

Wine evolution and spatial distribution of oxygen during storage in high-density polyethylene tanks

María del Alamo-Sanza¹, V. Felipe Laurie² and Ignacio Nevares^{1*}.

¹ Higher Tech. Col. of Agricultural Engineering, Universidad de Valladolid. Avda. Madrid, 44, 34004-Palencia, Spain.

² School of Agricultural Sciences, Universidad de Talca, Chile.

*Corresponding author: inevares@iaf.uva.es; +34-979108384.

Running title: Oxygen and compositional changes in HDPE tanks

Keywords: wine, aging, oxygen, HDPE, polyethylene, oak wood.

Background: Porous plastic tanks are permeable to oxygen due to the nature of the polymers with which they are manufactured. In the wine industry, these types of tanks are used mainly for storing wine surpluses. Lately, their use in combination with oak pieces has also been proposed as an alternative to mimic traditional barrel aging.

Results:

In this study, the spatial distribution of dissolved oxygen in wine-like model solution, and the oxygen transfer rate (OTR) of high-density polyethylene tanks (HDPE), was analysed by means of a non-invasive opto-luminescence detector. Also, the chemical and sensory evolution of red wine, treated with oak pieces, and stored in HDPE tanks was examined and compared against traditional oak barrel aging. The average OTR calculated for these tanks was within the commonly accepted amounts reported for new barrels. With regards to wine evolution, a number of compositional and sensory differences were observed between the wines aged in oak barrels and those stored in HDPE tanks with oak barrel alternatives.

Conclusion: The use of HDPE tanks in combination with oak wood alternatives remains as a viable alternative for ageing wine.

Introduction

For a long time, barrels have been used for transporting and storing beverages, including wines. Nowadays wine barrel maturation is a desirable process for many wine types, as it conveys the release of flavors (e.g. aldehydes and polyphenols), contributes to wine concentration due to evaporative losses of ethanol and water, and provides enough air exposure as to allow the occurrence of important chemical changes, such as colour stabilization¹⁻³.

In order to mimic some of the changes observed during wine barrel aging, but in a less expensive way, different solutions based on active or passive oxygen incorporation, and the use oak alternatives (i.e. oak staves, cubes, chips, etc.) have been proposed. Micro-oxygenation systems are the most widely adopted technology for active oxygen incorporation⁴, whilst the use of porous plastics materials in different parts of the winemaking process have been suggested as an inexpensive way of passive oxygen incorporation^{5,6}. Among the latest, the use of high-density polyethylene (HDPE) tanks, alone or in combination with oak wood alternatives (e.g. chips, cubes, staves), have been regarded as

potential inexpensive alternatives to barrel aging^{6, 7}. Currently, they are used for fermenting, storing and maturing wines, but their effects on the chemical and sensory properties of wines have not been well characterized. In fact, there is only one peer-reviewed paper related to this subject, in which the authors compared the effects of micro-oxygenation (MOX) in both stainless steel and HDPE tanks⁸. According to the manufactures of permeable HDPE tanks, they can be made with several controlled permeability levels to oxygen, thus providing an alternative way of oxygen incorporation into wines. Accordingly, the aim of this manuscript was to analyse the uniformity of the oxygen 2D-distribution and calculate the OTR of permeable HDPE vessels using a non-invasive and non-oxygen consuming opto-luminescence technology. Moreover, the chemical composition and sensory characteristics of red wines stored in HDPE tanks (treated with oak pieces) and oak barrels were analysed and compared.

Materials and methods

Oxygen 2D distribution within HDPE tanks

The analysis of oxygen 2D distribution was analysed in all four 190 L tube-shaped HDPE tanks (106 cm height and 48 cm diameter. Flextank International, Abbotsford, Australia). A model wine lacking of oxygen scavengers (15% v/v ethanol solution in water, pH=3.5) was used to check the formation and evolution of DO gradients inside the HDPE tank. After filling the vessel, the model wine was stripped from oxygen by sparging nitrogen gas (>99% purity) with a ceramic plate diffuser (220 mm diameter and 0.5 µm pore size) placed at the bottom of the tank.

DO was measured with eight optical sensors located inside the vessel, using a total of eight independent channels simultaneously. The eight oxygen immersion probes were placed at five heights and three different distances from the wall of the tank (Figure 1), thus representing different volume regions within the tank. The luminescence-based oxygen meter system selected for this work was an Oxy-trace (PreSens GmbH, Germany), with PSt6 oxygen sensor types (limit of detection: 1 ppb, 0 – 4.2% oxygen). The calibration of the oxygen measuring systems was done using a tonometer, as explained elsewhere⁹.

Considering that each of the oxygen probes was covering a different portion of the liquid (i.e. a different volume), the DO values recorded were weighted with the volume of liquid representing the area of influence of each measuring point, according to the following equation: $DO_{VM} = (\sum_{i=1 \text{ to } 8} DO_i * V_i) / V_{Total}$ (Equation 1). Where V_i is the volume of model wine represented by each probe (Figure 1). DO_i is the dissolved oxygen representing each of the eight volume zones monitored, and V_{Total} corresponds to the volume of the entire tank. In this case, the temperature of the model wine, and the cold room in which the tanks were stored, were adjusted to was stored at 15°C in order to avoid convection. Since the oxygen is incorporated by diffusion, no convection movements were expected due to oxygen ingress.

The tank containing the model wine was stored in a cold room where temperature and humidity were kept at 15±1 °C and 65-75% respectively.

Oxygen Transfer Rate (OTR) in HDPE tanks

As previously reported elsewhere for oak barrels¹⁰ the OTR measurements performed here represent all possible routs of oxygen ingress to the tanks and are not just a measurement of oxygen permeability through the HDPE material. In this case, to calculate the OTR of the HDPE tank, the partial pressure gradient of the oxygen permeating into the tank must be held constant. The method used is based on

the measurement of the increase in oxygen partial pressure (P_{O_2}) over time, after filling the tank with an oxygen depleted model wine (P_{O_2} between 0.01 and 0.1 hPa)¹¹. As previously explained, a porous ceramic plate diffuser (220 mm diameter and 0.5 μm pore size), sparging nitrogen gas (>99% purity), was used to remove the oxygen dissolved within the model solution. This gas was selected because the solubility of oxygen is smaller than that of nitrogen in water (Henry's constant of oxygen in ethanol-water mixtures at 0.15 Mole fraction: $k_{\text{Hatm}(O_2, 20^\circ\text{C})} = 23900$; $k_{\text{Hatm}(N_2, 20^\circ\text{C})} = 42600$)¹².

During the test, the amount of permeating oxygen in time is determined with the photo-luminescence device. The slope of the resulting curve of dissolved oxygen vs. time corresponds to the oxygen transfer rate (OTR). In order to evaluate the oxygen concentration in mg L^{-1} , Henry's law was applied, but considering an adjustment based on the solubility of oxygen in hydro-alcoholic mixtures¹³, thus avoiding an under estimation of the readings¹⁴. Therefore, the evolution of DO_{TM} in time was used to calculate the OTR for each of the four HDPE tanks used in the trial⁹.

Due to the long-term process of maturing wines, the rate of oxygen permeating through barrels is typically expressed in mg L^{-1} of oxygen per year.

Wine aging in HDPE tanks and barrels

A young-red wine (obtained 2 months after alcoholic fermentation) made from a single-variety (cv. Tinta del País), belonging to the Spanish Appellation of Origin Toro, was used to conduct the aging treatments. Some of the main chemical features of this wine were: 12.5% alcohol by volume, pH of 3.68, 5.2 g L^{-1} titratable acidity (tartaric acid eq.), 0.52 g L^{-1} volatile acidity (acetic acid eq.), colour intensity of 13 AU (calculated as the sum of the absorbances at 420, 520 and 620 nm), and a total polyphenol index of 51¹⁵. The sulfite content of the wine was adjusted to 35 mg L^{-1} of free SO_2 with potassium metabisulfite ($\text{K}_2\text{S}_2\text{O}_5$). These parameters were evaluated before the wine was transferred into the tanks (time 0), and 2 and 4 months after that, according to European Community Methods¹⁶.

The wine was aged for 4 month under the three following duplicated treatments:

- (a) Wine stored in 225-L new oak barrels.
- (b) Wine stored in 190-L HDPE tanks with 4180 g of oak staves each (100 x 8 x 1 cm^3).
- (c) Wine stored in 190-L HDPE tanks with 950 g of oak cubes each (1x1 cm^2).

The dosing of the alternative to barrel oak products, ABOP (i.e. staves and cubes), for each of the HDPE tanks was calculated according to the ratio between the inner surface and the volume of the barrels (2.01 m^2 in 225-L) resulting in a total of 1.7 m^2 of oak per 190-L tank. The wood was of *Quercus petraea* trees grown in Navarra, Spain, and provided by Tonelería Intona, SA (Navarra, Spain). The seasoning process was carried out in open air for three years as typically performed by the cooperage company. All wood used in this trial (i.e. barrels, staves and cubes) came from the same batch of wood, and was manufactured by the same cooper, with medium toast intensity (200 $^\circ\text{C}$ for 35 min) in an industrial-scale convection oven, with areas specially adapted to staves.

After completing the aging treatments, the wines were bottled in 750 mL green Bordeaux bottles, with premium natural cork closures, using a monoblock machine (PG97-M4, Agrovín, Spain), and stored for 2 months until the sensory evolution was performed. In this case, temperature and humidity conditions were controlled at 15-16 $^\circ\text{C}$ and 65-75 % respectively.

Wine chemical analyses

Phenolic compounds and colour parameters (Table 1) were analysed according to Zamora¹⁷. The wine's "chemical age", i (i.e. polymeric pigments/anthocyanins), was measured as described by

Somers and Evans¹⁵. Colour due to polymeric pigment (EP), free anthocyanins (TA) and colour due to copigmented anthocyanin (C) were determined according to the method proposed by Levensgood and Boulton¹⁸.

Low-molecular mass phenols (e.g. epicatechin, gallic acid, protocatechuic acid, gentisic acid, vanillic acid, caffeic acid, syringic acid, *p*-coumaric acid, ferulic acid, sinapic acid, and trans-caffeiltartaric acid) and aldehydes (e.g. syringic aldehyde, protocatechuic aldehyde and vanillic aldehyde) were quantified according to Gallego *et al.*¹⁹.

Volatile compounds were extracted and analysed using a method adapted from Fernandez de Simon *et al.*²⁰. Quantitative determinations were carried out using external standards, and the compounds evaluated were: furfural, 5-hydroxymethylfurfural (5HMF), *o*-methoxyphenol (guaiacol), 4-ethylphenol, 2-methoxy-4-(2-propenyl) phenol (eugenol), *cis* and *trans* 2-methoxy-4-(1-propenyl) phenol (isoeugenol), *cis* β -methyl- γ -octalactone (*cis* W lactone), *trans* β -methyl- γ -octalactone (*trans* W lactone), dihydro-2(3H)-furanone(γ -butyrolactone), maltol and 1-(4-hydroxy-3-methoxyphenyl)-ethanone (acetovanillone). The corresponding external standard calibration curves were made with 7 to 10 points for each compound, and linear regression coefficients between 0.98 and 0.999 were obtained.

In all cases, the samples were analysed in duplicate.

Wine sensory analysis

The wines were tasted by a group of ten expert oenologists from Valladolid University. Previously, two training sessions were carried out in order to agree on a set of sensory descriptors and to standardize the judging criteria. These sessions included the blind tasting of the wines of the study, the generation of a set of descriptors to be judged, and the evaluation of a larger set of wines in order to reach a consensus on the intensity of these attributes. The following sensory attributes were evaluated: (a) visual traits: colour intensity, purple colour; (b) aromatic traits: aroma intensity, aroma complexity, fruity aromas, wood-like aromas (i.e. perception of oak aromas over fruit aromas), toast-like aromas, eucalyptus/mint, sweet aromas (i.e. vanillin and coconut), spicy aromas (i.e. pepper and clove), cinnamon aroma; (c) taste and mouthfeel traits: weight (e.g. full, thin, etc.), acidity, tannin intensity, sweet tannins, green tannin, astringency, bitterness and after taste. The different terms were evaluated on a 1 to 10 scale (1, null; 10, very strong). Additionally, the judges were asked to evaluate their global perception of the wines based on the previously described scale.

Statistical analysis

The modelling of DO distribution was done according to distance-weighted least squares fitting, and the OTR determination were calculated using the slope of the curve representing DO evolution in time. The chemical and sensory comparisons of wines stored in HDPE tanks and barrels was performed using ANOVA, applying the Student New-Kleus multiple range tests using the STATISTICA program (version 8.0, StatSoft, Inc 1984-2007, USA)

Results and discussion

Oxygen 2D distribution within HDPE tanks

Following the oxygen depletion of the wine-like model solution, the concentration of oxygen was recorded continuously until the upper limit of the measurement range of the PSt-6 opto-luminiscence sensors was reached (1.8 mg L^{-1}). This data was used to simulate the dissolved oxygen evolution vs. time, using the volume of liquid under influence of each measuring point with regards to the whole tank volume (Figure 1). The modelling of dissolved oxygen distribution in time is shown in Figure 2 (see animation in supplementary material). For instance, probe number five and six, placed at the top of the tank, showed the greatest DO difference against the probes covering the center of tank (i.e. up to 0.3 mg L^{-1} , Figure 2, time=15000 min). Likewise, the DO differences observed between the wine near the walls and the center of the tanks were as much as 0.2 mg L^{-1} (Figure 2, time=15000 min).

Oxygen Transfer Rate (OTR) in HDPE tanks

The evolution of DO_{VM} in time is represented in Figure 3. As seen, the averaged DO_{VM} values fitted a straight line, from which an OTR of 21.71 mg L^{-1} of oxygen per year was calculated. Moreover, Table 1 shows the equations representing the DO evolution of each oxygen probe, covering different volumetric regions within the tanks (Figure 1).

The OTR calculated was not far from the nominal amount provided by the manufacturer ($\text{OTR}_N=28 \text{ mg L}^{-1}$ of oxygen per year), and was in the upper range of values previously suggested for new oak barrels (10 to 28 mg L^{-1} of oxygen per year)^{10, 21, 22}.

Also, the calculated OTR values are within the range of micro-oxygenation dosage used for red wines in contact with oak wood, after malolactic fermentation²³. However, under conventional micro-oxygenation systems, in large-volume vessels, much larger gradients of oxygen distribution have been observed, reaching DO differences up to 1 mg L^{-1} ⁹.

Comparable to oak wood containers, oxygen ingress into HDPE tanks works under a process of diffusion governed by Fick's law and the oxygen partial pressure gradient from the outside of the vessel and into the liquid. This mechanism is different from the dissolution process observed with active micro-oxygenation, in which Darcy's law and oxygen barometric pressure differences control the process.

Wine aging in HDPE tanks and barrels

After performing the OTR test for the HDPE containers, a red wine was stored under the three different aging systems indicated (i.e. oak barrels, HDPE tanks containing staves, and HDPE tanks containing oak cubes).

Table 2 shows that the chemical composition of the wines stored in barrels differ significantly from those aged in HDPE tanks containing oak barrel alternatives. The wines aged in HDPE + ABOP showed lower mean levels of anthocyanins and more colour due to polymeric pigments (Ep) than those aged in barrels. Like so, higher colour intensities and chemical age (i) values were observed for the wines aged in HDPE tanks containing ABOP. These results suggests that the typical reactions associated with oxidation that result in a loss of monomeric anthocyanins and the formation of polymerized coloured species prevailed in the wines aged in HDPE tanks with ABOP; most likely, as a result of a lower pace of oxygen incorporation within the barrels.

Furthermore, wines aged in HDPE vessels with cubes or staves had the highest values at A420 nm and A620 (Table 2) which are caused by the formation of compounds brought about by a higher evolution²⁴. This result agrees with previous research in which wines stored under alternative aging systems had more A420 nm and A620 nm^{25, 26}.

A number of important features of aged red wines result from a cascade of oxidation reactions in which acetaldehyde is produced. This carbonyl compound plays a pivotal role in the aging process, enhancing the polymerization of anthocyanins with tannins, or tannins among themselves²⁷, producing new and colour-stable pigments and influencing astringency²⁸. Based on the prior, different authors have proposed that a mild oxygenation regimes results in an enhancement of wine quality during storage, both in stainless steel tanks and oak barrels^{4, 29}. The loss of monomeric anthocyanins during red wine aging with ABOP (alternative to barrel oak products) has already been pointed out in previous papers^{25, 30, 31}.

With regards to the release of oak wood compounds, a different behavior between oak barrels and HDPE tanks with ABOP products was observed (Table 2). The concentration of HMF in wines aged in HDPE tanks with staves was almost twice as that of wines in HDPE tanks with cubes, and almost three times higher than for the wines stored in barrels. In this case, the oak cubes are manufactured from a portion of the same staves use in the other treatment, in which the entire surface was toasted by convection. Therefore, the results obtained here might be explained by the fact that after cutting the cubes, only a third of the wood surface (two of six sides of a cube) has been toasted by convection, while the other two thirds were toasted by conduction.

Instead, the maltol concentration of wines stored in barrels was about 5 times higher than those aged in HDPE tanks with staves, and 4 times higher than in HDPE tanks with cubes. Maltol is produced by breakdown of lignin during wood toasting and is responsible for the burn overtones of wine aroma³². With regards to oak lactones, only the *cis* β -methyl- γ -octalactone (*cis* W lactone) showed significantly higher concentration in the wines stored in barrels (Table 2). These compounds originate from oak lipids and directly contribute to woody and coconut character of wines³³⁻³⁶, as well as vanilla perfume, when in high concentration³⁶.

On the other hand, syringic acid, syringic aldehyde vanillic acid, and sinapic acid had significantly higher concentrations in the wines stored in HDPE tanks with ABOP than in barrels (Table 2), results that agree with those by Gallego *et al.*¹⁹.

As opposed as in barrels, when ABOP are used, the entire piece of wood is submerged and exposed to the wine, thus allowing a deeper infiltration and extraction along the two longitudinal and four radial axes of the wood³⁶. This might be the reason that explains the differences in extraction occurring in oak barrels and HDPE tanks containing ABOP. The results obtained in wines aged with cubes and staves were quite similar and can be explained according to the ABOP making process, in which the cubes were made from the same lot of staves after toasting.

Finally, the concentrations of epicatechin, *p*-coumaric acid, caffeic acid and ferulic acid, were significantly higher in wines aged in oak barrels than in those stored in HDPE tanks with staves or cubes. As with the results of wine colour, the prior could be the result of a lower rate of oxygen incorporation within the barrels as compared to HDPE tanks.

Wine sensory analysis

The results of the sensory evaluation showed that the barrel-aged wines had a significantly lower intensity of colour and purple tones (Figure 4) than the HDPE-aged wines; results that are consistent with the chemical measurements performed (Table 2). On the contrary, a greater intensity of sweet and cinnamon aromas was observed in the barrel-aged wines, as compared to the HDPE-aged wines. As for the taste and mouthfeel attributes, the barrel-aged wines were perceived as having more sweet

tannins and longer after-taste than the HDPE-aged wines (Figure 4). Some of the preceding differences probably contributed to the final global evaluation of the tasters in which the barrel aged wines rated higher (Figure 4).

Furthermore, if the two formats of ABOP in HDPE tanks are compared (i.e. oak staves and cubes), a similar trend of sensory patterns is observed. An interesting observation that should be noted is that although not significantly different, the panel seemed to detect a higher aroma and wood-like intensity (i.e. a higher perception of oak vs. fruit aromas) on the wines aged in HDPE tanks with staves (Figure 4), a result that coincides with the higher concentration of HMF measured in these wines. The perception of woody-like aromas depends on the synergistic effect of different compounds. For instance, the sensory attributes related with cis W lactone would be more or less noticeable depending on the intensity of other compounds such as vanilla^{37,38}. In our trial, higher levels of vanilla or furfural were detected in the HDPE+staves treatment, thus suggesting an effect of these compounds (and cis w lactone) on the perception of woody-like aromas.

Conclusions

As with other vessels used in winemaking, an asymmetrical DO distribution was observed within HDPE tanks, with regions near the lid and the inner walls of the tanks having more oxygen than the liquid in the center of the tanks. Moreover, the calculated OTR (21.71 mg L⁻¹ of oxygen per year) of the HDPE tanks used was in the upper range of values reported for oak barrels (10 to 28 mg L⁻¹ of oxygen per year). Furthermore, the chemical composition and sensory characteristics of the wine stored in barrels and HDPE tanks (treated with ABOP) showed significant differences that might be explained by disparities in oxygen incorporation, as well as with the way in which small pieces of wood (i.e. staves or cubes) release their compounds to the wine. Therefore, the use of HDPE tanks in combination with oak wood alternatives (e.g. chips, cubes, staves) remains as a viable alternative for storing wines that should be further studied.

Acknowledgements

This work was supported by the Spanish Government (project AGL2011-26931), the Regional Government of Castilla y León (project JCyL VA086A11-2), and Conicyt Chile through Fondecyt grant 1110655. The authors thank the assistance of L. Gallego and the support of Tonelería Intona S.A.

References

1. Singleton V, Some Aspects of the Wooden Container as a Factor in Wine Maturation, in *Chemistry of Winemaking*. Adv. Chem. Ser., Washington (1974).
2. Siau JF, *Transport processes in wood*. Springer-Verlag, Berlin ; New York (1984).
3. Singleton VL, Maturation of Wines and Spirits: Comparisons, Facts, and Hypotheses. *Am J Enol Vitic* **46**:98-115 (1995).
4. Moutounet M, Ducournau P, Chassin M and Lemaire T, Appareillage d'apport d'oxygène aux vins. Son intérêt technologique., in *Oenologie 95 : 5e Symposium International d' Oenologie*, Ed by Documentation T. Ed. Lavoisier., Paris, pp 411-414 (1995).
5. Schmidtke LM, Clark AC and Scollary GR, Micro-Oxygenation of Red Wine: Techniques, Applications, and Outcomes. *Crit Rev Food Sci Nutr* **51**:115-131 (2011).
6. Paul R and Kelly M, Diffusion - a new approach to micro-oxygenation, in *Australian Wine Industry Technical Conference*, Ed, Melbourne (2004).

M del Alamo-Sanza, VF Laurie, I Nevares. Wine evolution and spatial distribution of oxygen during storage in high-density polyethylene tanks. *Journal of the Science of Food and Agriculture* (2015) 95 (6), 1313-1320

7. Flecknoe-Brown A, How wine barrels work. *Aust GrapeWine*:93-96 (2002).
8. Nguyen D-D, Nicolau L, Dykes SI and Kilmartin PA, Influence of Microoxygenation on Reductive Sulfur Off-Odors and Color Development in a Cabernet Sauvignon Wine. *Am J Enol Vitic* 61:457-464 (2010).
9. Nevares I, del Alamo M and Gonzalez-Muñoz C, Dissolved oxygen distribution during micro-oxygenation. Determination of representative measurement points in hydroalcoholic solution and wines. *Anal Chim Acta* 660:232-239 (2010).
10. Vivas N and Glories Y, Modélisation et calcul du bilan des apports d'oxygène au cours de l'élevage des vins rouges. II. Les apports liés au passage d'oxygène au travers de la barrique. *Progrès Agric Vit* 114:315-316 (1997).
11. Piringer OG and Baner AL, *Plastic packaging materials for food : barrier function, mass transport, quality assurance, and legislation*. Wiley-VCH, Weinheim ; New York (2000).
12. Tokunaga J, Solubilities of oxygen, nitrogen, and carbon dioxide in aqueous alcohol solutions. *J Chem Eng Data* 20:41-46 (1975).
13. Mejane JV, Debailleul M and Lecerf J, Étude sur la solubilité de l'oxygène dans l'alcool. *Ind Aliment Agri* 90,:719-727 (1973).
14. Nevares I, del Alamo Sanza M, Waters E and Day M, La medida del oxígeno disuelto en vino y mostos, ¿Concentración o presión parcial?: estado actual del conocimiento, in *XIII Congreso Latinoamericano de Viticultura y Enología*, Ed, Santiago de Chile (2011).
15. Somers TC and Evans ME, Spectral evaluation of young red wines: Anthocyanin equilibria, total phenolics, free and molecular SO₂, chemical age. *J Sci Food Agri* 28:279-287 (1977).
16. EEC, Community Methods for the Analysis of Wines, Ed. Commission Regulation (1990).
17. Zamora Marín F, *Elaboración y crianza del vino tinto : aspectos científicos y prácticos*. Antonio Madrid Vicente. pp 57-66, Madrid (2003).
18. Levengood J and Boulton R, The variation in the color due to copigmentation in young Cabernet Sauvignon wines, in *Red wine color: Revealing the mysteries ACS Symposium Series*, Ed by Waterhouse ALK, J. . American Chemical Society, Washington, USA, pp 35-52 (2004).
19. Gallego L, Nevares I, Fernández JA and Álamo Md, Determination of low-molecular mass phenols in red wines: The influence of chips, staves and micro-oxygenation aging tank. *Food Sci Technol Int* 17:429-438 (2011).
20. Fernandez de Simon B, Cadahia E and Jalocho J, Volatile Compounds in a Spanish Red Wine Aged in Barrels Made of Spanish, French, and American Oak Wood. *J Agric Food Chem* 51:7671-7678 (2003).
21. Moutounet M, Mazauric JP, Saint-Pierre B, Micaléff J and Sarris J, Causes et conséquences de microdéformations des barriques au cours de l'élevage des vins. *Rev Oenol* 74:34-39 (1994).
22. Kelly M and Wollan D, Micro-oxygenation of wine in barrels. *Aust & N Z Grap Wine* 473a:29-32 (2003).
23. del Álamo M, Nevares I, Gallego L, Fernández de Simón B and Cadahía E, Micro-oxygenation strategy depends on origin and size of oak chips or staves during accelerated red wine aging. *Anal Chim Acta* 660:92-101 (2010).
24. Vivas N and Glories Y, Role of Oak Wood Ellagitannins in the Oxidation Process of Red Wines During Aging. *Am J Enol Vitic* 47:103-107 (1996).
25. del Alamo M, Nevares I and Merino S, Influence of different aging systems and oak woods on aged wine color and anthocyanin composition. *EurFood ResTech* 219:124-132 (2004).
26. del Alamo M, Nevares I, Gallego L, Martin C and Merino S, Aging markers from bottled red wine aged with chips, staves and barrels. *Anal Chim Acta* 621:86-99 (2008).
27. Cheynier V, Dueñas-Paton M, Salas E, Maury C, Souquet J-M, Sarni-Manchado P and Fulcrand H, Structure and Properties of Wine Pigments and Tannins. *Am J Enol Vitic* 57:298-305 (2006).

28. Vidal S, Francis L, Noble A, Kwiatkowski M, Cheynier V and Waters E, Taste and mouth-feel properties of different types of tannin-like polyphenolic compounds and anthocyanins in wine. *Anal Chim Acta* **513**:57-65 (2004).
29. Pontallier P and Ribereau G, Influence of aeration and of sulphiting on the evolution of red wine colour composition during the bulk conservation phase. *Connaiss Vig Vin*:105-120 (1983).
30. Piracci A, Bucelli P, Faviere V, Giannetti F, Lo Scalzo R and Novello E, Frammenti legnosi oak-chips e staves: contributo alla stabilizzazione del colore. *L'Enologo*:103-109 (2001).
31. del Alamo M and Nevares I, Wine aging in bottle from artificial systems (staves and chips) and oak woods: Anthocyanin composition. *Anal Chim Acta* **563**:255-263 (2006).
32. Chatonnet P and Dubourdiou D, Comparative Study of the Characteristics of American White Oak (*Quercus alba*) and European Oak (*Quercus petraea* and *Q. robur*) for Production of Barrels Used in Barrel Aging of Wines. *Am J Enol Vitic* **49**:79-85 (1998).
33. Mosedale JR, Puech J-L and Feuillat F, The Influence on Wine Flavor of the Oak Species and Natural Variation of Heartwood Components. *Am J Enol Vitic* **50**:503-512 (1999).
34. Boidron JN, Chatonnet P and Pons M, Influence du bois sur certains substances odorant des vins. *Conn Vigne Vin* **22**:275-294 (1988).
35. Spillman P, Wine quality biases inherent in comparisons of oak chip and barrel system. *Aus& New ZWine IndJ* **14**:25-33 (1999).
36. Crawford K, Benton A, Grigg A and Plumb D, Oak inserts. Grain orientation effect on extraction of oak flavor compounds. *Pract Win Vin Nov-Dec* (2010).
37. Sauvageot, F. and Feuillat, F. The influence of oak wood (*Quercus robur* L., *Quercus petraea* Liebl) on the flavour of Burgundy Pinot Noir. An examination of variation among individual trees. *Am J Enol Viti.*, **50**, 447–455. (1999)
38. Boidron, J.-N., Chatonnet, P., and et Pons, M. Influence du bois sur certaines substances odorantes des vins (effects of wood on aroma compounds of wine). *Connaissance de la Vigne et du Vin*, **22**, 275–294. (1988).

Table 1. Oxygen transfer rate values of HDPE tanks.

Measuring point	DO evolution regression line	R ²	µg L ⁻¹ .min	mg L ⁻¹ .year
Channel 1	y = 0.0496x + 144.65	0.889	0.0496	26.07
Channel 2	y = 0.0478x + 108.63	0.920	0.0478	25.12
Channel 3	y = 0.0493x + 167.01	0.891	0.0493	25.91
Channel 4	y = 0.0465x + 87.547	0.894	0.0465	24.44
Channel 5	y = 0.0531x + 267.70	0.554	0.0531	27.91
Channel 6	y = 0.0605x + 43.463	0.927	0.0605	31.80
Channel 7	y = 0.0444x + 94.272	0.823	0.0444	23.34
Channel 8	y = 0.0388x + 138.59	0.787	0.0388	20.39
OTR	y = 0.0413x + 102.83	0.964	0.0413	21.71

OTR: Volume Weighted Oxygen Transfer Rate

Table 2. Concentration of chemical compounds analysed in red wines kept under different aging systems.

	Oak barrels			HDPE + staves			HDPE + cubes			p level
total phenolics	1952.09	± 15.91		1945.14	± 23.76		1948.34	± 51.27		0.9793
low polymerised phenols	1130.84	± 68.94		941.69	± 41.86		978.34	± 49.50		0.0776
high polymerised phenols	821.25	± 84.85		1037.90	± 30.62		970.00	± 1.77		0.0536
catechins	785.20	± 59.40		694.55	± 33.02		639.20	± 33.94		0.0961
anthocyanins	447.56	± 16.71	a	320.23	± 13.58	b	288.31	± 21.66	b	0.0057
tannins	1.86	± 0.11		1.98	± 0.14		1.90	± 0.34		0.8705
colour intensity	9.22	± 0.79	b	13.79	± 0.35	a	13.46	± 0.27	a	0.0054
A420 nm (absorbance)	3.63	0.21	b	4.97	0.01	a	4.92	0.05	a	0.0030
A520 nm (absorbance)	4.48	0.45	b	6.59	0.01	a	6.54	0.13	a	0.0070
A620 nm (absorbance)	1.11	0.13	b	1.98	0.01	a	2.01	0.08	a	0.0030
Ep	3.68	± 0.13	b	4.85	± 0.07	a	4.88	± 0.14	a	0.0032
copigmentation (C)	1.56	± 0.45		0.87	± 0.21		0.59	± 0.08		0.0913
free anthocyanins (TA)	2.67	± 0.38		3.13	± 0.14		3.05	± 0.07		0.2671
polymeric pigment (Ep)	2.25	± 0.05	b	3.18	± 0.07	a	3.20	± 0.20	a	0.0073
epicatechin	12.29	± 0.34	a	10.58	± 0.28	b	8.80	± 0.47	c	0.0060
gallic acid	100.72	± 2.45		103.34	± 1.98		98.88	± 3.17		0.3529
protocatechuic acid	10.23	± 0.73		11.55	± 0.42		10.83	± 0.43		0.1985
gentisic acid	3.85	± 0.68		4.27	± 0.42		3.32	± 0.47		0.3410
vanillic acid	7.16	± 0.01	b	7.64	± 0.03	a	7.54	± 0.08	a	0.0044
caffeic acid	42.57	± 0.97	a	41.23	± 0.42	ab	39.80	± 0.18	b	0.0468
syringic acid	15.65	± 0.29	b	17.61	± 0.21	a	18.47	± 0.30	a	0.0041
p-coumaric acid	30.34	± 0.87	a	28.26	± 0.35	ab	26.29	± 0.06	b	0.0118
ferulic acid	1.19	± 0.05	a	0.65	± 0.14	ab	0.36	± 0.27	b	0.0404
sinapic acid	0.21	± 0.08	b	0.43	± 0.04	ab	0.28	± 0.01	a	0.0438
trans-caffeiltartaric acid	1.33	± 0.06		1.26	± 0.07		1.23	± 0.04		0.3929
syringic aldehyde	1.65	± 0.41	b	3.83	± 0.14	a	4.72	± 0.08	a	0.0026
protocatechuic aldehyde	0.62	± 0.29		0.44	± 0.14		0.36	± 0.16		0.5129
vanillic aldehyde	2.14	± 0.17		2.58	± 0.07		2.45	± 0.05		0.0574
Furfural	1.77	± 0.03		1.82	± 0.02		1.82	± 0.03		0.2345
5HMF	6.58	± 1.89	b	18.13	± 0.99	a	9.47	± 0.96	a	0.0070
guaiacol	0.41	± 0.01		0.14	± 0.06		0.23	± 0.17		0.1616
4 ethyl phenol	0.65	± 0.00		0.21	± 0.23		0.51	± 0.66		0.5912
eugenol	0.03	± 0.00		0.02	± 0.00		0.02	± 0.00		0.0557
isoeugenol	0.29	± 0.05		0.28	± 0.10		0.26	± 0.09		0.9407
cis W lactone	0.77	± 0.18	a	0.14	± 0.08	b	0.06	± 0.04	b	0.0162
trans W lactone	0.30	± 0.07		0.22	± 0.04		0.22	± 0.03		0.2871
butyrolactone	30.96	± 4.25		10.11	± 5.69		15.52	± 11.84		0.1556
maltol	1.07	± 0.04	a	0.20	± 0.04	b	0.25	± 0.08	b	0.0010
acetovanillone	0.12	± 0.0024		0.09	± 0.01		0.12	± 0.03		0.3625

Figure 1: Location of the oxygen probes within the HDPE tank (D= 500 mm diameter, h= 1000 mm height). Wine regions by volume under influence of each oxygen reading point.

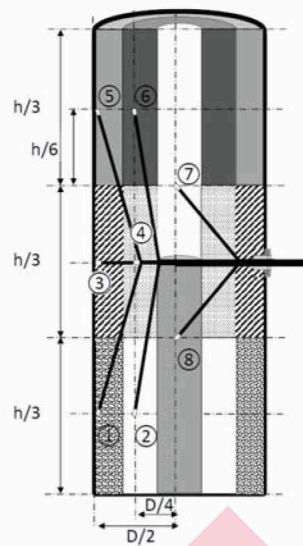


Figure 2: 2D distribution of dissolved oxygen ($\mu\text{g L}^{-1}$) in a HDPE tank at different times. DO iso-lines step size is $100 \mu\text{g L}^{-1}$. Each rectangle of the figure represent the map of the 2D-tank at a different time point

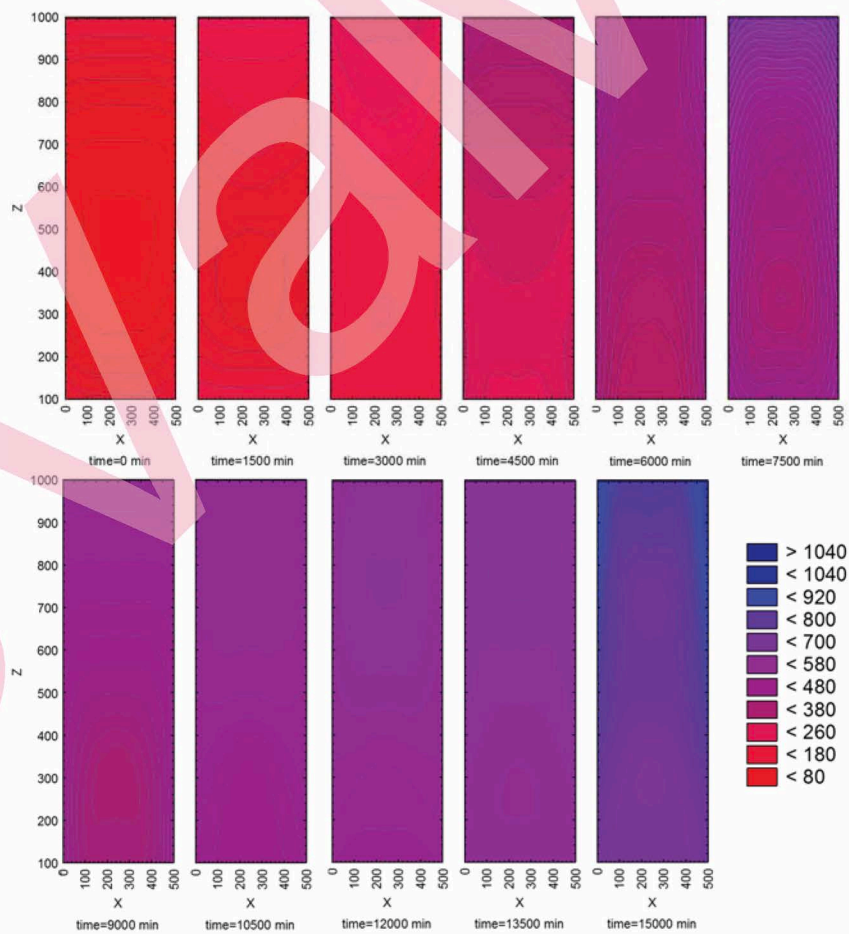


Figure 3: Calculated oxygen transfer rate (OTR) based on volumetric weighted dissolved oxygen measures (VoW-DO). The shadows around the DO evolution line represent the standard deviation within tanks).

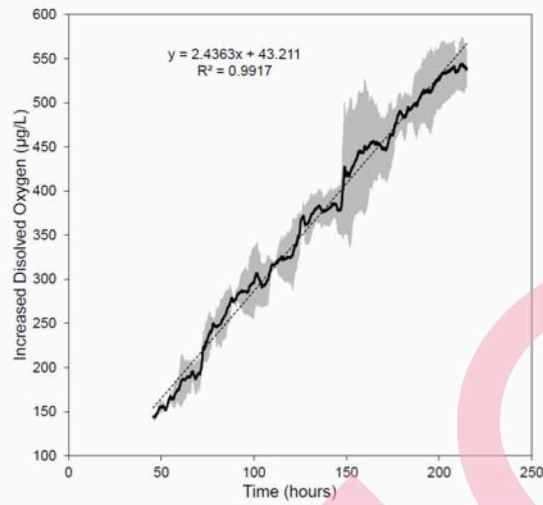


Figure 4: Sensory evaluation of wines aged in oak barrels and porous HDPE tanks containing red wine treated with oak cubes or staves after five months contact time (closed square= HDPE+cubes, open circle= HDPE+staves and open triangle=oak barrels).

