Micro-oxygenation of Wine in Barrels

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Abstract

The growing implementation of micro-oxygenation has increased our appreciation of the role of oxygen in the winemaking process. Indeed the technique of micro-oxygenation had its origin in the attempt to simulate in tank, the slow uptake of oxygen in barrel. However this process is not well understood and, we will argue, it may not be adequate to achieve the full maturation potential of small oak barrels. Our experience has shown that for some wines, micro-oxygenation dosing rates of 2 to 8 ml O_2/ litre wine / month are necessary. The barrel's own oxygen diffusion potential we calculate to be less than 2.5 ml/litre/month. Supplementing this may be necessary and beneficial.

Introduction

Traditionally, the first choice of many winemakers has been to mature wine in small barrels – generally the higher the quality aspirations for the wine, the smaller the barrel. There are many reasons for this, including:

- wine flavour improvement
- structure enhancement,
- winemaking tradition,
- sheer romanticism.

More and more attention is being focussed on the structural changes that occur in wine matured in barrels and there is ample evidence to suggest that at least some of these changes are due to the ingress of oxygen. The method by which this occurs has been a matter of some controversy, but the two most likely mechanisms are diffusion through the permeable wooden staves of the barrel and diffusion from the wine surface as a result of air exposure in the headspace. It is most likely that both of these mechanisms play a part, with diffusion through the wooden staves being more important in new barrels but decreasing in importance as the inner surface of the barrel becomes "winelogged".

Porosity and Permeability

In this regard, it is important to distinguish between porosity and permeability – concepts that are easy to confuse. Preferably, barrels are not porous - they are permeable. If they were porous, they would not hold wine and we would not experience the phenomenon of headspace vacuum.

Porosity is basically caused by the presence of holes or channels in a material, through which a fluid such as a gas will flow. The rate of flow of the fluid is controlled by several factors including its viscosity and surface tension (whether the fluid "wets" the surface of the material). In general flow through a porous material will be zero or very low up to some breakthrough point and will rise very rapidly thereafter; so there is no easy way of controlling or predicting flow rate.

Permeability, on the other hand, depends on the ability of very small molecules such as those of a gas to fit into the gaps between the molecules of the solid. This effectively allows the gas to dissolve into the solid. At equilibrium, an equal amount of gas will be dissolved in, and released from, the surface of the solid. If the material is relatively thin such as with a membrane, and there is a concentration difference of the gas on either side, gas will be transported across the membrane. This occurs because some of the gas which dissolves into the membrane on the high concentration side is released from the low concentration side.

Diffusion – Some Theory

The first work on this was done in the 19th century by Adolph Fick (1829 – 1901) the pioneering physiologist who investigated gas transfer in the lungs. He determined Ficks Law[1] which states that the diffusion rate of a gas through a given area of any permeable material (membrane) is proportional to the concentration gradient across the membrane:

- **dV/dt = k.d[V]/dx.**

Where:

- V = volume of gas diffused
- (dV/dt = rate of diffusion of the gas)
- [V] = concentration of that gas
- (d[V]/dt = concentration gradient across the membrane)
- x = thickness of the membrane
- k = constant

The concentration gradient in turn depends on the concentration difference between the two sides, which for gases equals the pressure difference, divided by the thickness of the material the gas must cross. Lastly, each material has a characteristic permeability to a given gas. This is related to how well the gas dissolves in the material and to how much "free space" is available for the gas within the matrix of the solid.

For a non-polar molecular gas such as oxygen, the lower the polarity of the solid the higher the solubility and therefore permeability will be.

For any gas, a material with a closely spaced crystalline structure (such as a metal) will have much lower permeability than one with a loosely packed amorphous structure. The characteristic permeability of the material is the proportionality constant in Fick's Law and is designated as μ (pronounced "mu" and usually measured in a fairly useless unit called the Barrer, which is equal to 10^{-10} $cm^3.cm.cm^{-2}.s^{-1}.cmHg^{-1}$ or volume x thickness / area / time / pressure).

Putting all of this together, the rate of diffusion (dV/dt) through a "membrane" is the product of the permeability μ, the pressure difference ΔP and the area A all divided by the thickness d, or:

- **dV/dt = m.A.DP/d**

Practical Implications

So how does this relate to wine in a barrel? With wine, small volumes of oxygen are rapidly consumed by chemical reactions so we can assume that the equilibrium vapour pressure of oxygen in the wine will be close to zero. In turn, this means the pressure differential (ΔP) across the oak "membrane" is equal to the partial pressure of oxygen in the atmosphere.

The permeability of oak wood is difficult to quantify as it varies with grain direction, wood type and preparation method and it declines rapidly as the wood moisture content rises. However we have considered previously published oxygen uptake rates in barrel[2,3] and calculated the permeability of oak to be no more than 20 Barrer (and probably a lot less).

From this we estimate that 2.2ml O_2/ litre wine / month is the <u>highest</u> diffusion rate that could be expected through the oak staves. For a typical barrel:

- 225 litre capacity,
- 2 square metres surface area (approximately),
- 27mm wall thickness,
- 18kPa atmospheric oxygen partial pressure,

the maximum diffusion rate of oxygen will be around 500 ml of oxygen over a period of a month. We would also expect this permeability to decline as the barrel ages and the surface fouls. So, practical rates over the life of the barrel will be lower.

Further, we estimate that diffusion from the headspace surface can account for a very low oxygenation rate of 0.4 ml / l / month. As an example, a barrique which loses 500ml to evaporation over a period of a month, and is opened twice in that period without being topped, will gain 90 ml of oxygen from the air in the headspace. Larger ullages will result in higher rates but this is definitely not recommended as it invites acetic spoilage.

We believe that these low levels of oxygenation in barrel are inadequate for the optimum maturation of wines in barrel, an opinion shared by many winemakers.

The traditional solution to this has been to rack the wine in an aerative manner one or more times through its life, allowing oxygen uptake around 4ml / litre on each racking.[3] This has the added benefit of separating a wine from its lees and providing a convenient opportunity to make additions to the wine. On the other hand it is messy, labour intensive, time consuming and expensive. On average, a racking operation in a medium sized winery costs about 20¢ per litre including product shrinkage. The control of oxygen uptake during racking is also rather coarse.

Alternatively, leaving the wine in barrel for longer extends maturation time and cost and can lead to excessive oak extraction.

Micro-oxygenation Background

Over a number of years of working with the micro-oxygenation technique, we have typically required rates of oxygen delivery of 2 to 8 ml / l / month to ameliorate reductive tendencies and achieve optimum maturation results. The theory and the practice therefore, suggest that a barrel, by itself, cannot deliver sufficient oxygen to match the demonstrably beneficial effects of micro-oxygenation.

Just over 10 years ago, Patrick Ducornau of Oenodev, invented the technique of micro-oxygenation to simulate the maturation characteristics of barrels for wine in tank. His original micro-oxygenation system, and its numerous imitators, allows the delivery of sub-saturation doses of oxygen to wine in tank. It relies on the formation of micro-bubbles by the injection of gaseous oxygen into the wine through a porous membrane or sinter. These bubbles rise through the wine, dissolving into it as they travel to the surface. Typically this system requires the bubbles to travel a certain distance to allow full gas exchange and dissolution to occur. Without this, oxygen will accumulate in the tank headspace and the oxygen delivery to the wine will be some unknown fraction of the expected rate.

Practically, this limits the applicability of standard micro-oxygenation techniques to wines held in vessels of approximately 2.5 metres depth or greater, thus making it unsuitable for smaller vessels such as oak barrels.

This meant that winemakers keen to enjoy the other benefits of quality oak barrels, had to forego the benefits of micro-oxygenation. This seemed unreasonable to us so we considered the possibility of simulating and supplementing the diffusion of oxygen through the barrel wall, using a smaller area of thinner membrane material with much higher permeability. By controlling the membrane's effective surface area and thickness, as well as the differential pressure of oxygen across it, we figured we should be able to deliver the benefits of micro-oxygenation to wine in barrel. We just needed to find the right material in the right form.

A Practical Solution

It turns out that several polymers have outstanding characteristics in this area, most notably some fluoropolymers and some forms of polydimethylsiloxane (silicone). Other fluoropolymers can be made to work, but require fairly high pressures to achieve good flow rates and then they risk deformation or bursting. Another limit on the performance of these polymers is their tendency to self foul – if the polymer absorbs significant amounts of polar material from the wine its permeability over time will be greatly reduced.

Our research found that a particular grade of polydimethylsiloxane has just the right balance of required properties:

- good and consistent permeability
- very low self fouling,

Further, we have been able to incorporate a tubular form of this into a practical system that has proven successful in selected Australian wineries. We are able to control the effective partial pressure of oxygen by balancing the diffusion through the membrane with the depletion of oxygen from the internal volume. We apply a control program to the replacement of gas in this volume and thus achieve effective control of the micro-oxygenation rate of the wine in barrel.

In trials, the treated wine has responded with the characteristics typical of micro-oxygenated wine: greater richness, less greenness and softer tannins than the control.

This technology is the subject of an international patent application[4] and is available commercially under the brand name **0_2mate**™. The system developed for the micro-oxygenation of barrels is known as **(barrel)mate**™.

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