THE OXYGENATION OF MUSTS AND WINES

In his Etudes sur le vin (1866), Pasteur notes that oxygen causes defects in wine (oxidative phenomena), but also acknowledges its ability to eliminate some unpleasant smells. He states "It is oxygen that makes wine; it is under its influence that wine ages; it is oxygen that changes the acid principles of new wine and makes bad tastes disappear; it is still oxygen that causes the common deposits in barrels and bottles."
Since then, many other scientists have studied the fundamental relationship between oxygen and wine, starting with Ribérau Gayon in the 1930s, followed by Amati in 1977, who determined the oxygen input in a white wine from preparation to bottling, taking into account the clarification and filtration stages, while in 1999, Vivas evaluated the input in the technological and elevage stages, and was followed by Ferrarini in 2011, Vidal in 2001, 2003, 2004, Valade in 2005, and others.

There have been many considerations in this regard, and the results obtained are often contradictory, but some basic steps can be summarized as follows:

- Wine is significantly enriched with oxygen, especially when it is kept moving.
- Oxygen solubility varies from wine to wine and will increase as the temperature increases.

However, its consumption, both chemical and microbiological, is the opposite, and the accumulation due to low temperatures represents a critical aspect of oxidative prevention.

- The amount of dissolved oxygen depends on the fineness of the emulsion; the more the gas bubbles are pulverized, the greater the dissolution rate.
- Some compounds, such as iron and copper, catalyze oxidation phenomena, while others, such as polyphenols, increase oxygen consumption capacity.
- At 20 °C (68 °F) and at atmospheric pressure, wines can incorporate 6ml/l or 8.4 mg/l dissolved oxygen. Concentration decreases exponentially with temperature and increases proportionally with pressure.

The basic steps and possibly the most appropriate times to perform targeted oxygen administration can be broadly summarized as follows:

- pre-fermentation stage (white musts)
- fermentation phase
- phase immediately following racking (red wines)
- beginning of aging (red wines)
- correction of any reduction states

The technique of contacting freshly pressed SO2-free must, exclusively from white grapes, with high amounts of oxygen, also known as hyperoxidation or hyperoxygenation, appealed to many oenologists, especially in the 1980s. The idea that violent oxidation of the must will reduce the risk of oxidation in the future wine seems contradictory, but it is not. In fact, it is a matter of making the oxygen react in advance with some oxidizable substances, which are then removed by transfer, clarification or filtration, thus making the wine less susceptible to future oxidative phenomena.

This technique is not suitable for all white musts, especially for aromatic grape varieties, and in particular Sauvignon, but it is used in several cellars and by renowned producers of classic method sparkling wines.

At the onset of alcoholic fermentation, all oxygen is used by the yeast to reactivate metabolic pathways and create the nutritional components for fermentation. Oxygen allows the yeast to synthesize sterols and long chain fatty acids (C16, C18), collectively and not coincidentally called "survival factors", which give the cell membrane greater fluidity and greater resistance to alcohol. In order to maintain efficient transport mechanisms within the cell, which are impaired by increasing alcohol concentration, membrane fluidity must remain constant. In the absence of oxygen, the cell membrane is weakened because the amounts of sterols and fatty acids available to it are insufficient. This leads to a gradual loss of function and inactivation of transport mechanisms: eventually the fermentation process stops or becomes sluggish, resulting in a lower quality final product.

However, it should not be forgotten that nitrogen is another important factor in yeast nutrition, and a nitrogen deficiency will also affect the quality of the future wine.

Sablayrolles (2000) estimated that the amount of oxygen required by yeast for the synthesis of membrane constituents ranges from 5 to 10 mg/l, depending on the lipid content of the must. As for the most appropriate time to make the addition, the same author has pointed out that it coincides approximately with the first quarter of the fermentation process. Adding too early would not be beneficial as the yeast still has survival factors available in its cells, while adding too late would find the yeast cells already partially compromised, negatively impacting the fermentation progress.

According to Salmon et al. (2000), once alcoholic fermentation is complete, yeast cells continue to consume oxygen if they remain in contact with the wine, even for more than three years. Hence the need to constantly monitor wines aging "sur lies" in order to avoid unpleasant moments of reduction and possibly act with precise, alternating oxygenations throughout the whole phase.

Malolactic fermentation, carried out by lactic acid bacteria, mainly Oenococcus oeni, is also influenced by the presence of oxygen. Practice shows that although these bacteria are microaerophilic microorganisms, i.e. capable of developing in the absence or presence of small amounts of oxygen, the addition of small doses of oxygen to the wine favors this process.

During the aging process, the oxygen that dissolves in the wine as a result of cellar operations, storage in wooden barrels, or targeted dosage is consumed by the noble lees and, in the case of red wines, especially by polyphenols.

Polyphenolic compounds are among the major constituents of wines and responsible for various organoleptic characteristics. They are very reactive compounds. Their reactions, which begin when the grape is crushed and continue throughout the fermentation and aging of the wine, produce a large variety of products that add to the great complexity of the polyphenolic composition of the grape. The newly formed compounds have specific organoleptic characteristics, often different from those of their precursors. Polyphenolic compounds are divided into two main groups, flavonoids and non-flavonoids.

Flavonoids include anthocyanins, composed of five anthocyanidins: cyanidin, malvidin, peonidin, petunidin and delphinidin, which are responsible for the color of red wines, and tannins, which are responsible for the organoleptic sensations of astringency and some important reactions with anthocyanins.

Non-flavonoids include benzoic and hydroxycinnamic acids, the latter being involved in oxidative browning phenomena, which are important in white musts.

Anthocyanins and tannins can combine in different ways to form polymers of varying degrees of polymerization. According to the literature, the presence of dissolved oxygen is critical to some of these reactions, namely:

- Anthocyanin-tannin bonding

This type of reaction, although slow, results in the formation of colored polymers.

- Condensation by ethanal bridge (acetaldehyde)

The acetaldehyde that is involved in this type of reaction is the acetaldehyde that results from the oxidation of ethyl alcohol. "In the absence of anthocyanins, this reaction evolves to form polymers of increasing molecular mass, which precipitate over time. Instead, when the two ends of the chain are occupied by anthocyanins, the process stops, allowing the color to stabilize." (Moutonet 1998). The ethanal bridge produces anthocyanin-tannin polymers that exhibit a pleasing purple hue.

In addition to the effects on color, the reactions of polyphenolic compounds can significantly modify the organoleptic qualities of wines, which are directly related to the structure of the tannins; in particular, the tannins become progressively less bitter and astringent, thus changing from hard to soft, when the degree of polymerization is high.

Reductive states, related to the presence of sulfur compounds, are dangerous moments in wine production, as they could significantly compromise quality. Their onset is easily noticeable by the presence of distinctly unpleasant odors reminiscent of rotten eggs, garlic, putrefaction, cooked cabbage, and burnt rubber.

They can have different origins depending on the time of their occurrence:

- During fermentation when, in nitrogen-poor must, the yeast suffers from nutrient deficiency.

In this case, the addition of nutrients and oxygen promotes the disappearance of hydrogen sulfide.

- During maturation on fine lees.

At this stage, the yeast cells go into autolysis, which promotes the release of their enzymes, called sulfite reductase, which causes the formation of reduced sulfur compounds. The addition of specific doses of oxygen, especially if done at the onset of the problem, can be a permanent solution.

- During normal aging of unclarified and unfiltered wines, by polyphenols and minimal amounts of residual lees.

Again, the addition of small doses of oxygen can prevent an off-program transfer.

The above is an indication of the importance of the role played by oxygen in the evolution of wines, especially red wines. However, in the presence of high concentrations of this gas, anthocyanins, tannins and other equally important molecules, such as aromatic compounds, can be affected by oxidative phenomena, with a significant reduction in wine quality.

It seems clear, therefore, that the amount of oxygen to be added to the wine should be rationally evaluated and duly measured. Micro-oxygenators are used for this purpose.

This equipment allows the continuous release of very small amounts of oxygen, in the order of ml/l/month, i.e. micro-oxygenation.

Macro-oxygenation instead occurs when using ml/l/day doses, or a single dose, injected in a single solution and in a short interval of time, similar to what happens when pumping-over in air or transfer.

Macro-oxygenation covers the fermentation phase and the phase immediately after racking, while micro-oxygenation is used in the aging phase and to correct any reduction states.

The micro-oxygenator must guarantee the reliability of the dosage. In other words, it must ensure that the wine to be treated receives exactly the amount of oxygen we have decided to add.

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This is achieved through automated balancing and controls, and by taking measures that minimize the risk of potential loss. It is also necessary for the equipment to be able to constantly and continuously release very small quantities of oxygen, duly atomized, i.e. reduced to microbubbles, through specially designed diffusers, so that the quantity of oxygen administered is completely absorbed by the wine itself. The entire system is controlled by a microprocessor, ensuring constant and continuous safety and precise repeatability of the set values.