

Wine and Juice Oxidation

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Introduction

The oxidative flaws of grape juices and wines are characterized by an increase in brown color and the development of the typical oxidative aromas of acetaldehyde, acetic acid, and ethyl acetate. Loss of pigmentation and tannins through precipitation can also occur. Oxidation is defined as the loss of electrons and relates to the status of the valence (outer shell) electrons; this definition has less utility for the average winemaker than the noticeable byproducts. Recent research in wine oxidation is demonstrating the importance of interrelated oxidative reactions and metallic cofactors in wine chemistry. Awareness of the chemistry and microbiology of these oxidative processes allow the winemaker to understand, prevent, control, or harness these reactions.

There are three main mechanisms of juice and wine oxidation: enzymic, chemical, and microbiological.

Enzymic Oxidation

Enzymic oxidation from grape (tyrosinase) or mold (laccase) enzymes present in the grape juice causes browning and, in extreme cases, aldehyde production. These reactions require the presence of the enzymes, the required substrates (phenolic compounds), oxygen, and metallic cofactors. Like most enzymes, they are more active at warmer temperatures. They are also more active at higher pHs, and although the grape tyrosinases are denatured by ethanol the mold laccases have continued activity in wine. These enzymic processes can be discouraged by judicious use of harvesting, crushing, and pressing parameters to minimize enzyme reaction rates and exposure to oxygen. Other control measures rely mainly on removal of the enzyme (via fining, usually with bentonite), reducing exposure to oxygen, and judicious use of SO₂.

Some winemakers use juice “hyperoxidation” as a production method to reduce the phenolic and color compounds of their product. Typically this relies on several saturations of the must or juice with oxygen and can be monitored with oxygen probes. This is particularly useful in some heavier press fractions or in sparkling wine bases; it has been used for reducing some varietal aromas and may be a factor in reducing “pinking” of white wine later but is also known to reduce some desirable aromas and could encourage microbial growth.

Concentration of grape tyrosinases will be dependant on maturity and grape varietal. Farming practices can affect the types and amounts of molds in the vineyard and is the first step in preventing oxidation from laccase. If laccase is already present (and can be tested for using a test kit and/or a botrytis “pregnancy test”) it can be controlled through similar treatments used for grape tyrosinase reduction: fining, temperature control, and pH control. Sulfur dioxide (SO₂) is less effective against laccase than grape tyrosinases.

Chemical Oxidation

Chemical (non-enzymic) oxidation is the process in which electrons are lost through stepwise reactions involving oxygen, phenols, and metal catalysts. Wine may be oxidized through simple exposure to air, which contains approximately 20% oxygen. Oxygen meters can be used to measure gross exposures

from wine transfers or bottling, but low rates of exposure are more difficult to measure as the oxygen may be below the level of the meters or be consumed at such a rate that the oxygen level does not rise. Recent research has demonstrated the vital importance of iron and copper as part of these reactions, but juices and wines all contain adequate minute concentration of these metals, and prevention of oxidation by removal of all metal is not a realistic approach. However, excess metals have been known to accelerate the reactions and thus copper, iron, brass, bronze, and other iron or copper containing metals are highly inadvisable as wine contact materials.

Phenolic compounds are required to start the reactions which result in the oxidation of other compounds which do not themselves react directly with oxygen. The numerous interactive steps (oxygen with phenols, production of peroxide, and reaction of peroxide with other susceptible compounds) occur at different rates and speeds depending on concentration of reactants, temperature, pH, etc and help explain the complexity of the oxidation and aging of wine. Alcohol is, second to water, the compound of highest concentration in wine and is thus the most likely compound to be affected. Classic symptoms of wine oxidation are the conversion of ethanol to acetaldehyde and phenols to brown pigments. Judicious use of SO₂ can be used as a substitute oxidative compound; ascorbic acid can also be used but depending on the circumstances can accelerate the oxidative cycle rather than stop it.

Microoxidation (MOX) is the term used to manage wine aging and development by slow and controlled use of oxygen additions to wines. Reactions are as yet difficult to predict and this process must be monitored closely to prevent the occurrence of oxidation spoilage rather than wine "development".

Microbial Oxidation

Microbial oxidation covers the whole range of oxidative spoilage aromas and is frequently seen in conjunction with both enzymic and chemical oxidation as the causes and situations are mutually conducive.

The most common yeast oxidation involve film yeasts (*Candida*) and wild yeast (*Pichia* and *Kloeckera*) that come from vineyard and winery sources, and under warm conditions ethyl acetate and/or aldehyde aromas can be produced within hours of harvesting. Some yeast strains are more tolerant to the cold and will also produce oxidative off odors at lower temperatures. SO₂ is effective against most early growth; normal fermentation and protection of the wine from air prevents most aerobic yeast growth from causing large scale films. During post fermentation aging, *Brettanomyces* can thrive under very low oxygen conditions, and the common ethyl phenol aromas are not addressed as oxidation in this summary, yet these yeast are also able to produce the classic oxidative spoilage aromas.

Bacterial spoilage through the action of *Acetobacter* and the related *Gluconobacter* species can produce large amounts of acetic acid, an oxidative byproduct of ethanol or a byproduct of sugar metabolism, during all stages of grape and wine production. *Acetobacter* can grow on damaged grapes, in juice and must, and can continue to thrive in wine throughout ageing. *Acetobacter* has even been implicated in post bottling spoilage of Australian wines which were sealed in such a fashion as to allow small amounts of oxidation in the headspace of a wine which contained adequate populations for spoilage. Because these bacteria are ubiquitous throughout the vineyard and winery, control of their growth and restriction of oxidative opportunity is the only method of management, as complete eradication of populations is not realistic.

Lactic acid bacteria are also capable of oxidation spoilage, depending on their status on homo or hetero fermentative organisms and on the available carbon sources (sugars or ethanol). They are also managed by controlling oxygen and maintaining adequate sanitation and SO₂.

Reducing opportunity for any microbial spoilage involves: managing the populations of microbes through reduction of inoculating sources (damaged fruit, unclean equipment, contaminated barrels, or unfiltered bulk wines); the control of existing microbial residents through cleanliness, pH and temperature management; reduction in oxygen ingress through barrel management/topping regimes, proper selection

of pumps/valves/fitting, proper tank materials; and maintenance of low oxygen headspaces in tanks and other containers. Judicious use of SO₂ is one of the winemaker's most valuable tools but cannot alone be a substitute for adequate sanitation and good enological practices (such as pH and temperature management). Judicious use involves a basic understanding of the relationship of pH to SO₂ chemistry.

Summary

Understanding the many and varied oxidative processes of wine and juice allows the savvy winemaker to carefully control the undesired processes with a minimum amount of effort and intervention. Prevention is critical in controlling wine and juice oxidative spoilage because it is expensive, unrealistic, or impossible to reverse.