

Oxygen & Fermentation

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An Introduction to Understanding Oxygen & Fermentation

This MoreManual![™] has been written to help explain how oxygen can be used as a tool during fermentation. Usually thought of as being problematic and something to avoid, oxygen, when properly understood and used correctly can be a handy element in creating a well-rounded, fruit foreward wine. We will begin by first looking at how oxygen interacts with yeast and the complex chemical compounds that make up the matrix of the wine. Then we will look at how these reactions can be used to help limit undesirable, sulfur-based off aromas and flavours from developing in the wine during fermentation. While not for every wine, understanding how to introduce oxygen during fermentation should prove to be an invaluable addition in your winemaking toolbox should the need arise!

The Effects of Oxygen Exposure

Oxygen makes up about 20% of the air we breath and is found everywhere in the winery. In general, we as winemakers are mostly aware of the detrimental effects exposure to oxygen can possibly have on our wines: at best, a dulling of the fruit with a loss of once-present vitality, with VA and sherry-like, aldehydic flaws developing in a worst-case scenario. In fact, it is because of these potentially negative reactions that most winery decisions (ex: processing fruit, racking, bottling, etc.) usually seek to carefully limit or even eliminate a wines' exposure to oxygen in the first place.

However, there is one time when oxygen exposure on the macro level is actually quite beneficial to any wines' development, and that is during the fermentation itself. When correctly applied, oxygen interacts with both the yeast and the wine/must in such a way that yeast health is improved, fermentations encounter less problems, and the resultant wine quality is often more approachable with fresher aromas and tastes than it had been previously.

While the reasons for this are complex, they are indeed accessible. Essentially, two separate elements: the yeast and the reduction-oxidation potential of the wine itself interact to form a symbiotic relationship. This combined system then has specific reactions when exposed to oxygen. By better understanding the quality and timing of these reactions, we as winemakers can hope to take advantage of the positive effects while avoiding the negative ones.

A Closer Look at the 2 Elements - Yeast & Oxygen

In order to best do this, we will need to be sure that we have a solid working foundation for each of the two elements in the system. So, let's begin by taking a closer look at the first of these two, the yeast itself.

Yeast - Element 1

The yeast cell is like a small balloon and it survives by selectively letting nutrients in and passing waste and by-products out through its skin, or membrane. The more healthy the membrane, the more efficient this transport mechanism will be and the yeast will be better prepared to handle whatever adverse conditions it may find itself in; and at various stages of a fermentation these can potentially be quite varied and challenging.

At the very beginning when the fruit has just been crushed there a great deal of sugar in the must. The presence of this sugar makes the juice thicker/heavier than water and this density actually creates stressful pressures that need to be regulated against if the yeast is to effectively survive. A helpful example would be to imagine how little effort it takes for us humans to take a couple of deep breaths while lounging by the side of a pool. Now try to take the same deep breaths while you are standing in the pool with the water up your neck and you can now see that the same action requires much more effort than before. This is because water is thicker than air and even though what you are doing is usually an easy action you are now having to fight against the pressure of the water and this requires more effort. Well, it is the same for the yeast in the must and the greater the sugar level, the greater the density will be and that translates to added physical stresses that the yeast will have to work against in order to survive. In fact, a must with a high enough °Brix level (≥25°Brix) should actually be thought of as being potentially toxic to the yeast.

Towards the end of fermentation, however, the yeast finds itself in quite a different set of conditions than it started out. At this point we see very little stress from the density of the sugar in the must since most of it has already been consumed. But now, along with a scarcity of nutrients, there is a fair amount of alcohol present. As was the case with sugar, at high enough concentrations alcohol is also toxic to the yeast and can therefore become an antagonizing factor, as well.

So, we can see that at various points in a fermentation there may be times when environmental conditions can come together and make it difficult for the yeast to do its job. It should be noted that the ability of yeast to gracefully work through

these adverse conditions will be directly related to its state of health. But, just why is this important? Well, the answer is simple: If the yeast becomes unhealthy and stressed it will lose efficiency and become sluggish, possibly running the risk of stopping altogether. In addition, it can start producing excess Hydrogen Sulfide (H₂S) and often Volatile Acidity (VA), as well. This H₂S and VA will have a negative impact on the must and will begin to mask the fruit flavours and aromas while causing the wine to appear harsh and aggressive on both the palette and the nose. Furthermore, this excess $\rm H_{2}S$ and VA, if present in large enough quantities can now begin to inhibit and stress the yeast itself (along with the subsequent ML culture, if desired), causing them to make even more of these undesirable compounds and the ugly cycle continues. Finally, if left unchecked, these flaws and their consequences can effectively lower a wine's final quality.

Oxygen – Element 2

Therefore, it becomes obvious that it makes sense for winemakers to try to do everything we can in order to keep the yeast as stress-free as possible. So, in addition to the common practices of balancing the must when needed, controlling the fermentation temperatures, and using a comprehensive nutrient schedule, we can now look at how the effects of oxygen can be used to lend a helping hand. When oxygen is present, yeast use it to synthesize fatty acids and sterols. These specific types of chemicals are then used for cell wall maintenance and population growth. This, in turn helps the yeast stay healthy and plentiful throughout the course of fermentation. It should be noted, however, that the yeast need the presence of oxygen to facilitate these processes and that in the absence of it production will stop. In the beginning, this is not a problem as oxygen is indeed present for the yeast both in the saturated form from being dissolved into must during the mechanical processing of the fruit, as well as from surface area exposure at the top of the fermentation vessel. However, once the fermentation starts in earnest, the yeast will have consumed the dissolved oxygen in the must and the top of the vat will be blanketed with CO₂, effectively cutting it off from the oxygen in the surrounding air. In short, if the yeast is to receive any more oxygen to help it stay healthy and limit the production of undesired sulfur compounds during the remainder of the fermentation, the winemaker must take measures to add it them selves.

Oxydation-Reduction Potential:

How It Effects The Chemical Matrix of Wine

Before we get into the technical aspects of adding oxygen to the must, now is a good time to review the other part of the system, the phenomenon of oxidation-reduction and how it effects the chemical matrix of a wine. The term "Redox Potential" effectively refers to a wine's state of balance between its level of off-smelling sulfur-based compounds¹ (ex: H_2S) and the amount of available oxygen. When present, oxygen beneficially counteracts these compounds. However, when a wine contains a higher amount of these negative sulfur-based compounds and not enough available oxygen to mitigate all of them, then by definition you have a reduced pool of oxygen from which the offending sulfur compounds could have been counteracted (but weren't). This wine is then referred to as being "reduced." Wines that are in this "reduced" state often have off-sulfur odour defects, so this term is usually used to denote a wine with these flaws. In addition to a wine's aromas being adversely affected by off-smelling Volatile Sulfur Compounds (VSCs), mouthfeel is also negatively impacted. Negative VSCs aggravate the perception of pH and tannin, and can actually render a wine more aggressive and harsh when they are present.

¹It is important to note that not all VSC's are bad. In fact many are quite desirable:

- Volatile sulfur based compounds known as "thiols" are found in Sauvignon Blanc and these are responsible for giving flavours of passion fruit, citrus zest, smoke and flint.
- Smoke, leather & spice are positive VSC's in Syrah. So, be careful as over-oxygenation can remove the good with the bad.

Oxygen, when added to the fermenting must helps to limit the impact of negative VSCs in two ways. The first, as mentioned above, by allowing the yeast to synthesize the fatty acids and sterols needed to keep their cell wall transport mechanisms healthy. This allows them to better cope with the stresses encountered during fermentation and therefore limits the amount of negative VSCs produced in the first place. Second, oxygen counteracts whatever amount of VSCs that may already be present by raising the redox potential of the wine. All fermentations produce sulfur-based compounds and it is not possible (or even desirable) to completely eliminate them from your winemaking. Rather, the goal is to try and limit the impact that the negative ones may have on your wine and oxygen can be a useful tool to help do just that.

Finally, as another positive chemical reaction, in addition to limiting the formation of off-sulfur compounds, oxygen has the added benefit of helping to stabilize color in a red wine. It does this by reacting with the alcohol in the must to form aldehydes, which in turn react with anthocyanin (blue pigment) and tannins to form more stable molecules. Tannins are also chemically changed through oxidative reactions and can evolve to become more complex and rounded.

Adding Oxygen to Must

There are many ways to get oxygen into fermenting musts, some more effective than others. In general, temperature and turbulence determine the rate and the amount that can be dissolved in the following ways:

The colder a liquid is, the more saturated with a gas (in our case, oxygen) it can become. A drop of $5^{\circ}C = +10\%$ of solubility. However, reactions are also slower with lower temperatures. The inverse holds true, as well, in that the warmer a liquid is, the less saturated it can become while reactions will be quicker.

- The greater the turbulence, the greater the amount dissolved. This is because when a wine is moving, more surface area of the liquid will come into contact with the oxygen and therefore will be available to react with it. It is interesting to look at how the various techniques of introducing oxygen into a fermenting must differ in the actual amount of O_2 delivered:
 - A closed circuit, pumping over in a tank = 0 mg/L oxygen.
 - Racking with aeration = 2 mg/L oxygen.
 - A pumping-over with an in-line venturi² = 2 to 2.5 mg/L oxygen.
 - Pumping the must (Red wine) so that it first falls into an open tray or bin, and then goes back into the fermenter (usually inundating the cap) = 1.5 mg/L oxygen.
 - Pumping the must (Red wine) into a tray or bin as noted above, but with a fan blowing on the exposed wine = 4 mg/L oxygen.
 - Using a Stainless diffusion stone with air = 4 mg/L oxygen.

¹The venturi effect is when a moving stream of liquid in a hose quickly passes over a small hole that has been voluntarily or involuntarily placed in the circuit, it will create a vacuum and the outside air will get pulled into and then mix with the stream of liquid. This can be voluntary, as when you use a specialized in-line fitting (actually called a "venturi") or slightly loosen a clamp on a connection to create a small gap. Or, it can be involuntary, as when something is worn down or bent and connections don't seal completely.

So, with the exception of the first example we can see how the rest of the above techniques do deliver some amount of O_2 to the must, but there is quite a variance. It is up to the winemaker, then, to decide which techniques may be viable options to integrate into the winery's fermentation schedule. Equipment costs need to be considered, but time and logistics should be taken into account as well. For example, you may like the convenience of an in-line venturi. But if, as can happen, you actually require more than 2 to 2.5 ml/L of oxygen at a given pump/punch down period, your only option is to run the pump for an extended period of time. The end result being that now you will have physically worked the wine for longer than was needed for that operation, and if you are sharing pumps between tanks this delay also dominos over into the rest of that days' processing. Depending on how many separate fermentation vessels you will be managing at a single time, along with the amount of staff and equipment available, this may or may not be a big problem, but it is worth consideration none the less. Therefore, in addition to a venturi, perhaps you might also want to have a diffusion stone or a tray with a fan around just in case more oxygen is needed at a given moment. In short, it's best to make choices that will keep as many options as open as possible, because you never know what may come up.

Determining Dosage Rates: How Much Oxygen?

When deciding whether you want to add oxygen to a fermenting must, it is important to realize that the exact amount needed is based solely on an individual wine's phenolic content (ex: red pigment, tannins, etc.). Therefore, young, dense red wines will be able to take more oxygen than delicate ones will. Oxygen can also be quite useful in both rosé and white winemaking, as well, but the amounts required are much lower than for reds with the timing more critical and the wine potentially less forgiving. The following are some good places to start when considering oxygen additions to the must, but these should not be considered a final formula. In fact, the oxygenation schedule that worked last year for a particular lot of fruit may or may not be valid for this year's crush and will more than likely have to be adjusted for:

Red wine: 5/10 mg/L at: 1) the start of fermentation, 2) the day after, and 3) maybe in the following days if needed*. With each addition you are looking to see a strong decline in the sharp and stinky negative VSC's. The wine should be noticeably fresher in aroma and flavour when you finish each treatment.

White wine: 5 mg/L at: 1) the start of active fermentation. At this stage, the wine does not oxidize as the yeast will take up the oxygen before it can react with the must. The wine should become noticeably softer and rounder after the dosage.

* It is important to note that while the above dosage rates are safe, they are being prescribed at the early, more active stages of the fermentation. Direct additions of oxygen are usually not recommended after the must has reached 10° alcohol. This is because in the early stages of fermentation, yeast take up oxygen as a nutrient, and they do this quickly. However, after 10% alcohol, they no longer uptake nutrients (oxygen as well), so whole dose impacts on the wine matrix itself.

A Quick Note on Oxygen and SO₂ Reactions

Finally, with regards to oxygen and SO_2 interaction: It is important to note that the dissolution of oxygen into a must is not affected by the presence of SO_2 . The SO_2 only inhibits the enzymes which cause browning (polyphenoloxidases), but it does not directly interact with the oxygen itself. In other words, the level of free SO_2 in a wine or must does not keep a wine from taking up oxygen in the first place, it only helps to deal with the potentially negative secondary effects (ex: browning, and microbial contamination.) SO_2 does, however, directly bind with acetaldehyde which is formed when alcohol is oxidized, which will result in a lowering of your free SO_2 .

References and further information

The information presented in this paper is intended to be an introduction to the many aspects of using oxygen during the fermentation. The goal was to create an initial, albeit well rounded stepping-stone, from which you can decide if you want to go further down this path or not. While a good deal of information regarding micro-oxygenation exists, information about macro-oxygenation in the ferment is often not easy to come by. Besides the various seminars and on-going conversations I have had about the subject over the past few years with Patrick Ducournau and Thierry Lemaire of Oenodev (www.oenodev.com), Dominique Delteil and Daniel Granes of the ICV (http://www.icv.fr/), and Jeff McCord of Stavin (www.stavin.com), some useful information can be found in the following texts:

- Boulton, Roger, V. L. Singleton, L. F. Bisson, R. E. Kunkee.
 Principles and Practices of Winemaking. New York: Chapman & Hall, 1996.
- Riberau-Gayon, Pascal, D. Dubourdieu, B. Doneche, A. Lonvaud. Handbook of Enology, volumes 1 & 2. John Wiley & Sons, February 2003.
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