MICRO-OXYGENATION – A REVIEW

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Introduction

Micro-oxygenation is the process of introducing minute, measured amounts of oxygen to wines with the aim of bringing about desirable changes in aroma and texture which cannot readily be obtained by traditional ageing techniques. The objectives of the process include improved palatability, enhanced colour stability and intensity, increased oxidative stability, decreased reductive character, and decreased vegetative aroma.

The technique and methodology of micro-oxygenation has been developed by Patrick Ducournau and Thierry Lemaire of the French company Oenodev. The process of micro-oxygenation is now used in the development of a range of wines, predominantly red wines, from premier cru - ultra premium wines through to vin de table-fighting varietals (pers. comm., Lemaire 2000).

Background

An understanding of the role oxygen plays in the maturation of wine is fundamental to understanding the process of micro-oxygenation. The role of oxygen and more specifically its interactions during the maturation process will now be discussed.

The role of oxygen

It has long been recognised that oxygen plays an important role in the numerous microbiological and biochemical events that take place during the life of a wine. These events not only facilitate the winemaking process but also ultimately affect the organoleptic characteristics of the finished wine.

The principles that govern the dissolution of gases in liquid also apply to the dissolution of oxygen from the air into wine. Therefore during wine conservation quantities of oxygen are constantly dissolved in wine as a result of contact with air (Lemaire 1995). This either occurs accidentally due to exposure of wine to air during processes such as filtering, or intentionally during processes such as splash racking.

The role of oxygen in the evolution of wines, especially red wines, has been studied for a long time by comparing the behaviour of new wine in tank and barrel (Riberéau-Gayon and Glories 1986). In tank, processes such as racking at a few irregular intervals during the maturation process result in the exposure of wine to large volumes of air for short periods. Alternatively wines stored in barrel are constantly exposed to small amounts of air which enters through the bunghole, during topping and arguably through the barrel staves. Sensory assessment of the same wine stored in tank and barrel, disregarding the obvious oak aromas and flavours, typically concludes that the wine matured in barrel is superior in terms of structure and flavour. Although the availability of oxygen by either means of storage is uncertain and variable it is considered to be a major factor in the preference of winemakers for oak ageing wines. Interestingly, analysis of wines stored in both environments has found that the dissolved oxygen levels are relatively comparable, typically 20 ppb (Lemaire 1995).

The comparable dissolved oxygen levels found in these experiments has two important ramifications:

1. It suggests that wine consumes practically all of the oxygen it absorbs.
2. It provides an indication of the level of dissolved oxygen found in wine under typical conditions.

These two points are fundamental to the principles behind Micro-oxygenation (Lemaire, 1995).

The role of phenolics

Phenolics are the principal substrates of juice and wine oxidation. It is the reactivity and diversity of phenolic compounds that results in their intervention in numerous biochemical reactions where they play the role of substrate, oxidant, catalyst and inhibitor. These substrates and the reaction products are major wine constituents that are largely responsible for the variations in wine types and styles (Allen 1998, Zoecklein *et al*. 1995).

Phenolics and organoleptic characteristics

Phenolic compounds elicit many of the organoleptic characteristics of red wines. Anthocyanins are responsible for red wine color, and their interactions with other grape skin-derived flavanoids largely determines the color changes observed in maturing wines. Polymerized phenolics or tannins are largely responsible for the sensory characteristics of astringency and bitterness both fundamental to wine mouthfeel (Walsh, 1998).

Astringency is predominantly a tactile sensation, and is believed to be the result of interaction between salivary proteins and polymers of diverse phenolic compounds, probably including anthocyanins. The sensory perception of phenolic compounds in wine is of great interest and continued speculation. It is unknown whether the various mouth-feel sensations generally termed as astringency are the result of phenolic diversity or of perceptual modification of phenol-derived astringency by other wine components, not to mention the quantity and properties of salivary proteins stimulated by the wine to enter the mouth (Gawel 1998).

Phenolic interactions

Following the extraction phases of fermentation, skin maceration and pressing, most grape phenolics are gradually modified. However, the total amount of phenols in wine remains constant for much of the wine's life, indicating that they are in fact converted to other species (Cheynier *et al*. 1998). Two main reactions are suggested to be responsible for this phenomenon:

The first reaction occurs in the absence of oxygen, and involves tannin-anthocyanin copolymerisation and tannin condensation. This mechanism is slow at temperatures below 20ºC and has been reported as influential on the development of red wines low in phenolics with high pH. However this reaction is not considered the main mechanism of phenolic modification in the normal evolution of Bordeaux style wines (Ribéreau-Gayon and Glories 1986).

The second reaction occurs via two main mechanisms, namely

1. Oxidative coupling (favoured at high pH)
2. Reactions involving anthocyanins and / or flavanols.

Oxidative coupling involves the oxidation of ortho-diphenols into a highly reactive 1,2-quinone species. As outlined in Figure 1 the by-product of this reaction is hydrogen peroxide. Hydrogen peroxide in turn oxidises trace amounts of ethanol to acetaldehyde.

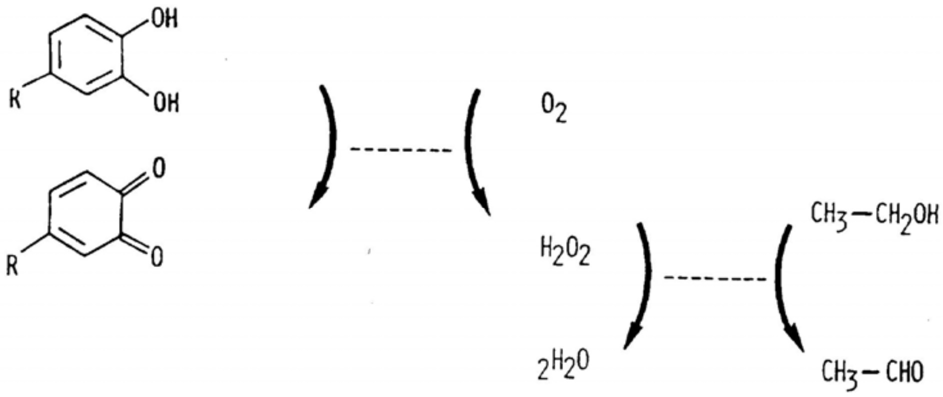

Figure 1. Oxidative coupling reaction (Source: Ribéreau-Gayon and Glories 1986 page 254)

The acetaldehyde produced from oxidative coupling is then involved in the condensation of anthocyanins and tannins via the Baeyer reaction, which utilizes the carbo-cationic form of aldehyde and thus proceeds more rapidly at low pH prior to malo-lactic). Polymerisation continues following the same mechanism as outlined in Figure 2 (Ribéreau-Gayon and Glories 1986). The reaction stops when both chain ends are occupied by anthocyanin moieties (Allen 1998).

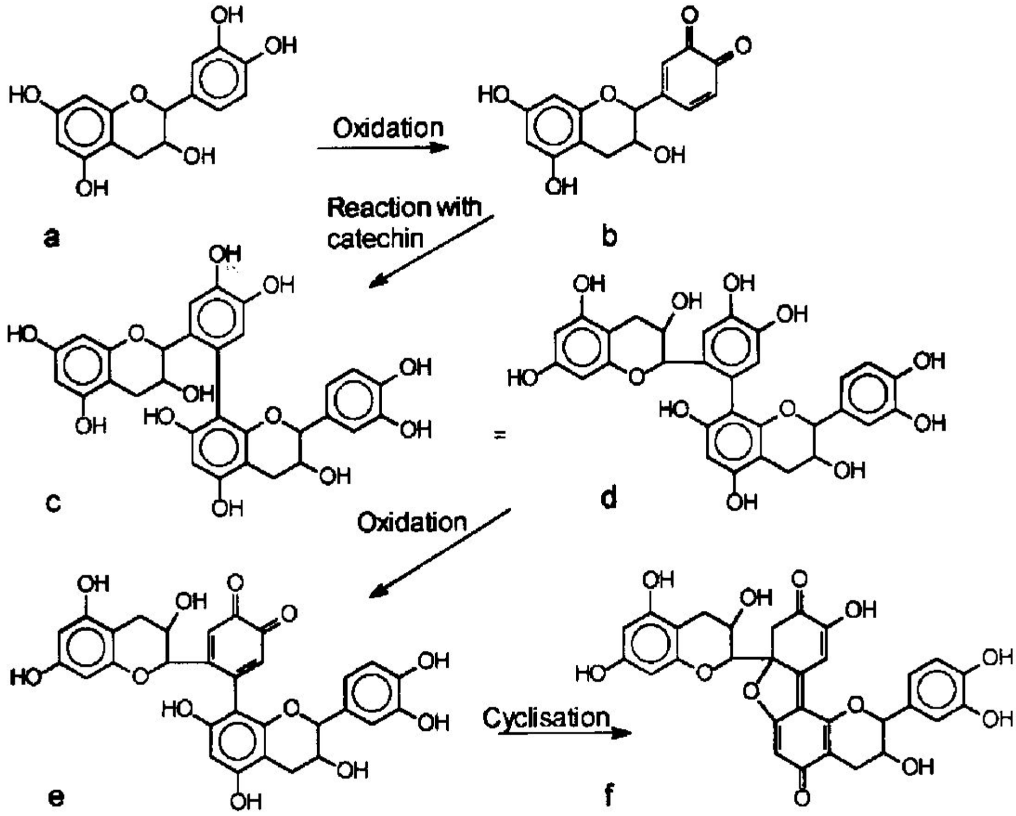

Figure 2. An example of oxidation of catechin (a) with further reaction of the 1,2-quinone product (b) by reaction with catechin to give a dimer (c) redrawn slightly as (d), which upon further oxidation gives a new 1,2-quinone (e) which can undergo cyclisation to structure (f) (Source: Allen 1998 page. 6).

It would appear from the kinetics of the various redox reactions in wine that phenolic compounds are preferentially oxidised. In a situation where the dissolved oxygen levels are surplus to the requirements of these reactions, the oxidation of a wide range of substrates occurs. Many of these oxidative reactions are irreversible and are reported to detrimentally affect the development and/or existence of many phenolic and aromatic compounds (Lemaire 1995).

Excessive amounts of oxygen during the late stages of maturation may also result in tannin polymerisation and condensation with anthocyanins causing precipitation (Ribéreau-Gayon and Glories 1986).

It should also be mentioned at this point that excess oxygen may lead to the risk of adverse microbial activity. The technique of Micro-oxygenation is designed to dose wine with oxygen at levels that do not encourage microbial activity.

The process of Micro-oxygenation aims to manipulate the rate and result of these oxygen requiring reactions in order to bring about desirable changes in wine texture and aroma.

Micro-oxygenation

The process of Micro-oxygenation begins with an assessment of the wine and a review of the winemaker's objectives. From this information a micro-oxygenation program can be developed. The technique of micro-oxygenation can be started at any stage during the winemaking process but is typically and most effectively begun at the end of alcoholic fermentation and prior to malolactic fermentation.

The treatment proceeds with changes to many of the organoleptic qualities of the wine. These changes in the wine can be separated into two distinct phases as illustrated in Figure 3:

1. Structuring Phase
2. Harmonization Phase

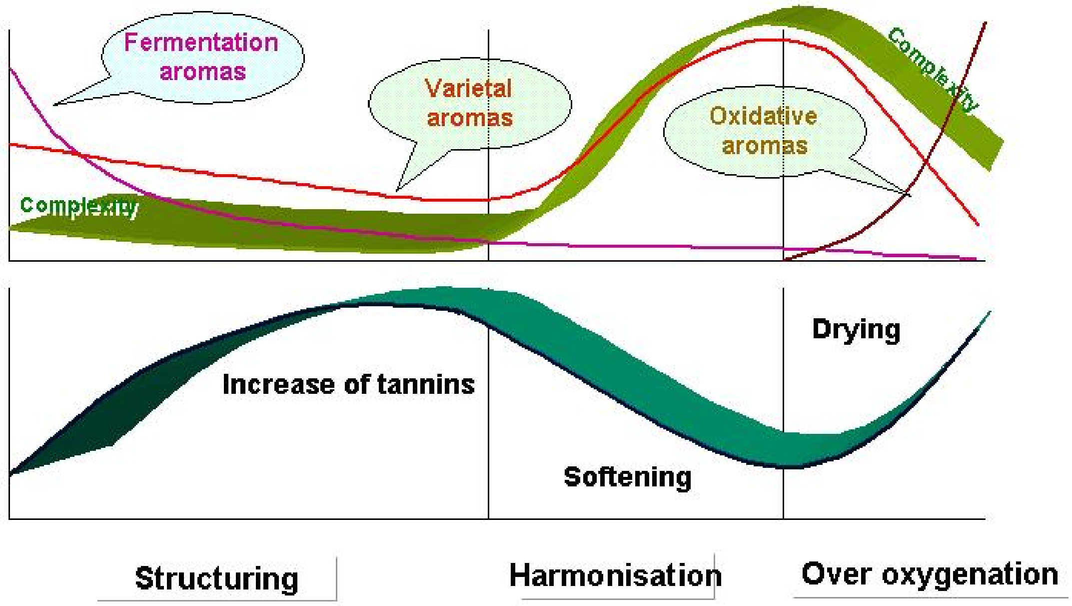

Figure 3. The organoleptic phases observed in wine during the process of Micro-oxygenation (Adapted from Lemaire 1995 page 112)

Structuring phase

The first phase of Micro-oxygenation is characterised by an increase in the aggressiveness and intensity of tannins on the palate. At the same time a corresponding decline in the aromatic intensity and complexity of the wine is observed. The end of this phase is determined by the inversion of these organoleptic tendencies.

The length of the structuring phase typically lasts between one and six months and is dependent on a number of parameters, namely:

1. The initial phenolic content of the wine
2. The timing of Micro-oxygenation
3. The quantity of oxygen added
4. The temperature
5. The level of sulphur dioxide
6. The extent of aeration

(Lemaire 1995).

Harmonization phase

The harmonisation phase is characterized by an increase in tannin softness and general wine complexity and length (see Figure 3). The optimum end point of the micro-oxygenation process is reached when the wine exhibits the maximum complexity and tannin softness and suppleness possible. Determination of this end point is difficult due to the reliance on sensory assessment of the wines detecting these subtle changes in wine characteristics. The winemaker's post-treatment intentions must be taken into account, and in some instances where considerable barrel ageing is planned, an earlier endpoint may be chosen to conserve more of the wine's reductive vigor than if near to bottling.

Over-oxygenation results in the perception of tannin dryness accompanied by the irreversible loss of wine freshness and oxidized aromatic expression. The same phenomenon is observed if the levels of oxygen addition is too large during the harmonisation phase (Lemaire 1995, pers. comm. Smith 2000).

During the harmonization phase the disappearance of vegetal and reductive characters in the wine may also be observed (Lemaire 1995).

Equipment

In order to deliver the controlled minute doses of oxygen necessary for the process of micro-oxygenation (typically 0.5 to 60 ml/l/month) specialised equipment has been developed by Oenodev. A schematic diagram of the internal workings of the equipment is detailed below in Figure 4.

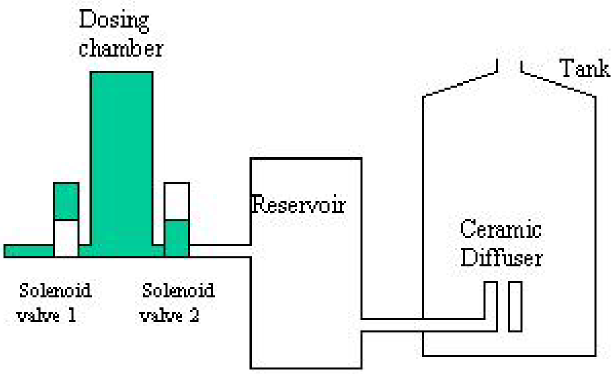

Figure 4. Schematic diagram of Micro-oxygenation set-up

The desired dose of oxygen to be injected into the wine is achieved by filling a chamber of known volume to a high fixed pressure. This volume is then transferred via a low-pressure circuit to the diffuser in the tank. In the diffuser, a ceramic filter converts the flow of gas into a stream of fine bubbles, which disperse rapidly into the wine. A programmable timer controls the filling of the dosage chamber and the low-pressure reservoir by means of two solenoid valves.

Commercial Application

Successful research and development of the technology since 1991 resulted in the commercial release of the system in 1996. Since 1996 over 1700 Micro-oxygenation systems have been put into operation worldwide. France is the major user of this technology followed by the United States; other users of the technology include Spain, Italy and Germany. The technology is now available in Australia and New Zealand through the coordinated efforts of Oenodev, Wine Network Australia and Air Liquide Australia.

Conclusion

The introduction of regular small amounts of oxygen to certain wines during the maturation phase has been shown to positively enhance certain organoleptic properties of the wine, typically wine aroma and astringency.

The mechanisms responsible for these changes involve the interactions of phenolic compounds and numerous other wine substrates between themselves and importantly with dissolved oxygen. To operate the main chemical mechanisms responsible for these beneficial changes in wine quality requires small amounts of oxygen for lengthy periods. Delivery of more oxygen than is necessary for these reactions results in the oxidation of numerous other wine substrates, a process detrimental to resultant wine quality.

The technique of micro-oxygenation is a new and exciting technology for winemakers. Significant opportunities exist for winemakers to improve the quality of their wines. The implementation of this technology in wineries will however radically change the way in which winemakers approach the manufacture of their wines.

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References

Allen, M. (1998) Phenolics Demystified. Proceedings of the Australian Society of Viticulture and Oenology Seminar – Phenolics and Extraction, Adelaide, Winetitles, Adelaide, pp. 4-11.

Cheynier, V., Fulcrand, H., Sarni, P. and Moutounet, M. (1998) Progress in Phenolic Chemistry in the Last Ten Years. Proceedings of the Australian Society of Viticulture and Oenology Seminar – Phenolics and Extraction, Adelaide, Winetitles, Adelaide, pp. 12-17.

Gawel, R. (1998) Red wine astringency: a review. Australian Journal of Grape and Wine Research 4, Winetitles, Adelaide, pp. 74-95.

Lemaire, T. (1995) 'La micro-oxygénation des vins' Report for the requirements of the Diplôma National d'Oenologie (Ecole Nationale Superieure Agronomique: Montpellier, France).

Ribéreau-Gayon, P. and Glories, Y (1986) Phenolics in grapes and wines. Proceedings of the Sixth Australian Wine Industry Technical Conference, Adelaide, Australian Winetitles, Adelaide pp. 247-256.

Walsh, B. (1998) Tannin Sensory Perception and its Relationship to Other Flavour Contributors. Proceedings of the Australian Society of Viticulture and Oenology Seminar – Phenolics and Extraction, Adelaide, Winetitles, Adelaide, pp. 24-27.

Zoecklein, W.B., Fugelsang, K.C., Gump, B.H. and Nury, F.S. (1995) Wine Analysis and Production. Chapman & Hall, New York.

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