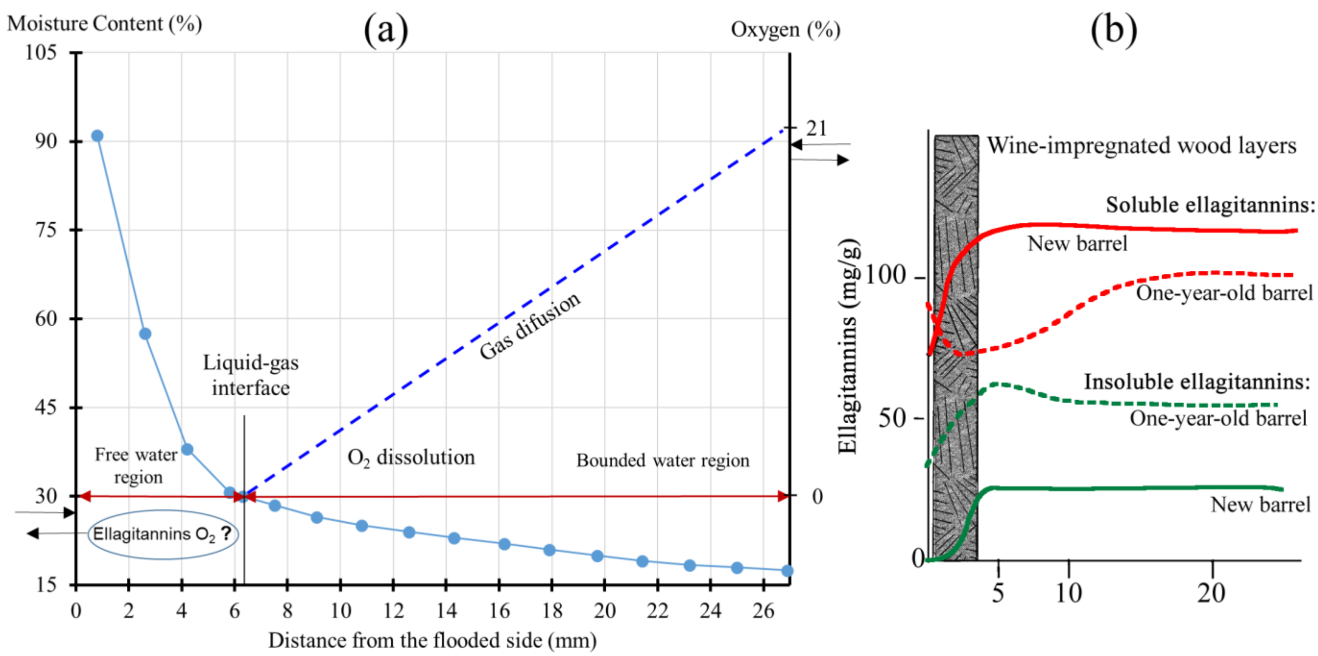

Figure 7: a) MC profile in the thickness of the oak stave in steady state and hypothesis of the transfer of oxygen through the pores of the wood (Feuillat, 1996), b)Ellagitannins evolution from new or old staves (one-year-old barrel) (Vivas and Glories, 1996).

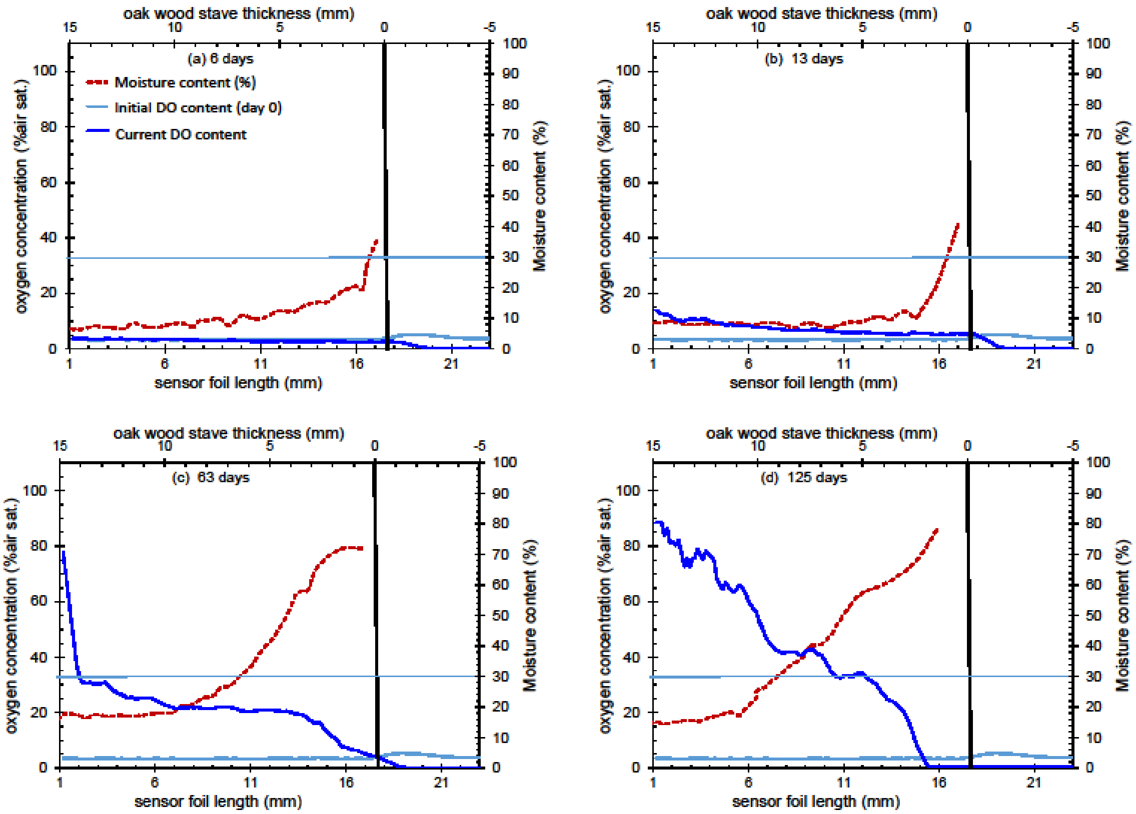

Figure 8: Profiles of the average oxygen concentrations and MC in the thickness of the stave and in the wine in contact with the wood during the 18 weeks measured. Progression of the oxygen concentration profile (% air sat.) (unbroken line) and the %MC profile of wood (dashed line) at 1, 2, 9, and 18 weeks (Nevares and del Alamo-Sanza, 2015).