Oxidative or Reductive? The Role of Oxygen in the Evolution of Red Wine

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and

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SWE Annual Conference 2018

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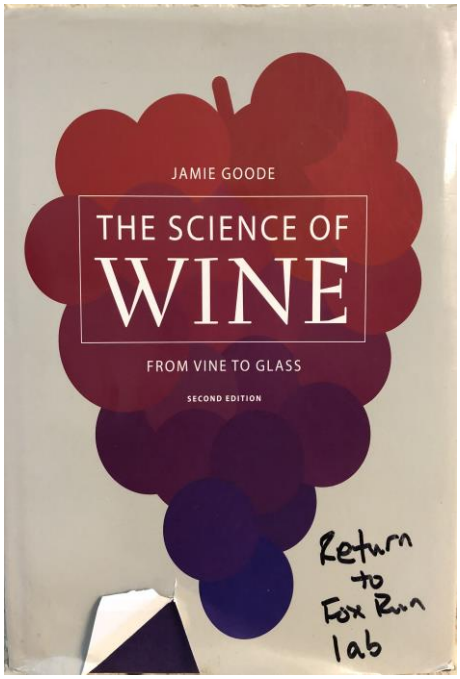


A whole chapter

10 Oxygen management and wine quality

Oxygen and wine is a big topic, and covers a great deal more ground than simply the topic of oxidation. Many years ago, no less an authority than Louis Pasteur described it as the "enemy of wine," but a more modern understanding of wine chemistry has shown that this is far from the truth. Yes, there are times when exposure to oxygen can be a bad thing, but there are other times when wine quality can suffer because of a lack of exposure to oxygen. A more correct view would be that oxygen is an important tool to shape wine style. Further, a good understanding of when, and how much, oxygen should be allowed contact with the developing wine is vital to the winemaking process.

We'll begin, though, by dealing with oxygen's negative effects. Of all wine faults, oxidation is the easiest for students of wine to experience. It's hard to touch someone about wine "faults," such as reduction, Brettanomyces, or even cork taint, unless you have examples on hand, and that's not always easy. If you want to experience oxidation, simply pour a glass from a bottle of wine, reseal the bottle, and a week later you'll have an oxidized wine. But as with the other faults—with the modest exception of cork taint—there's some gray area with oxidation. First of all, some wine styles involve deliberate exposure to oxygen to induce a degree of oxidation. The best example would be certain types of Sherry, Tawny Ports, and Madeira, where long aging in barrels that aren't fully filled to the top results in a kind of oxidation that is part of the wine style. Second, old wines are often greatly appreciated, and part of long aging in bottle involves a degree of oxidation. It's not always obvious, because one tasting's old claret aged to perfection may be considered over the hill and oxidized by another. In fact, it may be simplistic to think of oxidation as simply a wine fault. Even where there is no evidence of oxidation, there may be a significant quality loss to the wine through inappropriate exposure to oxygen.

Wine is a complex liquid consisting of a multitude of different chemicals, many of which are created by yeasts during the fermentation process. As with any mixture of chemical entities, they will rearrange themselves into the most favorable energetic state. This is the principle of entropy. What this means, in simple terms, is that the various molecules will swap tiny charged particles called electrons, and the nature of this swapping is determined by the reactivity of different components and what is known as the redox state of the wine. In any chemical reaction between two partners, one entity gains electrons (i.e. is reduced), and the other loses them (is oxidized). These processes occur in tandem, and it follows that you don't always need to have oxygen present for oxidation to occur. The redox (reduction-oxidation) potential of a particular wine determines what sort of state of its component molecules is most energetically favorable. That is, the reactions that take place in wine will be affected by the redox potential. This potential will shift according to how much oxygen the wine is exposed to. It follows that it will be lowest in bottled wine and highest in barrels after replenishing and stirring. It will also be lower in wines sealed with closures with lower oxygen transmission (such as tin-lined screw caps) than it is in those with higher gas transmission (such as most synthetic corks). Exposure to air results in the redox potential rising because oxygen will become dissolved in the wine and this will fuel oxidation reactions.

So what sorts of reactions happen when wine is exposed to oxygen? This is where it gets a bit complicated. Oxygen, which is often assumed to be highly reactive, doesn't react directly with wine, but requires an oxidizing agent to become truly reactive. "If we take the aroma compounds that we have in the wine and we put them in contact with oxygen in water, most of them will just stay as they are," explains wine scientist Maurizio Ugliano, previously of the Australian Wine Research Institute, now working for synthetic closure company Nomacorc. This is a remarkable statement, but it chimes with experience. There's something distinctive about wine that renders it susceptible to oxidation, and it means that it rapidly loses its fruitiness in a way that, for example, fruit juice or soft drinks don't.

So how is it that oxygen becomes reactive? "What happens is that the oxygen interacts with a lot of things that have nothing to do with the aroma fraction, particularly phenolics, and through that first interaction you will generate species that will then drive a lot of chemical reactions in wine," explains Ugliano. "You have a first interaction between oxygen and phenolics, and the outcome of this reaction will be the reactive species that will then be able to affect aroma precursors and aroma compounds, and push the wine toward oxidation."

Professor Roger Boulton of the University of California Davis adds to this: "As a wine is exposed to oxygen, the key initial reaction is the oxidation of monomeric phenols with a special reactive group to form hydrogen peroxide," he explains. Hydrogen peroxide is very reactive, and then goes on to interact with other wine components. "The peroxide can be consumed by a number of other reactions, either being quenched by tannins and other phenols (dominant in red wines, which less in whites) or forming acetaldehyde by reaction with ethanol," says Boulton.

Acetaldehyde is an important molecule in the oxidation of wine. Also known as ethanal, it's the oxidation product of alcohol, and has an aroma described to be like freshcut apples, and it tastes nutty and appleish. Sherry and Madeira, made in a deliberately oxidized style, have high levels of acetaldehyde, which gives wine a flat tartness in the mouth. Indeed, one description of oxidized whites is "sherried."

Transitionmetal ions are also a vital part of the process. "You need metal ions to start the reaction between phenolics and oxygen," says Ugliano. "In the absence of metal ions, such as iron or copper, this would not happen. What we have observed when we have tried to see whether the concentration of metals was one of the drivers for oxidation, was that the concentrations of metals that we seem to have today in the wine industry are not making any difference. If we add metals to different levels, staying in the range that is reported from studies, we don't observe a difference in oxidation." So it seems that the metal ions are necessary but they are not the limiting factor in oxidation in the concentrations seen in modern wines. Without them, there wouldn't be oxidation. But we can't eliminate them from wine to the level required to stop oxidation.

Phenolic compounds are necessary to generate reactive oxygen species that then go and do the damage, in both red and white wines. "There have been a lot of studies done recently in France, and we did one in Chile looking at catechin and epicatechin, the so-called flavonols," says Ugliano. "They interact with oxidation through this mechanism that involves iron and copper, and they form quinones. Quinones are very powerful reactive agents. For example, they can react with amino acids and form aldehydes. Today, a lot of what we observe as oxidation, especially in white wines, is not the consequence of aldehydes, but the loss of the fruity aromas that are due to thiols. In Sauvignon Blanc, oxygen plays a big role in the natural decay of the passionfruit aromas. We think that a lot of the oxidation concerns that exist in the wine industry today should be more directed to managing this loss of fruitiness, rather than simply

Above A red-wine barrel cellar at Thelema Stellenbosch, South Africa. Despite their inconvenience and cost, barrels are still used worldwide because of the way that they allow just a little bit of oxygen exposure during winemaking, in addition to their flavor impact.

"So what sorts of reactions happen when wine is exposed to oxygen?This is where it gets a bit complicated."

Dr Gavin Sacks, Cornell University

Gavin : Things ARE a bit complicated. There are just a few things that no one disputes…

1. Oxygen facilitates fermentation

It prevents stuck fermentations…

(especially in high sugar musts)

…by increasing kinetics
and
ethanol tolerance

Gavin, cont'd

2. Oxygen suppresses production of acetate esters by decreasing the activity of enzymes that produce them

Key esters give "red fruits" aromas to wine

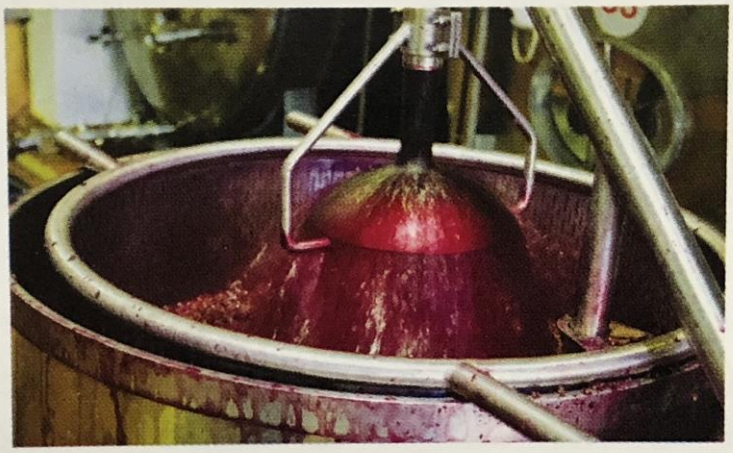
Beaujolais: lots of acetate esters

Gavin, cont'd

3. The macro-oxygenation effect does *something,* but…

during fermentation, yeasts

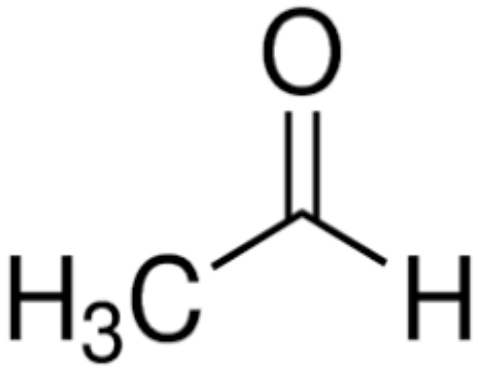
consume oxygen **instantly**



Above Splash-racking a fermenting red wine, in order to introduce oxygen.

Acetaldehyde
(key molecule in this discussion):
during fermentation there's always
as much of it as there is ethanol

Here it is



But…

How long does it stick around to react with phenolics before it's reduced to ethanol?

Gavin:
"I'm suspicious of oxygen increasing the lifetime of acetaldehyde during fermentation."

But…

At the **end** of fermentation, oxygenation **will** make a difference in terms of building acetaldehyde.

And that's when you have more polymeric pigments and tannins, especially if you employ things like extended maceration.

Building Polyphenol Content in Reds

1. Cold soak

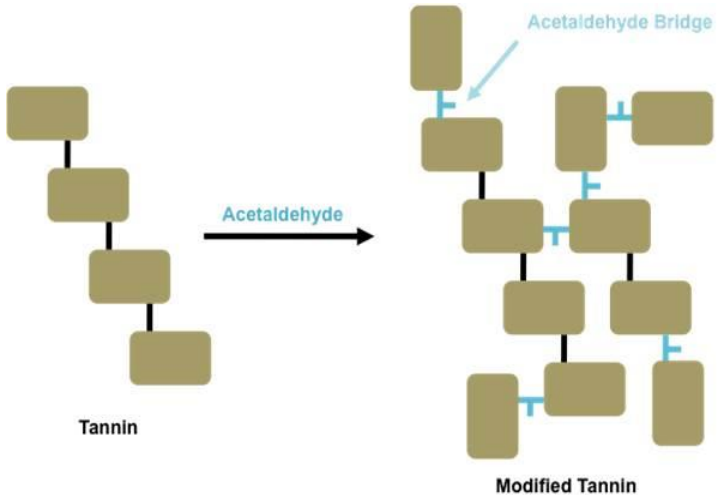
2. Bleeding (saignée)

3. Extended maceration

along with…

Fermentation temperature
+
Enzymes

The Role of Acetaldehyde in Polymerization of Phenolic Groups



What about limiting oxygen after completion of fermentation?

1. Less acetaldehyde generation

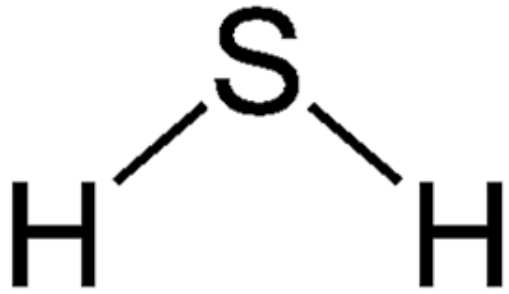
(oxygen oxidizes ethanol)

2. Retention of volatile sulfur

compounds that would otherwise

be oxidized or lost by entrainment

Hydrogen sulfide



“Reductive” winemaking

…is very loosely defined

At its most basic, it's the (near) exclusion of oxygen during winemaking

What is the role of H_2S in the evolution of 'reductive' red wines?

Is it a 'marker' chemical, or does it actually participate in desirable reactions?

But first – what does a reductive red wine smell like?

Glass #7

~~Rotten Eggs~~

Toasty / Roasty / Meaty

"I love young wines that start out very reductive like this, because by the time they've gone through élevage and bottling, then you've got this lovely 'ghost' of reduction. So you don't say, 'This is reduced.' But it's got this lovely framing to the wine that comes from having these volatile soft compounds in there at some stage, and then they've developed into something different."

H_2S is generated during fermentation,

generally when yeasts are stressed

Stress:

Nutrient deficiency
and/or
hot, fast fermentation

Even at sub-threshold levels, H_2S

reacts with other compounds

…and it will react with some oak

extractives*, even at ppb (H_2S)

and ppt (oak) levels,

to make new compounds

*lactones, phenols, aldehydes

Reduction is usually a temporary state

but it can persist in bottled wine for several years

Current thinking: treating with

copper is a BAD idea

Let's taste.

Wine	pH	TA	Alc %
Fox Run Cab franc ‘15	3.71	6	12.7
240 Days Cab franc ‘15	3.65	5.5	12
Fox Run Cab franc ‘16	3.76	6.2	12.5
240 Days Cab franc ‘16	3.8	6.3	13
Fox Rub Cab franc barrel sample ‘17	3.63	7.4	12.1
240 Days Cab franc barrel sample ‘17	3.6	7.1	12.7
Fox Run Lemberger tank sample ‘17	3.45	7.7	12.3