

THEORY AND APPLICATIONS OF MICRO-OXYGENATION

Section 3.

Why Micro-Oxygenation?

With all of the caveats suggested earlier, why would one want to use microoxygenation? The answer lies with the consumer and the bottom line. From a bottom line-standpoint, the acceleration of the aging cycle means that red wines can be programmed to achieve a 12-month cycle for release.

Thus, for many wineries, the grapes and wine do not have to be capitalized and carried from one financial period to the next, but can be expensed during the year and entered into inventory for sale. The interest saved by changing the release date of a wine, from 16 to 18 months, to one ready for sale in 12 months, might in some cases pay for the equipment, if that were the only saving that occurs.

There is another important reason for using micro-oxygenation, and that is customer acceptance of the finished product. It is well-known that the average time from the purchase of a bottle of wine to its consumption is about 48 hours; releasing ready-to-drink wines that are closer to their expected maximum development will mean that customer acceptance will be improved, which should translate into increased business for the winery in the months and years ahead.

1

Is Micro-Oxygenation for You?

Micro-oxygenation can be an important addition to a winemaker's tool box, but it must be used with discretion, and it will take a learning curve to determine how it will work in a given winery. There are several ways in which you can find out if micro-oxygenation should be in your future.

The easiest way is to arrange for a trial through one of the companies that sells micro-oxygenation equipment. The basic outline of the experiment is as follows, but the details would need to be developed in concert with your chosen supplier.

Pick a wine that will most likely give you the biggest income or quality boost, take one barrel of that wine and follow it through a cycle that ideally would begin postfermentation and pre-malolactic, and then treat it with low to medium levels of oxygen for each of the time frames. Take dual samples every week, and top off the barrel with wine to replace those samples.

Run the experiment through to the bitter end where the wine seems as if it is totally over the hill (it is important to work out the actual steps with your supplier). Take those samples, set them aside for several months, and then open them all at once and evaluate them against your control. You should see the influence of the oxygen on the wine and you should be able to make a judgment from that experiment.

Reductive Strength

Longevity, or the ability to age, is an important quality attribute. The reductive strength of a wine is a measure of the uptake of oxygen. This is influenced by the phenolic composition and lees, among other things.

2

Some phenols, including tannins, have the ability to react with oxygen, bind with another phenol, and recreate the original structure – thus allowing it to react over and over again.

Remarkably, the reaction of a young wine with oxygen can make that wine more resistant to later oxidation. This means young wines can consume oxygen and this actually increases reductive strength. This is a major reason why micro-oxygenation has become an important winemaking tool.

The key to micro-oxygenation is the diphenol (phenol ring with two -OH groups). This magical compound has the unique ability to adsorb oxygen and react with another compound to reform itself in a sort of daisy-chain arrangement.

Randall Grahm, of Bonny Doon Vineyards, considers reductive strength to be analogous to a wine's *chi* or, as the Chinese would say, *life force*. When a wine is young, it can share its *chi* with the world; when old, it must guard it so the wine does not diminish too quickly. Young wines have a capacity to adsorb oxygen, and that can actually increase their resistance to later oxidation. Irrespective of *chi*, we believe that reductive strength is related to the phenolic composition of a wine and, therefore, to longevity.

Fruit maturity has an impact on reductive strength. As suggested by Smith (2010), the problems with under-ripe fruit include the following:

- insufficient pigments
- limited extraction
- limited desirable flavors, which limits tannin capacity

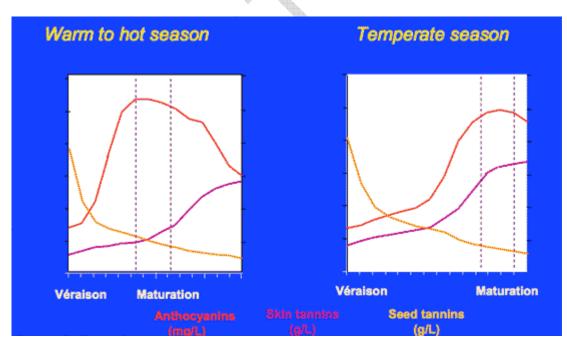
The problems with over-ripe fruit include the following:

- loss of color
- high alcohol capacity, which can destabilize color
- significant loss of reductive strength in the resultant wine

The change in the phenolic content, as a function of excessive fruit maturity, can lower the reductive strength by a factor of 10 (Smith, 2011).

Variation can occur between the skin tannins and anthocyanin concentration among seasons (Figure 7). While seed tannins (yellow line) are less affected, note the large potential difference in the ratio of tannins to anthocyanins (anthocyanins are shown in red in mg/L relative concentration, skin tannins are in purple in g/L relative concentration).

Figure 7. Effect of Climate on Relative Phenolic Concentration (source: Lallemande)



Grapes producing the most intense, balanced wines with the greatest longevity usually have a high anthocyanin-to-tannin ratio. Indeed, wine quality may be dependent, in part, on this ratio.

Tannins and Wine Quality

Kassas and Kennedy (2011) noted some interesting positive correlations in red wines. In their study, wines commanding the highest price in the marketplace had several attributes:

- highest concentrations of total tannins
- highest concentration of skin tannins
- degree of phenolic polymerization

The term *tannin* defines a very heterogeneous group of phenolic compounds that are identified, based on certain properties:

- astringency
- bitterness
- reaction with ferric chloride
- ability to bind with proteins, e.g., tannin leather hence, the term tannins

It was their characteristic interaction with proteins that traditionally differentiated tannins from other phenols. However, not all phenols that bind with proteins elicit an astringent response, and tannins are not the only compounds in wines that cause astringency.

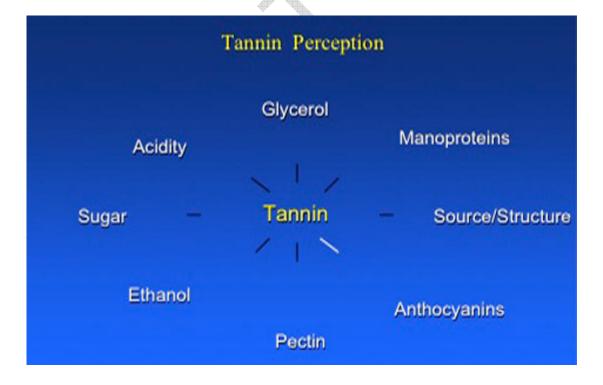
Some phenols, including tannins, have the ability to polymerize, or associate, with themselves and other compounds, including anthocyanin pigments. As

polymerization occurs, the molecule becomes larger. The number of subunits bound together is referred to as the DP number, or degree of polymerization. Socalled tannin "quality" relates to the following:

- degree of polymerization
- association of tannins with other molecules
- stereospecific nature of the molecule, which can make it harsh and hard, or supple

Grape tannins derived from the skin, seeds, and stems differ in their sensory properties, their DP number, and their overall subunit concentration. Tannin perception is a function of the factors shown in Figure 8.



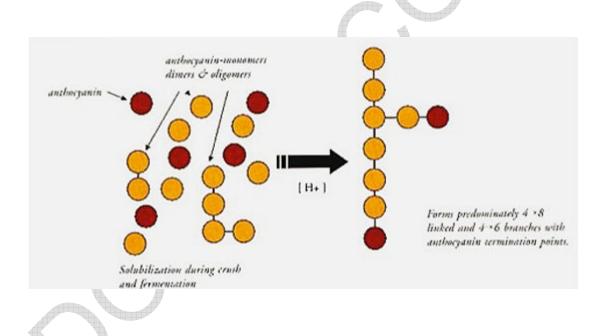


Pigment-Tannin Polymerization

In grapes and wines, anthocyanin pigments can be either free monomers, that is, unbound, or associated with other phenols to form polymers.

Anthocyanin-tannin polymerization occurs both, in the fruit during maturation, and in wines. Polymerization continues until an anthocyanin molecule binds the terminal end of the tannin chain, thus stopping the polymerization (see Figure 9).

Figure 9. Proposed condensation reactions under non-oxidative conditions (source: McCord, 1990)



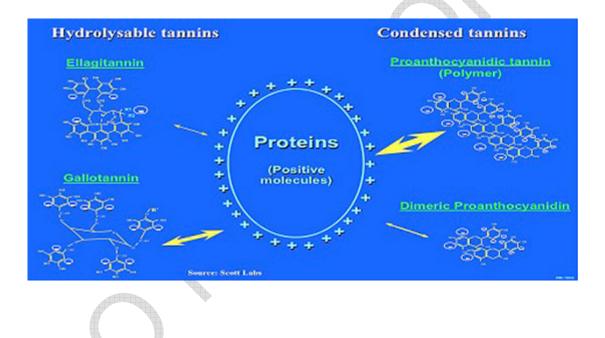
As such, the ratio of anthocyanins to tannins is important in impacting the extent of polymerization. This is highly crucial, because the degree of polymerization affects astringency.

Large tannin polymers provide a relatively large number of binding sites to interact with proteins, including salivary proteins (Figure 10). Wines with an

abundance of large polymers tend to lack softness, may lack color stability, and often possess a dry mouth sensation.

Smaller polymers, on the other hand, have fewer protein binding sites. As such, they produce less astringency, and provide a greater degree of soft tannins and more palate depth. Additionally, these smaller pigment polymers provide a greater reductive strength.

Figure 10. Reactivity of Tannins (source: Scott Labs)



The more anthocyanins, the shorter the resulting polymers and the finer the tannins. Smaller polymers lead to smaller colloids which have a softer mouthfeel.

Binding with phenols not only can involve other phenols like anthocyanins but also hydrogen sulfide, mercaptans and sulfur containing amino acids.

Factors Impacting Red Wine Color

Color is an important wine attribute, because humans are visually oriented. As such, wine color can certainly bias evaluations. A classic example of color bias is to change the color of a white wine, such as Chardonnay, with red food coloring. In blind evaluations, the color-adjusted wine frequently receives a different sensory rating for attributes such as fullness, body, and complexity.

As such, richly-colored wines are assumed to have high volume or body, and softer tannins. Conversely, a wine with less color is automatically assumed to have "green" or "harsh" tannins.

Spectral color in wine is a function of these three elements:

- anthocyanin concentration
- polymeric pigments
- concentration of cofactors, or certain non-colored compounds, which bind with anthocyanins

Hyperchromicity, also known as *copigmentation*, is an interesting phenomenon that allows more visible red color than would be expected from the anthocyanin concentration alone. Cofactors are non-colored compounds that have the ability to bind with anthocyanins, creating more color than the unbound pigment, hence the term *hyperchromicity*.

The concentration and type of cofactors vary greatly from variety to variety, season to season, but include some non-flavonoid phenols, flavonols, and the amino acid arginine. It is not likely that enological tannins contain compounds that act as cofactors.

Because red color is a function of three elements (anthocyanin concentration, cofactor concentration, and polymeric pigments), it is possible to have the following (Boulton, 2005).

- Change in grape anthocyanin concentration = Change in wine color.
- Change in grape anthocyanin \neq Change in wine color.
- No change in grape anthocyanin = Change in wine color.

The above highlights several points:

- Variation in cofactors and polymeric pigment concentration may be more important to spectral color than simple anthocyanin concentration.
- Grape pricing based on anthocyanin concentration alone may not be desirable.
- Harvesting based on anthocyanin concentration will not necessarily assure desirable red wine color.

Young wines have a high concentration of unbound pigments. Once they are incorporated into polymers with tannins, they are stabilized. Early stabilization via oxygen exposure is a significant benefit to color, texture, and aromatic properties. Because much of the phenolic polymerization is oxidative, anything that depletes the oxygen content early may be detrimental. As discussed by Smith (2010), lees contact can lower the oxygen content and, therefore, may reduce the incorporation of anthocyanins into stable pigment polymers.

Practical Summary of Winemaking Issues

- It has been determined that a molar ratio of 4:1 total phenols to anthocyanins is ideal for good structure. This means the ideal polymer has about six units, with anthocyanins on each end.
- Intentional encouragement of oxidative polymerization in young red wine is a main role of micro-oxygenation.
- This requires equipment which produces extremely small bubbles of oxygen that readily dissolve before reaching the wine's surface. This activity is not the same as splash racking.
- Oxygenation the early stage of winemaking does not shorten the life of a wine. Instead, it increases the anti-oxidative power by stimulating phenolic reactivity.



With micro-oxygenation, there are commonly four mistakes that are made:

- 1. too much oxygen
- 2. too much time
- 3. too late in the life of wine
- 4. too much microbial contamination

List and discuss the result(s) of each of the above. What, if any, corrective action can be undertaken?