Gas released from cork after bottling

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Abstract

The evolution of wine after bottling may be affected by the continuous supply of oxygen through the closures. In the case of cork, oxygen may come from two different sources: permeation from outside through the cork and the release of gas from inside cork cells. In this work we studied this later issue.

The typical compression rate (volume change / uncompressed volume) of a cork stopper is about 40%. Taking in account that cork has a void volume ranging 70 to 80%, cork cells pressure after bottling may reach 2 atm. This pressurized gas will 'escape' to both sides of the closure along many weeks.

In this work we measured the gas flow coming from cork stoppers in 3 typical starting headspace pressures: 60 mbar, 1000 mbar and 3000 mbar (absolute pressures). These conditions correspond roughly to vacuum bottling, balanced pressures bottling and bottling without any prior pumping. These experiments were performed by continuous monitoring the pressure, with a high accuracy gauge, in the headspace along several weeks keeping the bottleneck volume at constant temperature.

In the case of vacuum bottling the headspace pressure continuously rises for many weeks. With balanced pressures, the pressure rises for a few days and then starts decreasing. In the case of bottling without pumping the headspace pressure is typically higher than the cork cells pressure leading to a continuous pressure loss.

These results together with those from permeation of cork provide a useful picture to those who need to know quantitatively the amount of oxygen in contact with wine in the post bottling period.

Keywords: cork, oxygen, permeation, bottling

Introduction

The wine industry has promoted an increased education on closures namely the parameters that affect the quality of the wine until consumption.

In a way, this approach has resulted from statistics in international wine tastings (Wine & Spirit Association, 2006) suggesting that almost 25% of faulty wines dealt with oxidation issues. Following these observations an increased interest on oxygen management developed in the wine industry.

On the other side the competence between the traditional cork closures and the alternative closures, stirred the debate namely over whether oxygen ingress through the closure is a requirement for proper bottle development. In addition to this, it is for sure that every variation of wine bottle closure has its drawbacks and it is the role of the closures' suppliers to commit with better understanding, better assuring and better performing products.

Yet the value and necessity of oxygenation are still not definitive and shall depend even on a few subjective variables such as the expected aging of bottled wine, and if wine is intended for quick consumption or a lengthy cellar life.

On a quantitative perspective, different methods have been developed for the measurement of oxygen flow through the closure, therefore approaching to the impact of the closing system on the oxygen introduced to the wine during bottle aging - oxygen transfer rate. From the determined figures, expected shelf-life of a wine can be calculated.

It is understood that not only the closure material act on shelf life of a wine in bottle. Several experiments and examples have been published dealing with key parameters related to the wine preparation, bottling practices and bottle storage; examples of which are free SO_2 at filling, dissolved oxygen - Vidal & Moutonet (2008), headspace oxygen - Jung (2009), bottle ullage - Kwiatkowski (2007), position of bottle at storage - Lopes (2006).

Guidelines to bottling have been named and include minimizing dissolved oxygen in the wine, reduce headspace oxygen and other oxidants during filling and careful attention to antioxidant levels. From measuring dissolved oxygen for quality assurance, the wine industry continued to calculations of the total packaging oxygen (TPO) at bottling, to determining how the wine will develop over time.

Some examples of the sorts of levels of oxygen that might be introduced to wine bottles during different filling procedures have been given by Jung (2009).

Permeability measurements on corks have revealed a wider range of results when compared to alternative closures. Data demonstrates oxygen permeability is essentially identical to other closing systems, and in most cases it is unimportant compared to other sources of the oxygen in bottled wine; however it also reveals the required improvement on the consistent performance of the natural product - Macku (2010), despite the vast improvement on wine corks in recent years, due to research and screening.

An interesting review has been published by Karbowiak et al. (2010) where several factors are discussed, including the use of diffusion Fick's models for oxygen flow driven by molecular kinetics and the mass transport / transfer driven by pressure gradients named the permeation. These aspects deal with oxygen from outside to the inside of the bottle.

Lopes (2005) has identified distinct patterns of oxygen flow through the corks along time, recording a higher oxygen input during an initial period of 1 month; an identical decreasing trend over time was observed by Brajkovich et al. (2005) through indirect measurements (free SO_2).

Such observations suggest that the initial higher oxygen ingress might be related to oxygen contained in the cork, being released due to compression of the material. However this theory was not proven before.

In fact, when it comes to closuring a bottle of wine, three sources of oxygen are identified: the actual oxygen initially in the wine, the headspace oxygen and the permeation through the stopper. The system increases in complexity when reviewing that on the corks stand point, oxygen does not only deal with permeation from outside through the cork but also to the release of gas from inside cork cells.

No extensive research has yet been concluded regarding corking parameters such as the compression rates or application of the closures, as the impact of headspace pressure. An accurate evaluation of the whole scenario should take these factors in mind.

The achievement of the available information herein presented deals with the understanding on how these issues interfere. Available results, together with those from permeation of cork, provide a useful picture to those who need to know quantitavely the amount of oxygen in contact with wine in the post bottling period.

Materials and Methods

The experiment design had in mind that the typical compression rate (volume change / uncompressed volume) of a cork stopper is about 40%. Taking in account that cork has a void volume ranging 70 to 80%, cork cells pressure after bottling may reach more than 2 atm, becoming a source of (pressurized) gas that may 'leak' to both sides of the closure along many weeks.

To evaluate the kinetics of this process the headspace pressure was monitored for several days after the introduction of a cork stopper in a bottleneck like holder specially built for this purpose in stainless steel. This holder was kept inside a climatic chamber adjusted to maintain a constant temperature of 23.0℃ with a variation lower than 0.1 ℃. The bottleneck was slightly conical 18 mm to 19 mm in diameter The stoppers were introduced slowly with the help of a screwable cylinder (about 10 seconds), later removed. All parts, including the stoppers were thermalized in the climatic chamber before experiment start.

Three typical starting headspace pressures were used: 60 mbar, 1007 mbar and 3020 mbar (absolute pressures) – corresponding roughly to vacuum bottling, balanced pressures bottling and bottling without any prior pumping. Since ethanol vapor pressure is about 60 mbar at room temperature, vacuum bottling of wine cannot be processed at lower pressures. In this case a rotary vane vacuum pump was used to produce the starting conditions. In the case of balanced pressures, the valve was kept open to atmosphere during cork insertion to keep the headspace pressure the same as the barometric pressure in that time. The starting pressure of 3020 mbar resulted from the compression induced by the stopper in the closed headspace volume.

The pressure was monitored by baratron type, high accuracy gauges, manufactured by MKS Instruments. These gauges are temperature controlled and are well known for their accuracy and long term stability. Moreover, these gauges are used in our accredited metrology laboratory and, therefore, its traceability is easily assured. Connections outside the climatic chamber were chosen to be as small as possible to minimize temperature effects on the headspace volume. Fig. 1 schematically illustrates the experimental set-up. The outside pressure was the barometric pressure with the normal weather fluctuations. The results were not corrected for a constant atmospheric pressure. This pressure fluctuation may have slightly affected the results of the experiment performed with balanced pressures.

The experiments were performed with three different stoppers 45 mm x 24 mm, from the same lot ("Superior" from cork supply) with a density ranging 160-190 kg/m^3. Due to the natural variability of cork, results among distinct samples should be compared with caution.

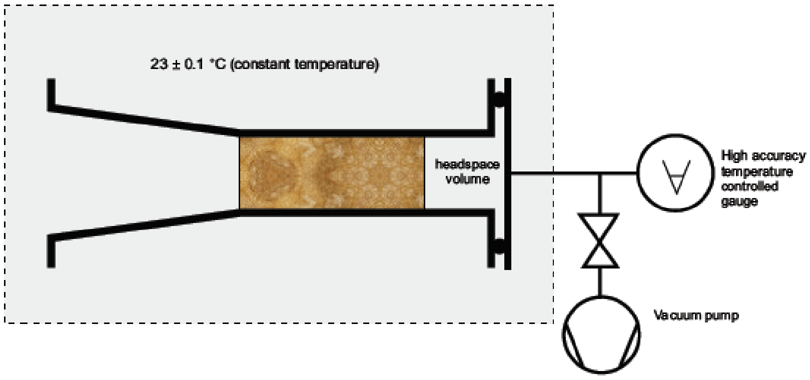

Figure 1- Experimental set-up used to monitor the pressure in the headspace after bottling.

Results and Discussion

The results are graphically shown in Fig. 2 for the three different starting pressures. The air flow rate, the total volume of air went through the closure and the pressure are plotted as function of the time.

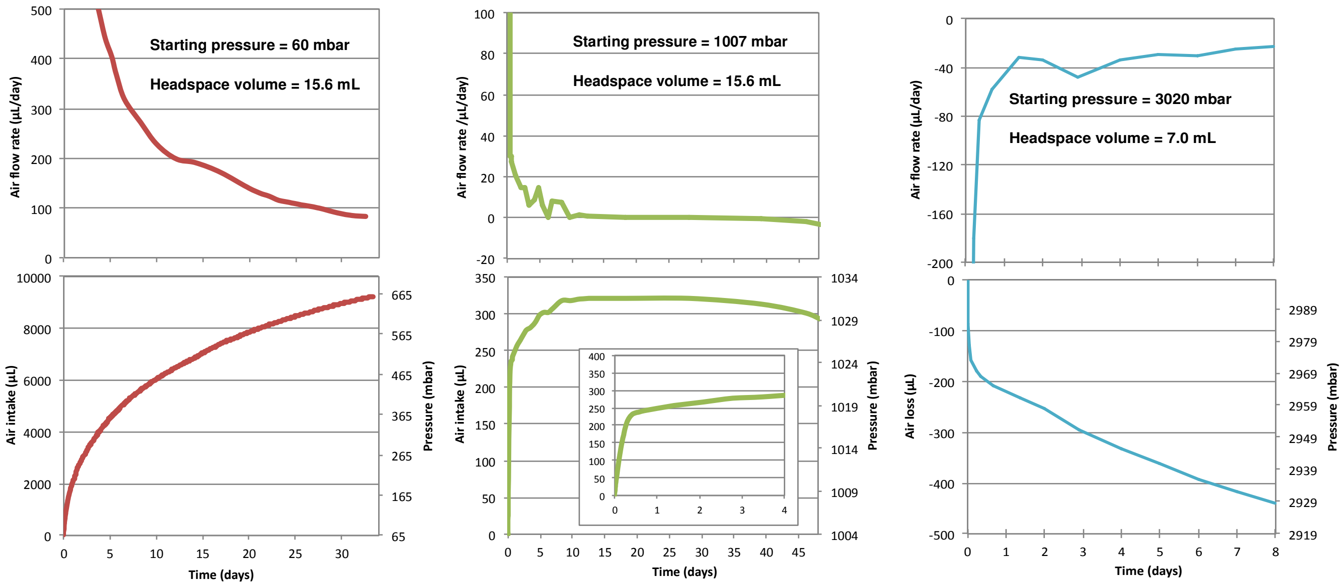

Figure 2 – Experimental results for three different starting pressures. Note the difference in the time scale and the headspace volume. The insert in the 1007 mbar lower graph is a scale expansion for the first 4 days,

Differences between the three experiments are outstanding. The flow of air into the headspace volume can be positive, quasi-null or negative (air loss). In the case vacuum bottling (60 mbar starting pressure) the flow rate has a huge maximum in the first few hours reaching peak of 10 mL/day (not shown). This intense flow is mainly due to the release of the highly compressed air inside the cork cells, after cork insertion. Then, the flow decreases approaching an exponential variation as the headspace pressure tends to the atmospheric pressure. Under this situation the closure works as a permeable membrane between two volumes at different pressures.

If the closure is inserted avoiding compression of the headspace volume (1007 mbar starting pressure) a peculiar pressure evolution is observed. First, air flows into the headspace resulting in a 3% pressure increase and then pressure is kept quite stable for about 2 weeks. Finally, the flow is inverted and the pressure starts to decrease at a very slow rate. A flow rate peak of 4 mL/day (not shown) is reached in the first hour for a very short time.

If the cork is inserted without any pumping (3020 mbar) the air flows in the opposite direction, from the headspace to outside. In this case the flow starts to be very small since the headspace pressure needs to overcome the cork internal pressure. Then, the air flows at constant rate, approximately, resulting in a slow pressure decrease.

The stopper volume is about 20.4 cm^3 prior to insertion and 11,5 cm^3 after insertion. Assuming that cork is made of 75% void volume (empty cells) and the rest in uncompressible, the absolute pressure inside cork cells after bottling is about 2.4 bar. This corresponds to 1.4 bar above atmospheric pressure. The amount of compressed air inside such typical closure is about 8.9 mL (STP). This pressure is the main source of flow in the first hours after bottling and is evident in the case of vacuum bottling and even more evident in the case of balanced pressures bottling. In this later situation, the inner pressurized volume is the only source of air. However, it flows to both sides of the closure. In the experiment performed only 0.35 mL of air went into the headspace.

A closer look in the first days of the 1007 mbar flow plot (insert in graph, Fig.1) shows two distinct regimes. The first steeply slope is maybe due to a quick release of gas from cork defects. Note that, although the flow rate is very high at this time, the total amount of release gas is smaller than 0.25 mL. The second slope should correspond to gas liberated from the pressurized cells that slowly flows towards lower pressures.

The data plotted in Fig. 2 can be also discussed in terms of cork permeation. In a recent paper (Faria et.al., 2011) showed that, besides the huge variability, the higher the cork density the lower the average permeability. Table 1 confirms this correlation — the closure with higher density showed a low permeation rate and the lighter stopper was the one that permeated more. Tabled permeabilities were calculated by the slope of the flow rate at the end of the experiment.

Table 1- Sample and experimental data

Starting pressure (mbar)	Manufacturer class	Mass (g)	Size (mm)	Density (kg/m^3)	Permeability (µL/(cm.atm.day))
60		3.3605		165	416
1007	Superior	3.6431	44 x 25	179	269
3020		3.7534		184	21

Conclusions

In this work the amount of gas liberated by a cork closure after bottling was addressed. The pressurized cork cells are a source of gas until pressure equilibrium is achieved. This source of gas (oxygen) maybe important in the wine evolution after vacuum bottling.

The gas is released in the first few weeks and then the cork behaves as permeable membrane. There is an intense flow rate in first hours, slowing down in next days. While the headspace pressure is lower than the cells pressure the gas inside the cork is an additional and significant source of gas, speeding up the headspace pressure increase. Then, the gas flow becomes ruled by cork permeability.

In the case of bottling without prior pumping, the gas released by cork is towards the atmosphere since the typical headspace pressure after bottling is higher than the cork inner pressure.

The total amount of gas released by cork seems to less the 1 mL as shown in the experiment performed at balanced pressures.

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