Oxygen Transfer Rate in Oak Barrels

Annual evaluation for dynamic oxygen intake and entry

Maria Del Alamo-Sanza and Ignacio Nevares
UVaMOX-Universidad de Valladolid, Avda. de Madrid 50, 34004 Palencia, Spain

Aging wine and other alcoholic beverages in oak barrels is a common practice in most wine regions of the world. The interactions between wood compounds and wine have been extensively studied. However, information regarding the supply of oxygen into wine in barrels is limited.

Oxygen directly or indirectly determines the phenomena experienced by wine during *élevage*, such as polymerization of tannins and anthocyanins, which improve the stability and quality of astringency and color, consumption of free sulfur dioxide, oxidation of ethanol to acetaldehyde and general modifications of the phenolic wine profiles. These phenomena reflect changes in wine compounds and their interactions with wood-extracted compounds.

In addition, these changes are often led by oxygen and may be beneficial or harmful. In general, the more controlled these reactions are, the better the results. Therefore, to control this process, it is important to know how much oxygen is entering a barrel of wine, the mechanisms that govern this process and the factors that affect oxygen transfer rate.

Different theories have developed in the past 100 years regarding how oxygen enters wine barrels. In 1931 J. Ribereau-Gayon confirmed that O_2 entered the barrel by assessing the formation of SO_2 after filling a barrel with an aqueous SO_2 solution. Ribereau-Gayon found that the oxygen transfer rate (OTR) through the oak wood was limited (2 to 5 ml/L per year) and that the main route of O_2 entry occurred where the wine was in contact with the gas in the headspace of the barrel. The total rate at which oxygen enters wine barrels varies with the time of year from 11.08 to 14.77 mg/L per year (based on 1 mg ≈ 1.35 ml at 15° C) in hermetically sealed barrels and from 1.48 to 3.69 mg/L per year in unsealed barrels.[9]

M. Moutounet wrote: "If we examine the results of the studies of Ribereau-Gayon (1931) on the penetration of oxygen, we observe that in a situation of permanent topping-up at atmospheric pressure, the oxygen transferred is evaluated at between 2 and 5 ml/L per year, whereas in barrels with an airtight bung the oxygen that penetrates is around 15 to 20 ml per year. This data can be explained by the existence of negative pressure inside the barrel, which favors gas entry."

R. Peterson worked on this topic and argued that the oxygen present in wine barrels was mainly introduced during barrel filling and racking, which adds approximately 2.8 to 7.0 ml/L per year to the oxygenation capacity of the barrels based on the previous work from Prillinger in full 50-gallon barrels.[6]

V. Singleton postulated that O_2 primarily enters the barrel through dry wood.[4] Therefore, wine only would receive oxygen from the air in the headspace at the top of the barrel during *élevage*. In addition, wine would receive atmospheric oxygen incorporated during barrel topping.[3]

V. Vivas and G. Glories measured the sulfate concentrations formed within barrels filled with a 500 mg/L solution of sulfur dioxide, allowing them to quantify oxygen entry after six months of élevage.[2] Data from these authors indicated that the rate of oxygen entry into new barrels was greater than the rate of oxygen entry into used barrels.

In addition, the rate of oxygen entry depends on the type of oak and the position of the bung. They found oxygen entry rates of 10 mg/L per year for two used French oak barrels and 28 mg/L per year for two new barrels from central France. Regarding bung position, the authors found that if the bung is closed without sealing, the annual rate of oxygen entry is 28 mg/L per year. In contrast, if the bung is closed with the traditional technique, with the bung- hole on the side, the rate of oxygen entry is 36 mg/L per year.

Furthermore, if the bunghole is sealed with a silicone bung to ensure an airtight seal, the rate of oxygen entry is 45 mg/L per year. The authors determined that 21% of total oxygen entered through the bunghole, 63% of oxygen entered between the staves, and 16% of oxygen entered through the wood itself. This result was made possible by performing the study in two barrels that were sealed differently for individual quantification.[2]

Oxygen transfer rate

For our study, there were 12 new Bordeaux (225 liter) barrels comprising both French and American oak that were either fine or medium grain with medium toast level. The American oak barrels were from Tonelería Victoria (Spain) and the French oak barrels from cooperage Radoux (France). The daily increase of oxygen within each barrel was determined by considering the mean values that were obtained from two optical probes installed in each barrel through a silicone bung.

Figure 1: four American oak barrels were tested 23 times within one year to determine the evolution of oxygen uptake velocity, which demonstrated in a slowdown of the oxygen transfer rate. An airtight bung (inset photo) was created to introduce two optical submersible dissolved-oxygen probes, a gauge for vacuum measurement, inert gas inlet (N_2) and gas outlet to evacuate dissolved-oxygen content in a synthetic wine before every test.

The position of the probes in the barrel — in the lower half and at the top (156 mm and 468 mm from the bung)—was determined in the first part of this study, in which eight probes were immersed at various depths in a barrel. Readings from the probes showed that dissolved-oxygen (DO) concentrations decreased as the distance from the bung increased. The two submergible oxygen probes (PSt6 sensor, detection limit = 0.001 mg/L, PreSens GmbH, Germany) used for the next stage of the study were chosen after being assessed as being representative of the evolution of DO within an entire barrel.

All trials were carried out in a cellar with controlled temperature and humidity (15° to 16° C and 70% to 80% relative humidity). The possible temperature gradient inside the barrels was checked, but there was no difference within the liquid inside the barrel.

Daily values from the two probes were added to determine the cumulative concentrations of dissolved oxygen that reached the model wine in each barrel for each day of the test. It was important to use a non-oxygen scavenger liquid with the same pH and ethanol content as wine that allows for oxygen mass balance calculations.

By using a model wine (pure water and ethanol at 15% v/v, 3.5 pH), we were able to calculate the exact OTR in each barrel because there were no compounds to consume the oxygen. We evaluated the oxygen reaching the liquid, if wood phenolic reaction with oxygen in the wood really blocks oxygen transfer (our actual measurement suggests the opposite). During wine *élevage* the same effect occurs as well, therefore we evaluated the oxygen reaching the wine inside the barrel through the oak considering oak wood phenolics.

The potential roles that the compounds in wood would have in oxygen consumption were considered in these trials,5,6 allowing for determination of the true OTR of wine barrels. That is, the amount of oxygen that would receive the real wine measured in the no oxygen- consuming liquid. The measurement technology and procedures are detailed in a scientific report Recent Advances in the Evaluation of the Oxygen Transfer Rate in Oak Barrels, *J. Agric. Food Chem.* 2014, 62, 35, 8892–8899.

Annual rate of oxygen entry into barrels

Stage two of this study involved measuring DO concentrations during the first 24 hours and for three weeks after filling the 12 barrels (data not shown). The concentrations were not significantly statistically different between the American and French oak barrels, although concentrations were higher during the first 10 hours for the American oak. No statistically significant differences were observed between the fine-grain and medium-grain American oak barrels, although the fine-grain barrels provided more oxygen to the model wine during the first few hours (del Alamo-Sanza and Nevares 2014).

To evaluate the overall rate of oxygen entry into wine-soaked oak barrels, the OTR in four fine-grain American oak barrels was analyzed over 12 months. Figure 2 shows the OTR (mg/L per day) in the tested barrels throughout the year. Analysis of the cumulative daily intake indicated that the dissolved oxygen in oak barrels continued to increase, but at a decreasing rate for the first six to eight weeks (see Figure 3). The OTR becomes approximately constant through- out the remaining year of *élevage.*

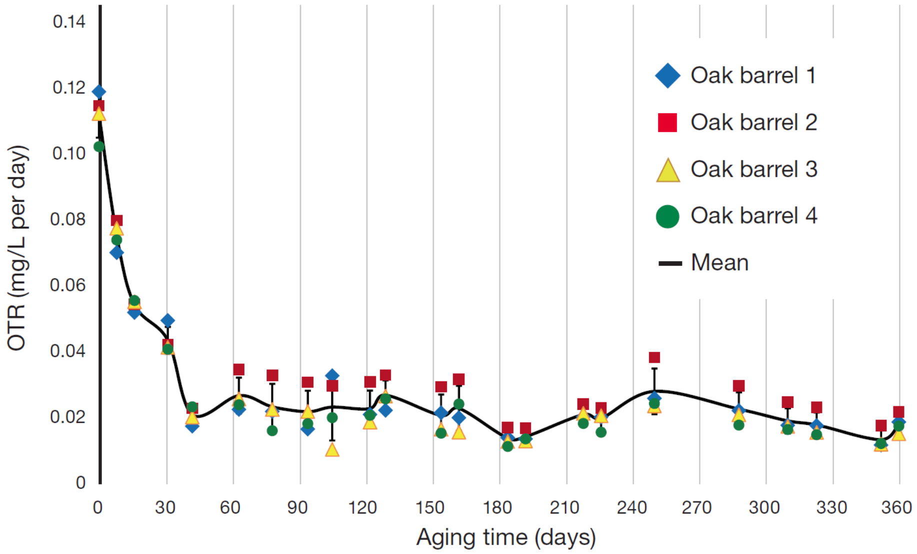

Figure 2: The evolution of the oxygen transfer rate (mg/L per day) of four oak barrels throughout one year.

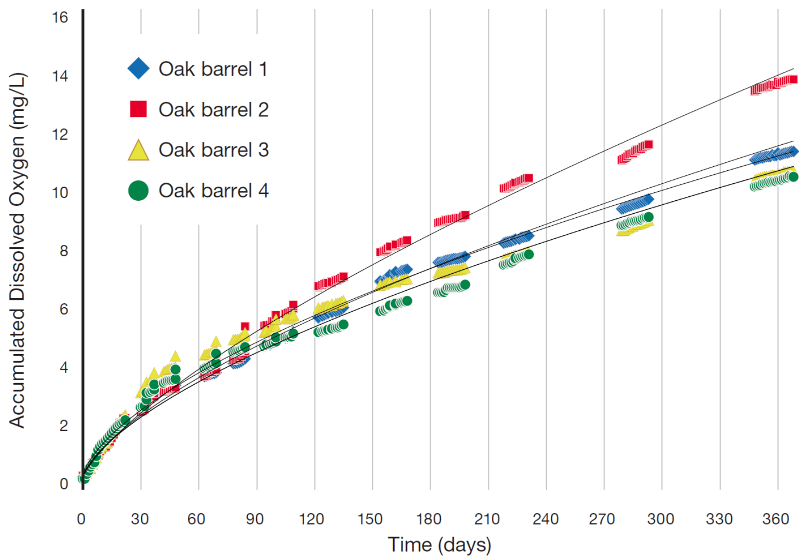

Figure 3: The accumulation of oxygen taken up in each studied barrel for one year.

In addition, the OTR decreased after the first three to four weeks. These results indicated that the actual rate of oxygenation per year is much lower than the rate that would be estimated if measuring only during the first weeks of testing. Therefore, it is important to test the evolution of oxygen entry kinetics for one year.

The daily average dose throughout the year was 0.32 mg/L. After the first month of *élevage*, the fine grain American oak barrels continued to provide the wine with between 0.029 mg/L and 0.038 mg/L of oxygen daily for the remainder of the year. Based on these results, we calculated the total dose of oxygen that a wine would take up in a fine-grain American oak barrel was 11.62 mg/L per year.

These results were significantly lower than results published previously by other authors who measured oxygen entry into new barrels.

J. Riberau-Gayon observed an oxygen entry rate of 21 to 28 mg/L per year,[1] and N. Vivas and Y. Glories observed an oxygen entry rate of 20 mg/L per year in two new Limousin coarse-grain barrels from central France.[2]

In both of these studies, the sulfate formed from SO_2 in the solution inside the barrel was evaluated at six months. The methodologies of these studies may explain the postulated high rates of oxygen entry by the above authors, given they did not consider the influences of progressively increasing wood moisture content leading to decreasing OTR.

The results we obtained also were lower than those estimated by M. Kelly and D. Wollan.[8] These authors treated the wood as a semipermeable membrane that allowed for oxygen diffusion according to Fick's law. Based on their calculations, the maximum amount of oxygen that could enter a barrel was 36.4 mg/L per year. However, this approach is erroneous because wood is a porous membrane that does not always function the same way.

Specifically, the moisture content of wood can modify its properties and oxygen permeability. The Kelly and Wollan study did not assess the amount of oxygen entry into the barrel for an entire year.[8] Instead, these results were obtained from theoretical approaches or extrapolated from six months of *élevage* data at different times of the year.

Based on the annual dose results of oxygen in our four-barrel study, the percentage of daily oxygen intake for each barrel (shown as a percentage) was calculated relative to the oxygen that was supplied throughout the year (which is considered to be 100%). On average, the fine-grain American oak barrels supplied wine with 7% of the total yearly oxygen in the first week. After one month, 23% of the total oxygen was supplied. Four months were required to dose the wine with 50% of the total oxygen received in one year. These results suggest that adding wine to new barrels before the filling or development of young oaked wine (which corresponds with maintaining these wines in new barrels for two to four months) reduces the potential for barrel oxygenation. For example, if barrels are used for two to four months for one batch of wine and are used for nine months for a second batch of wine, the latter batch would receive only 50% of the potential oxygen that these barrels would provide in one year. We used these results to extrapolate the behavior and annual rate calculations for the other eight barrels (four medium-grain American and four fine-grain French oak barrels) between 19 and 24 days during the second phase of the study. After approximately three weeks, the oxygen received by wine in a barrel represents 17% to 20% of the total oxygen that will be received in one year (observed in fine-grain American oak barrels and valid for medium-grain American and French oak barrels). We extracted these and calculated the annual oxygen entry rates for the eight barrels analyzed only during a few weeks instead of one year.

Four medium-grain American oak barrels would provide an average of 11.3 mg/L of oxygen per year (B1 = 10.46 mg/L, B2 = 10.64 mg/L, B3 = 11.96 mg/L and B4 = 12.14 mg/L). The annual rate of oxygen supply for four French oak barrels was 8.18 mg/L per year (B9 = 7.93 mg/L, B10 = 8.01 mg/L, B11 = 7.81 mg/L and B12 = 8.97 mg/L per year).

For the medium-grain American oak barrels, it took 19 days to dose with 17.3% of the total yearly oxygen dose. Therefore, these barrels would provide an average of 11.3 mg/L per year of oxygen to aged wine. Fine-grain French oak barrels were measured after 24 days and provided an average of 1.66 mg/L. Thus, the annual rate of supply for these barrels was 8.18 mg/L per year.

Summary

We analyzed the kinetics of oak barrel oxygen permeability for one year to establish the kinetics of the annual OTR of a barrel. The results of this study indicated that American oak barrels resulted in greater oxygen doses than French oak barrels. In addition, different wood grains (fine and medium) did not significantly affect the oxygenation rates of the barrels.

Authors

María del Álamo-Sanza is associated professor in the department of Analytical Chemistry at the University of Valladolid (Spain), where she has been since 2007. She received a Ph.D. in chemistry in 1997 at the University of Valladolid. Her research has always been related to wine chemistry, wine phenolics, oxygen and wine, and the characterization of wine aging in different aging systems and oak woods.

Ignacio Nevares Domínguez earned a degree for agricultural engineering specialists in agricultural and food industries from the Polytechnic University of Madrid (Spain) in 1991 and a Ph.D. in agricultural engineering from the University of Valladolid in 2003. He is an associated professor at the Department of Agricultural and Forestry Engineering of the Higher Technical College of Agricultural Engineering at the University of Valladolid since 2008. For more information, visit oxygenandwine.com.

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