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Oxygen desorption and oxygen transfer through oak staves and oak stave gaps: an innovative permeameter

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Abstract

During wine aging, several complex phenomena take place in barrels according to oak's intrinsic physical properties. This research aims to better understand oxygen desorption and oxygen transfer phenomena through oak staves and especially through stave gaps in order to reevaluate the importance of barrel-making in barrel's oxygen supply. Experimentation was based on the development of an innovative permeameter. With this permeameter, we could estimate gas transfer through oak staves and between oak stave gaps. With a specially developed tightening system, the existing pressure at stave gaps in a barrel could be reproduced on a laboratory scale in order to estimate its influence on oxygen transfer efficiency. Results proved that oxygen transfer through intact oak wood is limited; the main oxygen transfer takes place (i) through weak zones caused by fragile contact between staves and (ii) with low pressure between two staves (mainly in the middle of the side pieces). So, it is identified that oxygen transfer through stave gaps is largely impacted by applied pressure and by contact conditions on the surfaces of adjacent staves. This research also proves that oxygen desorption plays an important part in total oxygen ingress. These results confirm that the barrel-making process has a strong impact on a barrel's oxygen supply during the aging process.

Keywords: oxygen transfer, desorption, barrel, permeameter

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Introduction

Nowadays, 5% of all wine in the world is aged in barrels for at least six months in order to improve wine complexity (Giraud, 2009). Barrel aging has many beneficial effects on wine. It provides wine with up to 75 kinds of volatile compounds (Hernández-Orte *et al.*, 2014), enhanced color stability (Fulcrand *et al.*, 1996; Fulcrand *et al.*, 1998; Rentzsch *et al.*, 2007; Pechamat *et al.*, 2014) and reduced vegetable character (Lemaire, 1995; Ghidossi *et al.*, 2012) while enhancing organoleptic qualities. Barrel storage allows wine to undergo processes known as 'low oxidation conditions' (Vivas and Glories, 1996). A controlled dose of oxygen is crucial for maintaining the desired characteristics of a wine and preventing negative effects such as the growth of acetic bacteria (Delsart *et al.*, 2015, 2016), color change and the development of oxidative aromas.

Ribereau-Gayon (1931) was the first to consider the oxygen transfer through barrel over a long period. The barrels were filled with a diluted SO_2 solution for six months. With this methodology, the oxygen ingress could be estimated by regular SO_2 concentration analyses. The author estimated the amount of oxygen supply to be 15 to 45 $mg.L^{-1}.year^{-1}$. This range is still largely mentioned in the literature. Later, Peterson (1976) studied the characteristics of six American white oak (225L) wine barrels filled and sealed (lying on their side with the bung up) at ambient cellar conditions (10-24°C). The vacuum gauges were read periodically over several months. The author considered that the amount of oxygen pickup during barrel aging may depend as much on the physical soundness of each barrel, and imperfections in the wood, than on the relative oxygen porosity of the wood. It seems likely that oxygen pickup may vary widely from barrel to barrel during aging, even though the barrels are cleaned, filled and stored side by side. Singleton (1995) also argued that if the barrel were permeable enough it would be impossible to maintain a vacuum within its walls. He suggested the only possible oxygen transfer passage was the upper area of the barrel where staves remain dry due to the continuous loss of wine by evaporation.

Qiu (2015) determined the depressive values that appear during aging in three oak barrels. The author proved that pressure values can reach -350 mbar after one week. Then, this pressure becomes less important and stable, ranging from 150 to 200 mbar after one month. Indeed, this induced driving force could generate gas transfer phenomena through oak wood. Vivas and Glories (1997) studied dissolved oxygen in a barrel over a period of six months by measuring the concentrations of sulfuric acid formed inside barrels that were filled with a solution of SO_2 (500 $mg.L^{-1}$). They considered that the oxygen transfer depends principally on barrel age and the position of the bung. They also observed that if the bung is closed without being hermetically sealed, the oxygen transfer could reach 28 to 36 $mg.L^{-1}.year^{-1}$ if the bung is closed in the traditional manner (bung-hole on the side) and 45 $mg.L^{-1}.year^{-1}$ if the bung-hole is sealed with a silicone bung to ensure an airtight seal. Improved airtightness was proved to be able to reinforce the oxygen supply capabilities of a barrel. It is thus possible that a vacuum helps to increase the permeability of oak, or simply creates micro-deformations. The authors also considered that 21% of the total oxygen entered through the bung, 63% entered between the staves, and 16% entered through the wood itself. This was the first time that oxygen entering through stave gaps had been precisely quantified.

Vivas *et al.* (2003) also determined the permeability to gas of a piece of oak stave using a permeameter equipped with two chambers. The first interior chamber was separated from the exterior chamber by a piece of oak fixed in the center. The two chambers were filled with nitrogen gas at the beginning of the experiment and the exterior chamber was in contact with ambient air. The thickness of the oak was 2, 4, 8 and 16 mm. It was concluded that the water content of oak is the principal factor at play in the oxygen transfer rate. For oak wood with 2 mm thickness, the transfer rate was 16 times higher in dry wood during the 4 days of measurement. It was found that for both fineand widegrain wood the transfer rate increased as thickness diminished. For oak pieces of 2 to 16 mm thickness, the transfer rate diminished 4 times as thickness doubled. The authors proved that humidity is also a very important parameter to take into account.

In 2014, del Alamo-Sanza and Nevares (2014) followed up the hypothesis of the 'oxygen transfer theory' proposed by Ribereau-Gayon. The authors had equipment able to measure the gas permeability of oak wood. Their results proved that the actual average rate of oxygenation per year was much lower (11.62 $mg.L^{-1}.year^{-1}$) than the rate measured during the first weeks of testing. This implies that the oxygen supply of a barrel is a non-linear phenomenon. Oxygen transfer through stave gaps was also estimated to represent between 28 and 54% of the total oxygen supply of a barrel. During the first 120 days, a transfer of 50% of the annual oxygen

influx could be supplied to wine. The results proved that if barrels are used for 2-4 months for one batch of wine and then used for 9 months for a second batch of wine, the latter receives only 50% of the potential oxygen that these barrels would provide in a year. These results are very interesting and should be explained.

In another study on the same subject, Nevares and del Alamo-Sanza (2014) classified 69 rough staves according to their permeability to oxygen by measuring their transmission rate in order to assess the possibility of building barrels of different oxygen transmission rate (OTR). The authors developed a device that measures the OTR of rough staves with the same conditions as those in a 225L barrel. In the device, the stave is in contact with a liquid solution on one face and with gas on the opposite face.

Analysis of the correlation between the OTR and the grain type indicated that the correlation is very low. The same result was obtained when the OTR was analyzed with the grain classified according to the method developed by Vivas. The authors concluded that these results showed the possibility of classifying rough staves using the innovative device and the possibility of producing barrels with different OTR characteristics.

Two barrels with staves of different OTR were built with the stave gaps well sealed, and oxygen ingress was measured over 11 days. Over this short period, the high-OTR barrel contributed a total of 116 mg of oxygen (225 L × 519.02 µg/L) while the low-OTR barrel contributed 105 mg of oxygen (225 L × 471 µg/L). These results pointed out that the barrel with a high OTR would transfer only 10% more oxygen to the wine than the low-OTR barrel. These results are very interesting and the possibility to propose barrels with high or low oxygen flux is possible.

Del Alamo-Sanza and Nevares (2014) used optical sensors to study the oxygen diffusivity of oak wood staves in wine barrel aging for four months. The authors measured the 2-D oxygen with planar optodes in combination with a color RGB camera. This methodology allows the authors to visualize how oxygen diffuses through different microstructure elements of wood, and to analyze the oxygen dynamics in different kinds of wood considering the grain size classification commonly used in cooperage. The authors observed that oxygen reaches successive growth rings through late and early wood. By considering these results, the authors concluded that latewood has a bigger role in oxygen transfer and thus woods with high growth rates, with coarser grain, lead to greater wine oxygenation.

All these results could explain the transfer occurring through the oak wood but there is, to date, a lack of precise knowledge on oxygen desorption and oxygen transfer through stave gaps. The present study aims to answer the question of whether or not oxygen could pass through an oak stave/barrel wall, and to establish the principal factors at play in oxygen transfer through stave gaps. Desorption phenomena will also be investigated to explain the non-linear phenomena of oxygen transfer during the first months. This research will guide barrel-makers in the adjustment of their manufacturing processes.

Materials and methods

1. The innovative permeameter

Oxygen transfer through oak stave was studied with a permeameter co-developed by the Institut des Sciences de la Vigne et du Vin (ISVV) and Taransaud (Figures 1 and 2). The oak samples were cut from oak stave (fine-grain untoasted) supplied by the cooper Taransaud. Samples were 9 cm diameter and 2.3 cm thickness, either whole or cut into two pieces down the middle to imitate joints between staves. Samples were placed in the intermediate chamber of the permeameter, airtightness being further ensured by vacuum grease on joints. In our specific case, the joints between staves have a 90 degrees' union, and it represents an approximation because the side pieces have an angle between 4 to 6°. However, we developed a methodology using Prescale band that could reproduce the contact and pressure applied in real conditions between two staves. The Prescale band result was always checked before each experiment. The results obtained in our experiment and in real conditions cannot be discriminated. So, we consider that the approximation is very low. The upstream, intermediate and downstream chambers are equipped with a gas inlet and outlet permitting a preliminary step of nitrogen scanning; the downstream chamber could be linked to a bottle of model wine. The pressure measurement is realized online by using a Keller pressure transmitter and transducer (Series 21R) on each chamber. The flow of solution is facilitated by a pump (Pump drive 5001, Heidolph, C8 -524 – 40810 – 00, Germany). The flow induced by the pump is very low (0.100 $L.h^{-1}$) and is used to limit the concentration gradient that could occur in our permeameter. This concentration gradient is also limited in a real oak barrel because convection phenomena are also observed (Qiu, 2015). This is the

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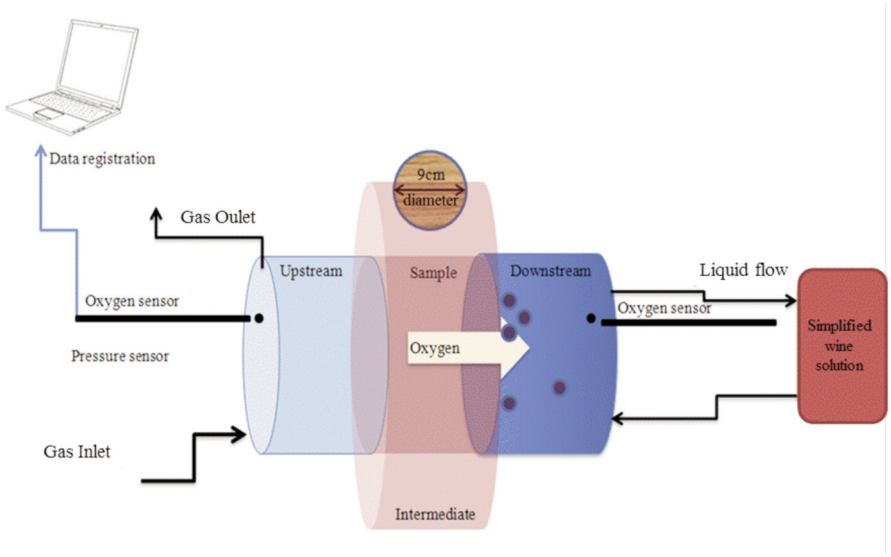

Figure 1. Schematic representation of the Oxygen Permeameter co-developed by ISVV and ENSAM.

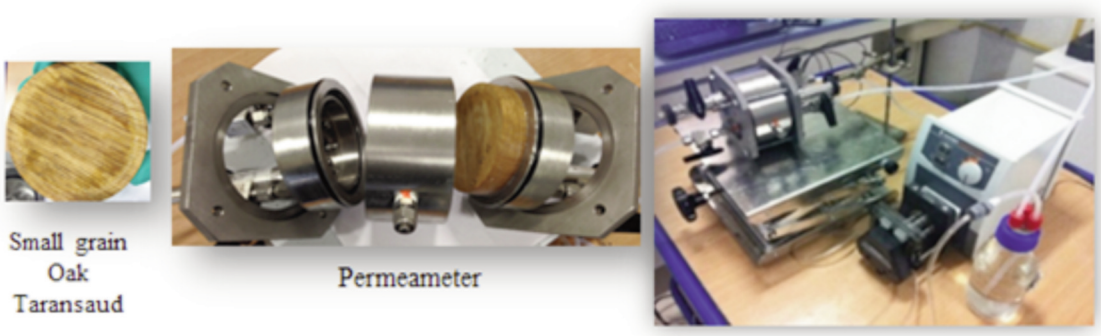

Figure 2. Oxygen Permeameter co-developed by ISVV and ENSAM.

reason why we decided to use this pump. The volume of solution (640 mL) put into contact with the oak sample is calculated with the same volume / surface ratio as in real conditions (225 L / 2 m^2).

The oxygen concentration in upstream and downstream chambers is detected using a mobile optical fiber coupled with a sensor device. The luminescent system is an Oxy-trace type (PreSens GmbH, Germany), coupled with a PSt3 type oxygen sensor (detection limit = 15 $\mu g.L^{-1}$, 0-100% oxygen). The sensors are spot sensors placed inside the upstream and downstream chambers, thus permitting the detection of the oxygen concentration in the gaseous or in the liquid phase without opening the system. Data are recorded and retrieved from a linked computer. Preliminary tests were realized to ensure that no oxygen could transfer through our permeameter (pump or weak point). To that end, a piece of metal replaced the piece of wood and the experimentation in real conditions was carried out over a period of two months. No oxygen transfer (lower than 60 ppb) was observed during this period. Moreover, the permeameter is positioned in a hermetic chamber filled with N_2. So, no oxygen can be transferred in our upstream and downstream chambers during our experiment.

Three different series of experiments were conducted with the permeameter to evaluate the oxygen diffusion through oak staves:

Series a: oxygen diffusion through oak when it is not in contact with liquid. This experiment represents the dry area close to the bung-hole in a barrel. In the downstream chamber, oxygen is measured.

Series b: oxygen diffusion through oak when it is put into contact with liquid. This set of experiments imitates the inner surface part of the barrel in contact

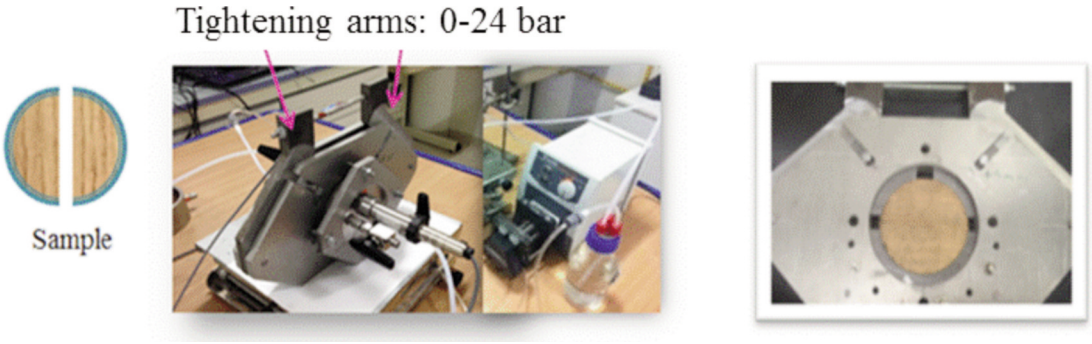

Figure 3. Oxygen Permeameter equipped with a tightening system.

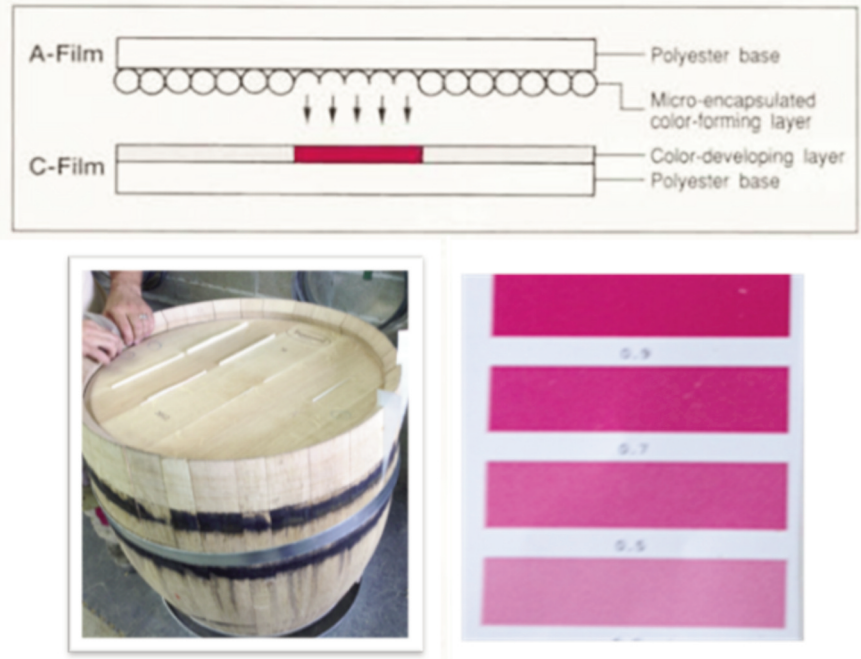

Figure 4. Measuring principle of Fuji Prescale film.

with wine. In the downstream chamber, oxygen is measured.

Series c: oxygen diffusion through potential preferential passages at stave gaps when oak pair is put into contact with liquid. Experiment c imitates the stave gaps in contact with wine. In the downstream chamber, oxygen is measured.

For experiment c, a tightening system was specifically developed to test the oxygen transfer rate through stave gaps with the permeameter (Figure 3). A selected piece of oak was cut into half, the two halves being pressed together within the tightening system.

2. Gases employed in the upstream chamber

Previous studies have shown that during wine-oak contact, oxygen contained within the oak structure is released into wine or solution (Pons *et al.*, 2014). The impregnation of liquid into the oak fibers accelerates oxygen dissolution into liquid phase. In order to observe real oxygen transfer, pure oxygen was used in the upstream chamber.

The advantage of using pure oxygen gas in the upstream chamber is that its saturation point in a liquid at 20°C is 42 $mg.L^{-1}$ instead of 8.4 $mg.L^{-1}$ for ambient air and for air trapped inside the wood. Therefore, a phenomenon of oxygen transfer could be proved to exist once oxygen concentration in the downstream chamber exceeds 8.4 $mg.L^{-1}$. So, we could differentiate desorption from real transfer by using these methods.

All applied gas is under 0.5 bar overpressure in order to simulate the vacuum conditions present inside a barrel. The pressure is higher than that encountered in real conditions (350 mbar) but a compromise

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should be found between the pressure gauge and experimental time. By using 0.5bar overpressure, we could have answered effective gas transfer in a period lower than 15 days. The pressure in the downstream chamber is also measured and is always close to 0 so the gradient pressure is stable during the experiment.

3. Prescale membrane for pressure range measurement

Prescale membrane (Fujifilm super low type LLW, Fujifilm Corporation, Japan) was used for pressure range tests in a French oak barrel. To be able to recreate stave gap conditions on a laboratory scale, the natural pressure range present in a barrel is tested with a Prescale membrane. The membrane is inserted into stave gaps in the back piece and side piece of a barrel. Two barrels were used and 50 membranes were placed between the staves at different places (side pieces and back pieces) (Figure 4).

The membrane is a two-sheet type composed of A-film and C-film. A-film consists of a PET base coated with micro-encapsulated color-forming material, while C-film consists of a PET base coated with color-developing material. The microcapsule on A-film breaks when A-film and C-film are placed together for 2 minutes under applied pressure and colors the C-film; the color intensity appearing on the C-film is proportionate to contact conditions and pressure applied. The precision of the Prescale membrane is ± 10% (measured at 23°C, 65% relative humidity), with a recommended temperature range of 20-35°C and humidity range of 35-80% RH during application.

The membrane selected for the in-situ test in a barrel is the super low pressure (LLW) type rather than the ultra super low pressure (LLLW), low pressure (LW), or medium pressure (MW) type, each type having a different pressure range. These membranes are positioned between two staves at different places on a real barrel. Any pressure applied onto membranes can be estimated by using the standard continuous pressure chart supplied by Fuji. The LLW type covers the pressure range which can be found in a barrel (Figure 4).

Throughout the experiments, the permeameter is maintained in a climate-controlled room (18 ± 1°C) with 80% RH. These conditions are close to those encountered in real conditions. All the experiments have been done in triplicate. Analyses are realized in triplicate and three different oak woods for each experiment are considered.

4. Oak staves, solution composition and measurement conditions

The oak staves used for experimentation are of small grain (<1.5 mm) from the Allier region of France, supplied by Taransaud, France. The samples for the permeameter are taken from staves throughout their length. The thickness of the samples is 23 mm. The sample's total surface of the tangential side in contact with the solution in the downstream chamber is 64 cm^2 (Ø = 9 cm). This surface is put into contact with 640 mL solution, representing the surface / volume ratio in a barrel. The humidity was measured with Wood Moisture Meter PCE-MMK 1.

To ensure that no oxygen is consumed by wine compounds during the experiment, the solution employed to be in contact with the oak sample is a simplified version of wine, comprising pure water, 12% ethanol and 5 $g.L^{-1}$ tartaric acid at pH 3.5 (adjusted by adding NaOH). The solution was previously degassed with nitrogen gas in order to guarantee the absence of oxygen from air, which may have masked the phenomenon of oxygen desorption from oak sample. The experiment also integrated the use of antibiotics in order to eliminate any risk of microbial growth (penicillin, chloramphenicol, biphenyl, pimaricin). This solution could ensure microbiological stabilization without consuming oxygen. Experiments have been realized in triplicate (1 L of this solution with oxygen content at 9.2 $mg.L^{-1}$), and oxygen consumption is always lower than 70 ppb after one month. For longer experiments, to avoid the consumption of oxygen by the polyphenols released, the solution was changed every 5 days and the oxygen concentration was readjusted to the last measurement. This short 5-day period does not permit sufficient release of polyphenols to induce oxygen consumption (Pechamat *et al.*, 2014; Pons *et al.*, 2014; Qiu, 2015).

5. Oxygen desorption

In order to assess the quantity of desorbed oxygen in oak wood, a specific vacuum system that reproduces the internal pressure inside barrels is set up on a laboratory scale (Figure 5). 500-mL vials equipped with oxygen sensor are connected to a vacuum system (depressurized at -0.2 bar). In order to simulate the real conditions, the volume / surface ratio is respected by considering an exchange surface of 54 cm^2 of wood in each bottle filled with the model solution previously degassed of oxygen.

The oxygen concentration in vials is detected using a mobile optical fiber coupled with a sensor device (PreSens GmbH, Germany - PSt3 type oxygen

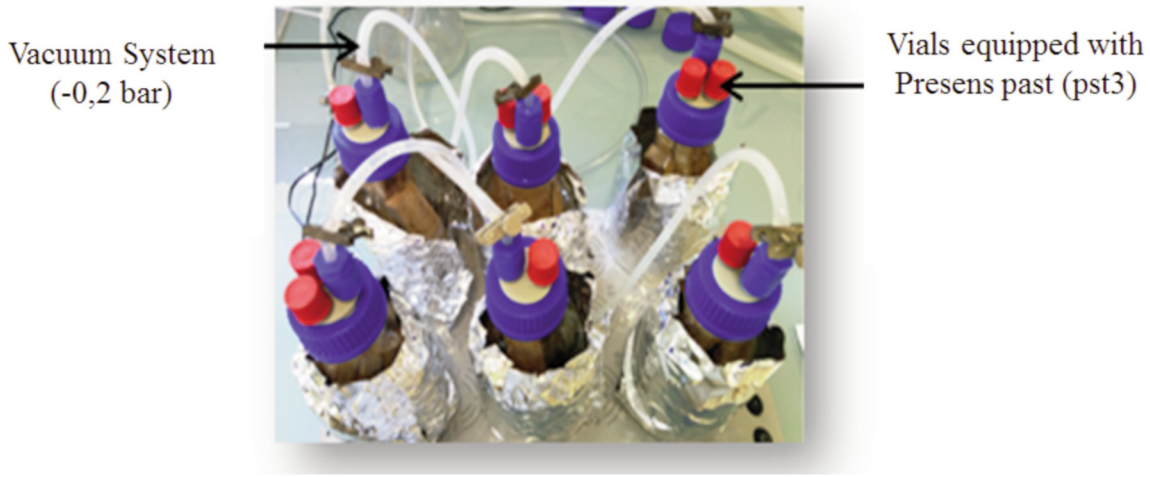

Figure 5. Oak's diffusivity to oxygen for 18 samples tested (N.1-14, nitrogen gas in the upstream chamber; N.15-17, compressed air in the upstream chamber).

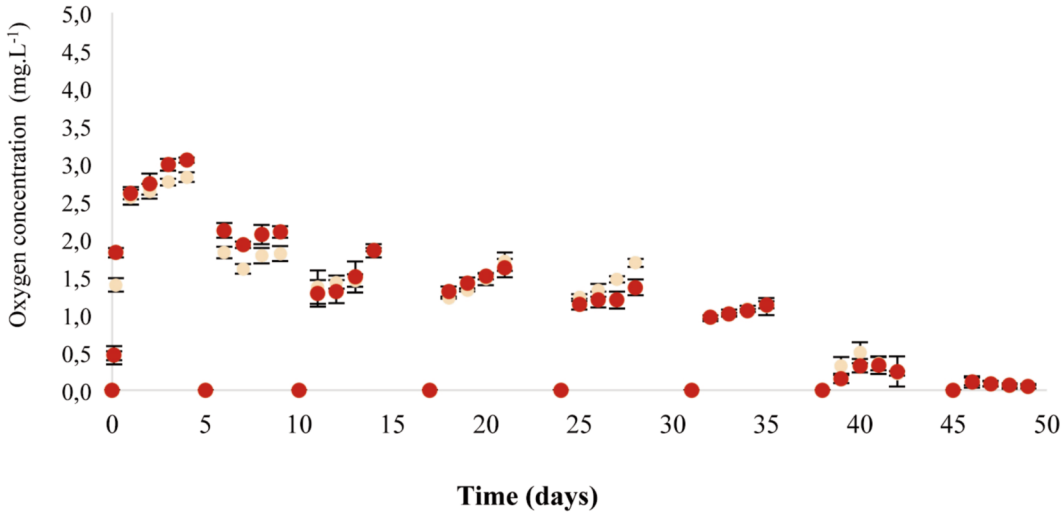

Figure 6. Example of oxygen diffusion curve of series a (oak sample N.14).

sensor). The spot sensors are placed inside the vials. The oak surfaces are covered with silicone gel with the exception of the internal face. This procedure allows to desorb only oxygen in contact with the liquid. To validate this hypothesis, various trials (15 vials) have been realized with oak wood completely covered with silicone gel and no desorption have been observed (<300 µg.L^{-1}). The oxygen desorption kinetics is followed by using the Presens probe with a reading of the content every day during 50 days.

6. Statistical analysis

The differences were interpreted using the results of a variance analysis (ANOVA - Duncan) carried out on each of the parameters. Statistical processing was carried out using Excel software (Microsoft Seattle, Washington, USA). The results were regarded as different for a probability lower than 1%.

Results and discussion

1. Oxygen desorption

Oxygen desorption is quantified over a 50-day period. During this follow-up, there are several cycles of observations, each cycle corresponding to 5 days of measurement. After each cycle, each bottle is emptied and filled with a new inert model solution. This methodology is realized to avoid the oxygen consumption kinetics of the released oak wood polyphenols. Figure 6 shows the oxygen desorption of oak pieces with various averaged toast (M and M+) during 50 days of measurement.

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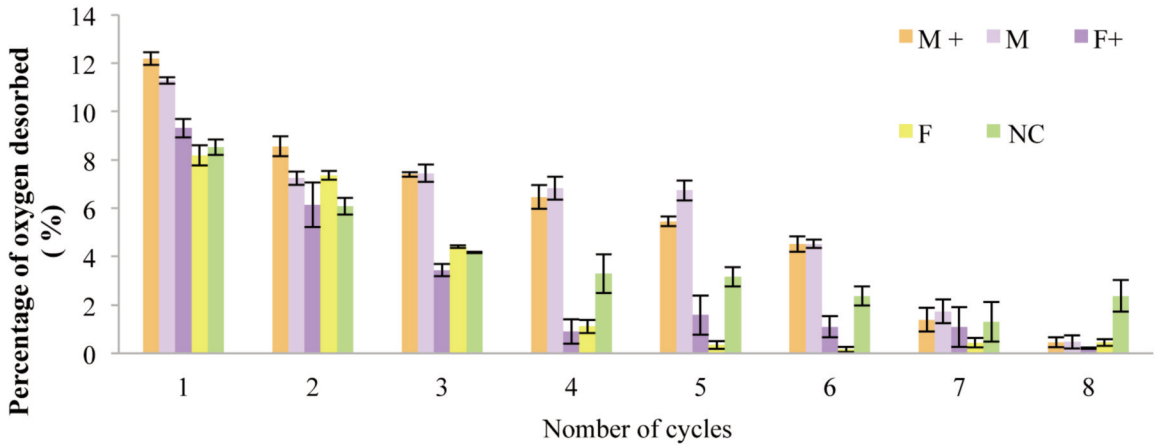

Figure 7. Evolution of oxygen concentration in model solution for three repetitions (upstream chamber condition: nitrogen gas at 0.5 bars).

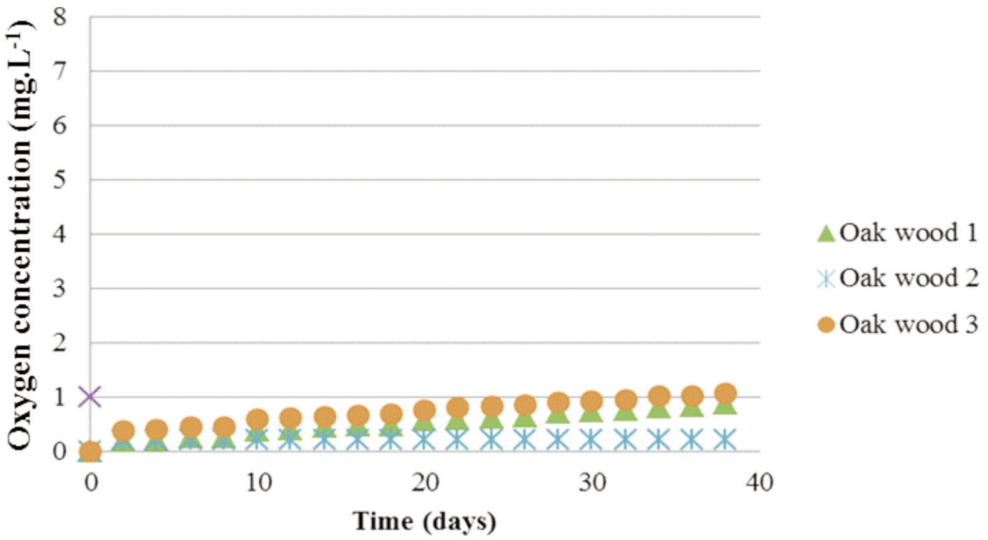

Figure 8. Comparison of oxygen concentration evolution in the downstream chamber with different types of gas applied in the upstream chamber.

First, we observe an increase in the dissolved oxygen concentration at the beginning of each cycle. After five days, we change the model solution and we reintroduce the pieces of staves into a new inert solution. The two curves are very similar. From the 7th cycle (37th day), the wood does not release oxygen any more. We can estimate the total amount of desorption for these two cases to be between 10 and 13 $mg.L^{-1}$.

The following results are expressed as percent desorbed oxygen for several different toast levels. This representation gives the opportunity to compare cycles of desorption between them. Figure 7 presents the synthesis of desorbed oxygen percentage values for medium toast (M), medium + (M +), strong (F), strong + (F +) and unheated (NC).

After 8 cycles, all the experimental woods desorbed between 11.2 and 13.6 mg of oxygen. Structural heterogeneity could have an impact on these results and should be investigated. However, this desorption must be taken into account on the global oxygen transfer balance because it represents a high percentage of the estimated intake in the literature. In comparison with the results obtained by Ribéreau-Gayon (1931), desorption phenomena represent 18 to 60% of the global oxygen transfer in a barrel during one year. This phenomenon could explain the non-linear oxygen transfer observed in the literature during the first month and should be taken into account.

2. Experiment a: oxygen diffusion through oak when it is not in contact with liquid

Experiments “a” are realized to define the permeability of oak wood close to 12% humidity. The natural humidity content when a barrel is first put to

use is close to this value. An intact piece of oak wood sample is set in the middle of the permeameter.

The permeameter is filled with nitrogen gas to ensure that no oxygen trace would be present in the system at the beginning of the experiment. Pure oxygen is introduced into the upstream chamber for the samples tested, at 0.5 bar overpressure. The downstream chamber is inerted with nitrogen. A measurement example is presented in Figure 8.

It is observed for the three samples tested that oxygen molecules present in oak were released into the downstream chamber. However, no global transfer is observed across the oak wood. The diffusivity of a material is largely influenced by its inner-connectivity. In the case of oak tissues, the inner-connectivity depends on the availability of un-encrusted perforations and punctuations on vessel walls. It was observed that the diameter of spring vessels and summer vessels in oak is highly variable in samples taken from the same stave as well as in samples taken from different staves (Qiu, 2015). This variability can also be found in the number of medullary rays (the most impermeable layer in oak tissue) and in the proportion of springwood-summerwood in oak pieces. If the connections are not filled with liquid, the gas cannot pass through the porous media because the diffusion is too low.

These results are significant because the part of the barrel close to the bung (no contact with liquid) is known to allow important gas transfer but with these results, we can consider that the transfer is not realized through the oak wood.

3. Experiment b: oxygen diffusion through oak when it is put into contact with liquid

In this part, the oxygen transfer rate is evaluated with a stave of 23 mm thickness. The oak woods considered have been in contact with model solution prior to these tests to limit oxygen desorption. The downstream chamber is filled with degassed model solution in contact with the wood.

To evaluate the possibility of oxygen transfer through impregnated oak piece representing the lower part of a barrel, pure oxygen gas is used in the upstream chamber at 0.5 bars for 45 days. To avoid oxygen desorption phenomena, oak pieces were pre-wetted (inner face put into contact with the model solution for one month). As the saturation point of pure oxygen gas is equal to 42 $mg.L^{-1}$ at 20°C, any sign of dissolved oxygen level above 8.4 $mg.L^{-1}$ in the downstream chamber would prove the existence of gas transfer (oxygen transfer through the oak wood). To avoid problems of oxygen consumption by the polyphenols, the solution is changed every 5 days. We control the oxygen and we readjust the oxygen content before reintroducing the solution.

So, this experiment with pure oxygen applied to the upstream chamber has been extended to 45 days in order to find out if an oxygen transfer could take place (Figure 9).

Over this long period of observation, no transfer has been observed: pure oxygen gas has not migrated through the 23-mm-thick sample. At the end of the measurement period, the dissolved oxygen level is lower than 0.5 $mg.L^{-1}$. We can consider that oxygen transfer through imbibed oak wood is seriously limited because no oxygen transgresses through this porous material after 45 days.

4. Experiment c: oxygen diffusion through preferential passages at stave gaps when oak pair is put into contact with liquid

A barrel's side is made up of approximately 30 pieces of oak stave. Eight metal hoops are put around the

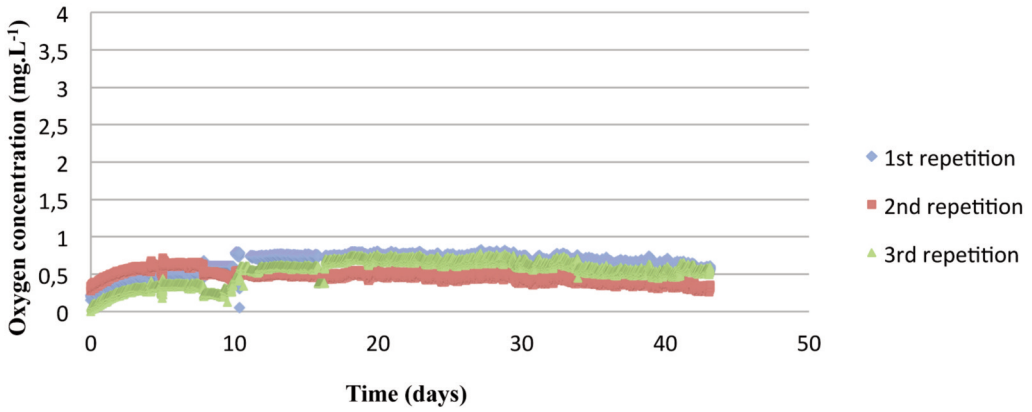

Figure 9. Dissolved oxygen concentration in the downstream chamber over 45 days.

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barrel to hold the staves together. Thanks to these hoops and the toasting process, oak staves can be bent into an egg-shape and become an impermeable barrier for the liquid inside the barrel. According to Moutounet *et al.* (1996), during aging barrels suffer from micro-deformation caused by the weight of wine. This micro-deformation is, in most cases, found at the back piece of a barrel, suggesting an uneven distribution of inter-stave pressure around the circumference of the barrel. It is possible that the uneven distribution of pressure is already present when a barrel has just been made. The mechanical forces caused by the metal hoops are not yet precisely known but a difference in curvature over the length of a stave is clear enough to the naked eye to allow the deduction of the uneven distribution of pressure.

A deformation immediately forms a passage for the transfer of gas and liquid. It can lead to a stronger bond or, in the worse case, a weaker contact between staves, leaving air only a shorter migration distance away. For this reason, this part of the present study examines the pressure range naturally present at stave gaps in a barrel before reproducing the same conditions on a laboratory scale. 50 Prescale membranes were placed between the staves at different places (side pieces and back pieces) in two barrels filled with model solution during one month and after disassembly; the pressure was evaluated by colorimetry.

It was considered that for stave gaps located in the two end-pieces, the pressure is between 25-35 bars, whereas in side piece gaps, the pressure is between 3-24 bars. By using Prescale membranes, we could estimate that 3 bars represent the pressure between two staves in the middle of the side pieces. Eight bars represent the pressure close to the metallic hoop, 14 bars represent the pressure at the bottom of the side pieces, and 24 bars represent the pressure between two staves of the back pieces. The Prescale results comparison between the results obtained in real conditions and the results obtained with our tightening arms are always realized and no differences could be detected. This approach allowed the recreation of stave-gap conditions on a laboratory scale (Figure 10).

These pressures are applied on four pairs of oak pieces and placed in our permeameter to reproduce real conditions.

With the permeameter and tightening arms, stave gap conditions are recreated in the laboratory. The pressure applied is able to reach 24 bars by pressing the two mechanical arms closer to each other. The applied pressure on stave samples (3, 8, 14, and 24 bars, chosen according to the results obtained with the Prescale membrane) was controlled by using a torque wrench. Four pairs of oak samples were made, each pair from one piece of fine-grain oak cut in half. These four pairs were taken from the same stave in order to reduce the heterogeneity factor. Tests are carried out on the influence of applied pressure on oxygen transfer rate at stave gaps using pairs A, B, C and D. Pairs A and B are both tested at 8 and 14 bars; pairs C and D are both tested at 3 and 24 bars. All the pairs were put into contact with model wine solution.

The different transfers with different operating condition are shown in Figure 11 for two stave gaps (pairs A and B) with two different applied pressures (8 and 14 bars).

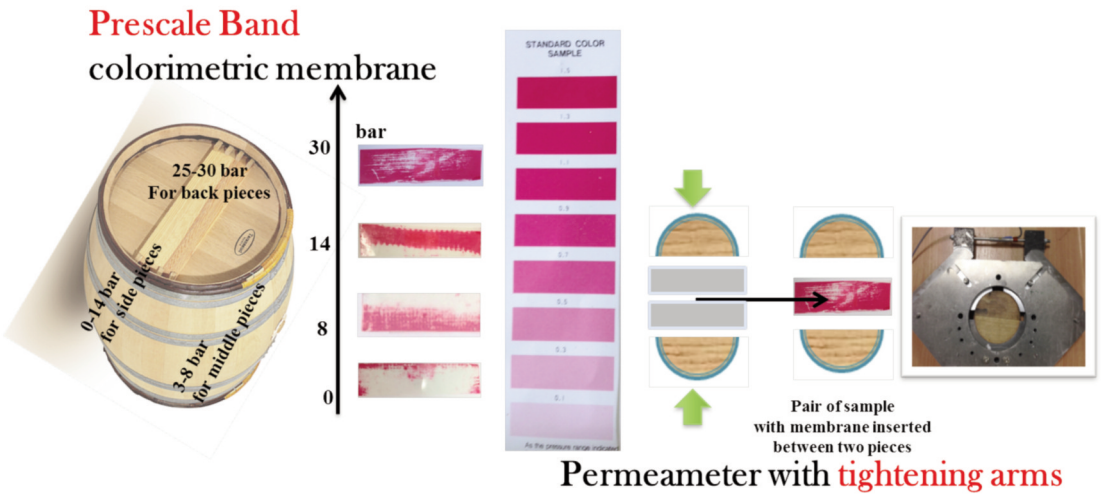

Figure 10. Dissolved oxygen concentration in the downstream chamber over 25 days.

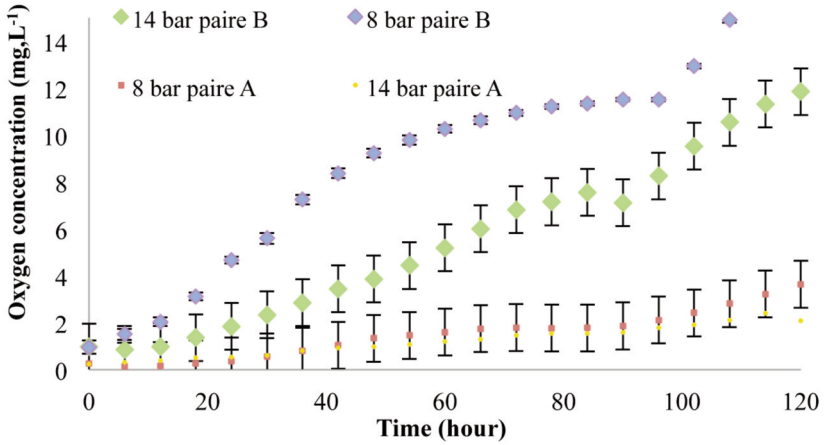

Figure 11. Pressure distribution in barrel and contact conditions according to different pressure.

In the pair B experiment, oxygen transfer through stave gaps is clearly observed. The dissolved oxygen concentration in the downstream chamber exceeded 8 mg.L^{-1} from 70 hours, either tightened at 8 or 14 bars. A difference in applied pressure at 14 and 8 bars has resulted in a better oxygen transfer rate for this pair. The same conclusion is drawn for pair A, although the difference between the 8 bars and 14 bars curves was relatively small. So, significant differences were noticed between the results obtained for 8 and 14 bars for these experiments. This shows that between the two halves of pair A the contact is of better quality. Contact traces were also visible on the Prescale membranes. For all the stave gaps tested, some had a perfect contact surface over their entire length and others had an irregular contact (Figure 12). These results prove that the contact (homogeneous repartition of the pressure applied on the two oak wood samples) is also very important. A good repartition seems to improve the limitation of the gas transfer. The concentration obtained for pair B is higher than 8 mg.L^{-1} and proves that oxygen transfers through the oak wood in this case.

A further reduction of applied pressure to 3 bars could lead to enhanced oxygen transfer. In pair C, at 3 bars, pure oxygen gas could saturate model solution in the downstream chamber within 5 hours (Figure 13). It proves that a pressure is required to limit the oxygen transfer (up to 8 bars) and that 3 bars of pressure between two staves (in the middle of the staves) represents a weak point where oxygen can easily be transferred to the wine. These same results are shown in Figure 14 for 24 bars of applied pressure for pairs C and D. The transfer is clearly influenced by the pressure applied. From these results, it has become obvious that the contact conditions have an important influence on oxygen

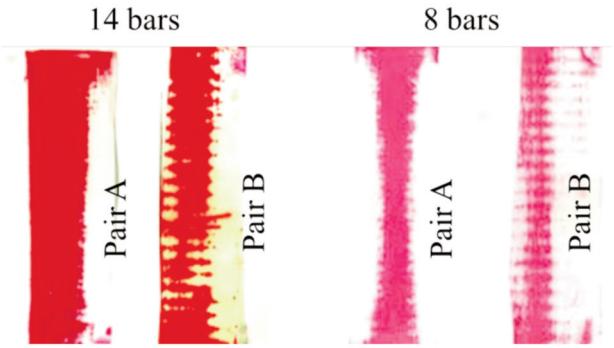

Figure 12. Oxygen concentration in the downstream chamber (pairs A and B tightened at 8 and 14 bars).

transfer efficiency through stave gaps. Tightened at both 8 and 14 bars, pair B allowed more oxygen to be transferred compared to pair A, reflecting a lesser quality of finish at the interface of pair B which allowed the formation of more passages for air exchange. Compared to pair C, pair D has better contact and thus allowed less oxygen to be transferred during the measurement period.

When pairs C and pair D are tightened at 24 bars, the dissolved oxygen concentration at the end of the measurement period reached 1.76 mg.L^{-1} for pair C and only 1.4 mg.L^{-1} for pair D. The contact condition influence is clearly limited when the pressure applied increases. If the pressure between two gaps is higher than 14 bars, the contact influence decreases.

With these results, it is noticed that in the case of a poor contact between stave gaps, for example in pair B or pair C, oxygen transfer could be slowed down by increasing the pressure and could be accelerated by releasing the pressure; but for pair A, which had

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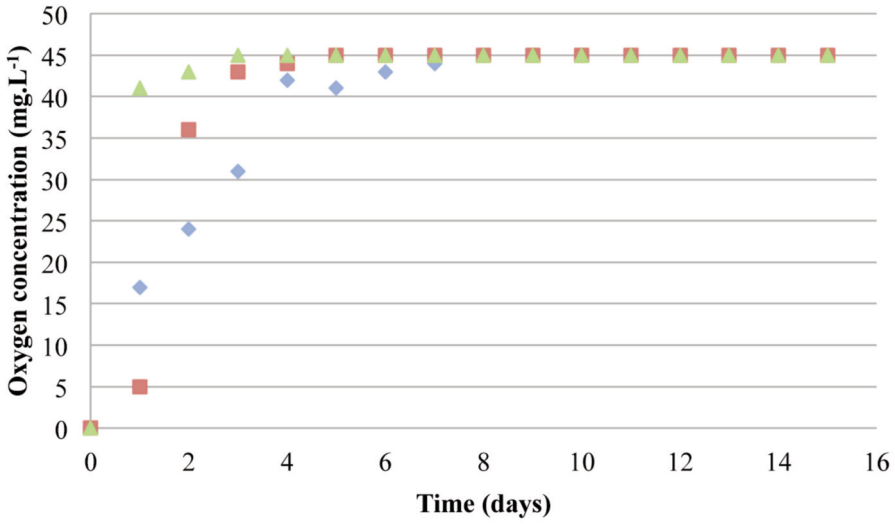

Figure 13. Oxygen concentration in the downstream chamber (pair C tightened at 3 bars; 3 repetitions).

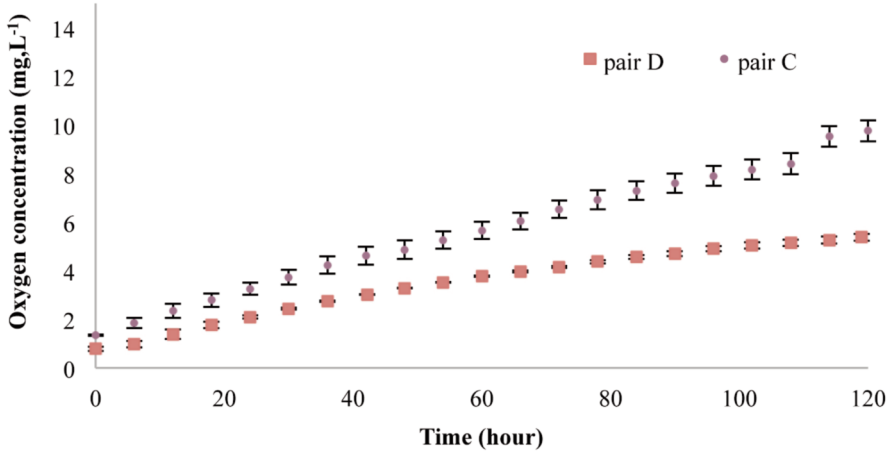

Figure 14. Oxygen concentration in the downstream chamber (pairs C and D tightened at 24 bars).

good contact, a pressure of 8 bars was already sufficient to restrain oxygen transfer. This suggests that oxygen transfer is influenced by contact conditions. During cellar work, it is often observed that the weak contact points in a barrel are around the bung-hole and in the middle of staves where they have the greatest curvature. 3 bars of pressure can be observed in these areas while pressures of 8, 14 and 20 bars exist mainly throughout the length of a stave, with 20 bars at each extremity. All these results could be summarized with the next figure (Figure 15). So, oxygen transfer efficiency depends on the pressure created between two staves and also on the contact conditions existing between the staves. An irregularity along the length of a stave or a micro-deformation will inevitably lead to an influx of air. Thus, these two parameters ought to be given consideration during the manufacturing process in order to better control the influx of undesirable gases during barrel usage.

Conclusions

Many complex transfer phenomena occur in oak barrels, due to the physical and chemical properties of oak wood. The aim of this research was to improve the knowledge of oxygen transfer through staves and between two staves. Oxygen transfer evaluation is possible thanks to the development of an innovative cell allowing us to place a piece of stave in various operating conditions and to measure the flux of oxygen on both sides of the cell. The differences of pressure between two staves have been determined between all the oak staves (3 and 25 bars for side pieces, 25 and 30 bars for back pieces). It is

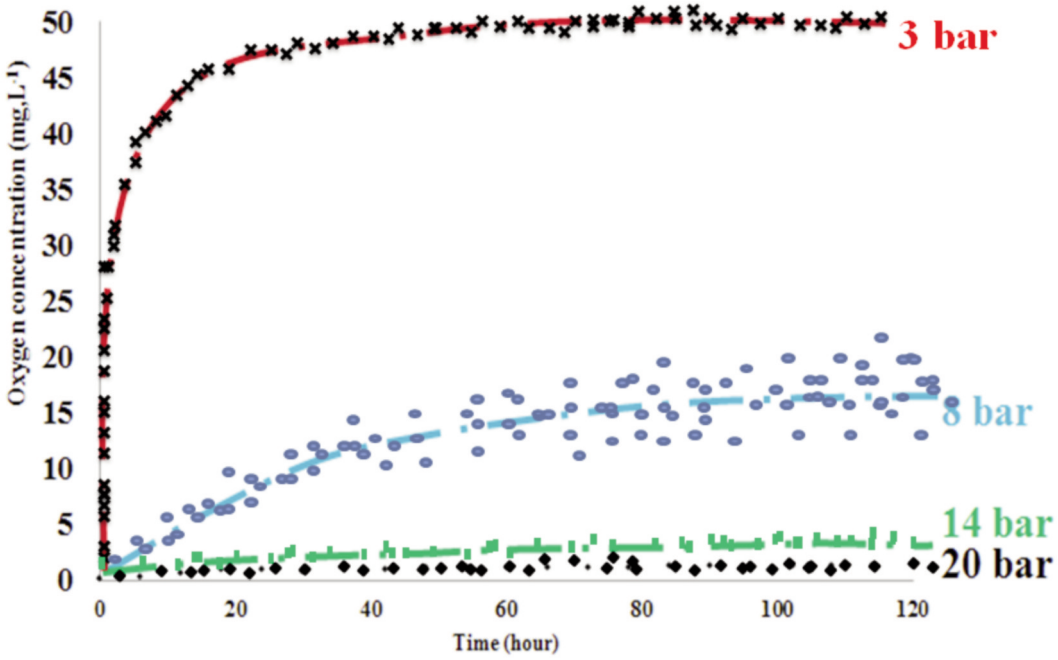

Figure 15. Oxygen concentration in the downstream chamber (pair B at 3, 8, 14 and 20 bars).

determined that an increase of pressure between two staves results in a decrease of oxygen transfer. At 20 bars, the transfer is seriously limited, but a further decrease of pressure to 3 bars (middle of the side pieces) leads to an extreme efficiency of oxygen transfer. These pressures are obtained in the middle of the side staves that represent weak points. The contact condition proves to have also a major influence on oxygen transfer efficiency. So in the case of oxygen transfer through stave gaps, two parameters both influence oxygen transfer efficiency: applied pressure and contact condition. Experiments also proved that the transfer through the complete oak wood is seriously limited. These results prove also that desorption of oxygen from oak wood represents a large amount of total oxygen transfer and should be considered in future studies.

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References

del Alamo-Sanza M. and Nevares I., 2012. Device for measuring the permeability and di□usivity of gases in porous materials and method for measuring said parameters using the device. World Intellectual Property Organization patent PCT/ES2012/070084.

del Alamo-Sanza M. and Nevares I., 2014. Recent advances in the evaluation of the oxygen transfer rate in oak barrels. *Journal of Agricultural and Food Chemistry*, 62, 8892-8899. doi:10.1021/jf502333d

Delsart C., Grimi N., Boussetta N., Miot Sertier C., Ghidossi R., Mietton Peuchot M. and Vorobiev E., 2015. Comparison of the effect of pulsed electric field or high voltage electrical discharge for the control of sweet white must fermentation process with the conventional addition of sulfur dioxide. *Food Research International*, 77, 718-724. doi:10.1016/j.foodres.2015.04.017

Delsart C., Grimi N., Boussetta N., Miot Sertier C., Ghidossi R., Vorobiev E. and Mietton Peuchot M., 2016. Impact of pulsed-electric field and high-voltage electrical discharges on red wine microbial stabilization and quality characteristics. *Journal of Applied Microbiology*, 120, 152-164. doi:10.1111/jam.12981

Fulcrand H., Doco T., Es-Safi N.E., Cheynier V. and Moutounet M., 1996. Study of the acetaldehyde induced polymerisation of flavan-3-ols by liquid chromatography-ion spray mass spectrometry. *Journal of Chromatography* A, 752, 85-91. doi:10.1016/S0021-9673(96)00485-2

Fulcrand H., Benabdeljalil C., Rigaud J., Cheynier V. and Moutounet M., 1998. A new class of wine pigments generated by reaction between pyruvic acid and grape anthocyanins. *Phytochemistry*, 47, 1401-1407. doi:10.1016/S0031-9422(97)00772-3

Ghidossi R., Poupot C., Thibon C., Pons A., Darriet P., Riquier L., de Revel G. and Mietton Peuchot M., 2012. The influence of packaging on wine conservation. *Food Control*, 23, 302-311. doi:10.1016/j.foodcont.2011.06.003

Giraud W., 2009. *Étude physico-chimique de l'interface bois-vin pendant l'élevage en barriques*. Doctoral thesis, Université de Toulouse.

Hernández-Orte P., Franco E., González Huerta C., Martínez García J., Cabellos M., Suberviola J., Orriols I. and Cacho J., 2014. Criteria to discriminate between wines aged in oak barrels and macerated with oak fragments. *Food Research International*, 57, 234-241. doi:10.1016/j.foodres.2014.01.044

Lemaire T., 1995. *La micro-oxygénation des vins*. DNO (National Diploma of Enology) dissertation, ENSAM, Montpellier.

Moutounet M., Mazauric J.P., Saint-Pierre B., Micaleff J.P. and Sarris J., 1996. Causes et conséquences de microdéformations des barriques au cours de l'élevage des vins. *Revue des Œnologues*, 74, 34-39.

Moutounet M., Mazauric J.P., Saint Pierre B. and Hanocq J.F., 1998. Gaseous exchange in wines stored in barrel. *Journal des Sciences et Techniques de la Tonnellerie*, 4, 115-145.

Pechamat L., Zeng L., Jourdes M., Ghidossi R. and Teissedre P.-L., 2014. Occurrence and formation kinetics of pyranomalvidin-procyanidin dimer pigment in merlot red wine: impact of acidity and oxygen concentrations. *Journal of Agricultural and Food Chemistry*, 62, 1701-1705. doi:10.1021/jf4052754

Pons A., Prida A.B., Darriet P. and Dubourdieu D., 2014. Étude de la contribution des « morceaux de bois de chêne » à l'apport d'oxygène dans les vins au cours de l'élevage sous bois de chêne. *Revue des Œnologues*, 153, 45-48.

Qiu Y., 2015. *Phénomènes de transfert d'oxygène à travers la barrique*. Doctoral thesis, ISVV, Université de Bordeaux.

Rentzsch M., Schwarz M. W.interhalter P. and Hermosin-Gutierrez I., 2007. Formation of hydroxyphenyl-pyranoanthocyanins in Grenache wines: precursor levels and evolution during aging. *Journal of Agricultural and Food Chemistry*, 55, 4883-4888. doi:10.1021/jf0702491

Ribéreau-Gayon J., 1931. *Contribution à l'étude des oxydations et réductions dans les vins*. Doctoral thesis, Université de Bordeaux.

Singleton V.L., 1995. Maturation of wines and spirits: comparisons, facts, and hypotheses. *American Journal of Enology and Viticulture*, 46, 98-115.

Vivas N. and Glories Y., 1996. Modélisation et estimation du bilan des apports d'oxygène au cours de l'élevage des vins rouges. I. Les apports technologiques et liés au mode d'élevage. *Progrès Agricole et Viticole*, 113, 222-227.

Vivas N. and Glories Y., 1997. 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 Agricole et Viticole*, 114, 315-316.

Vivas N., Debèda H., Ménil F., Vivas de Gaulejac N. and Nonier M.F., 2003. Mise en évidence du passage de l'oxygène au travers des douelles constituant les barriques par l'utilisation d'un dispositif original de mesure de la porosité du bois. Premiers résultats. *Sciences des Aliments*, 23, 655-678.