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Chapter 4

IMPACT OF WINEMAKING TECHNIQUES ON PHENOLIC COMPOUNDS COMPOSITION AND CONTENT OF WINE: A REVIEW

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ABSTRACT

Phenolic compounds play an important role in the quality of wines. The composition of these compounds is not stable and evolves during winemaking. Winemaking techniques play an important role in the extraction of polyphenols from the grapes and consequently in the further stability of wine properties. In the course of winemaking and aging, changes in polyphenolic composition occur due to the participation of these compounds in numerous reactions such as copigmentation, cycloaddition, polymerization and oxidation. In this chapter, we will present the impact

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of traditional and n and new processes of winemaking on wine phenolic composition. It will be focused on maceration type and time, fermentation process, Aging step, finning and clarification methods, membrane processes and filtration techniques as well as the microoxygenation step on wine polyphenols.

Keywords: phenolic compounds, maceration, fermentation, membrane processes, aging.

INTRODUCTION

Phenolic compounds or polyphenols represent a large group of molecules which are present in grapes and wines. These compounds constitute a decisive factor in red wine quality and contribute to wine organoleptic characteristic such as color, taste, astringency and bitterness. They also confer to the wine the capacity of aging. The chemical composition of these compounds is discussed in other chapters. The antioxidant properties of phenolic compounds have been associated with health-promoting effects. Nowadays, the anticarcenogenic ability and the neuroprotective effect of these compounds are slightly proven and still under investigation.

Scientific papers showed clearly that several factors affect polyphenols biosynthesis and accumulation through berry ripening (Koundardas et al., 2009; Spayd et al., 2002; Zoecklein et al., 2008; Poni et al., 2009). Among these factors, the cultivars varieties (clones, and rootstock), the environmental factors (agro-pedological, topographical and climatic factors) and the cultural practices (training system, row vine spacing, pruning, bunch thinning, bud and leaf removal, water, fertilizers and pesticides management) play a crucial role in the determination of the quantitative as well as the qualitative phenolic composition.

After grape harvest, the winemaking process begins. Regardless the geographical zone, the winemaking process scheme is almost the same with some steps modification. The general scheme of winemaking is presented in figure 1. During this process, the diffusion and extraction of the grape polyphenols take place and a perpetual evolution of the phenolic composition of the must at the beginning and of the wine later, occurs with the participation of biochemical and chemical phenomena. New technologies and processes (membrane processes, flash release, etc) have been introduced to wine industry in response to various challenges as climate change, wine with low alcohol content, better quality, higher production, new products etc. It is obvious that the traditional and new processes hugely impact the qualitative and quantitative composition of phenolic compounds.

Therefore, in this chapter, we will review the impact of traditional and new processes of winemaking on wine phenolic composition. It will be focused on the incidence of maceration type and time, fermentation process, aging step, finning and clarification methods, membrane processes and filtration techniques as well as the microoxygenation step on wine polyphenols. The factors influencing the grape polyphenols content will not be discussed despite their importance.

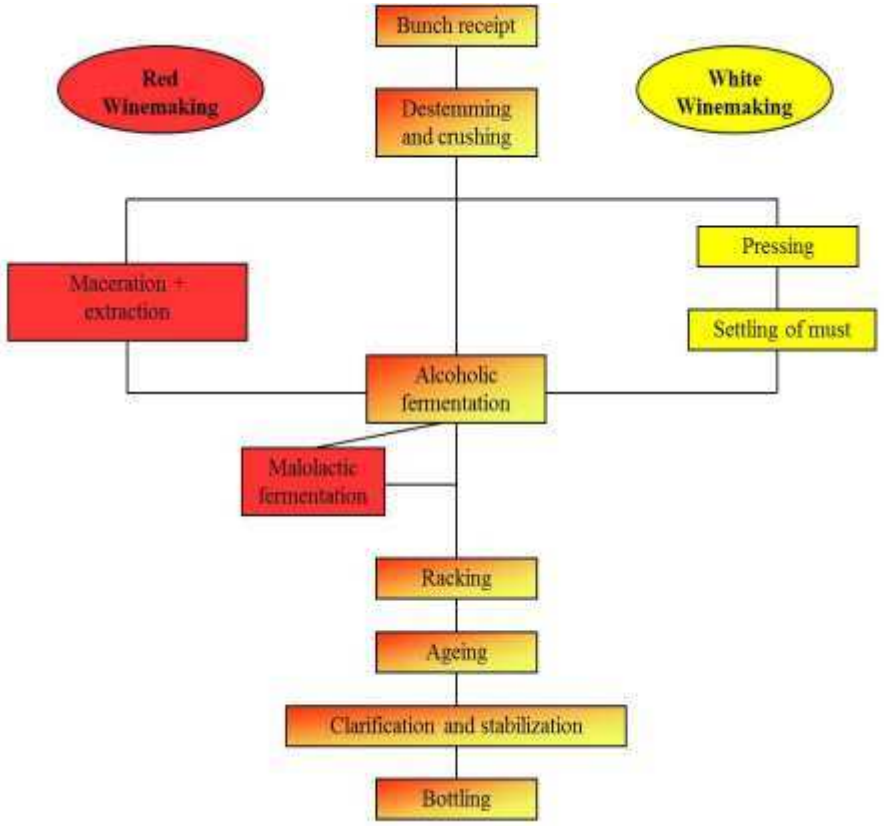

Figure 1. The winemaking process of red and white wines

IMPACT OF EXTRACTION PROCESSES AND PROCEDURES

Most grape phenolics are localized in the skins and seeds. During winemaking, phenolic compounds and other compounds contained in the grape are transferred to the wine by diffusion while the contact between the juice and the solid part of grapes is established.

Diffusion is the process by which a compound moves from a region of high concentration toward a region of lower concentration. The diffusion period in winemaking is called maceration and it is affected by several factors as grape variety and maturity, temperature of must or wine, duration of juice and grape skin and seed contact, concentration of alcohol and sulfur dioxide and use of enzymes.

In order to extend the extraction that occur during conventional maceration, and to achieve organoleptic properties beyond those offered by conventional maceration during fermentation, extended contact with skins may occur before (pre-fermentation extended maceration) or after fermentation (post-fermentation extended maceration). Depending on the temperature levels, the pre-fermentation extended maceration could be divided into two categories: i) cold maceration or cold soak for low levels of temperature, ii) heating maceration.

The effect of cold soak technique as regards with control vinification on the concentration of anthocyanins and proanthocyanidins in Monastrell wine, was studied by

Busse-Valverde et al. (2010) and the results have shown an increase in the anthocyanin extraction, mainly the extraction of malvidin-3-glucoside with higher grade of co-pigmentation and polymerization, therefore better stabilization than traditional wines. Gómez-Míguez et al. (2006) and Gordillo et al. (2010) reported a similar anthocyanin concentration after seven days of low temperature pre-fermentation maceration of Syrah and Tempranillo wine. Gil-Muñoz et al. (2009) found that cold maceration technique led to the highest anthocyanin content at the end of alcoholic fermentation in Cabernet Sauvignon wines. Consequently cold macerated wines tended to show higher chromatic stability than traditional maceration (Gordillo et al., 2010). When the results of the different practices were compared in Monastrell wines (Busse-Valverde et al., 2010), the proanthocyanidins concentration was greatest when cold soak was used (an increase of 33% in the proanthocyanidins concentration). In Cabernet Sauvignon wines, the proanthocyanidins content was higher when cold soak was used, with a total increase of 13.2%. Alvarez et al. (2006) also found a positive effect of low temperature pre-fermentative maceration on the concentration and polymerization of proanthocyanidins and on the stability of Monastrell wine color. Cold soak increased the ratio of anthocyanin to proanthocyanidins (67%) in the wine after maceration, suggesting a possible increase in the proportion of the anthocyanin-proanthocyanidin adducts against total polymers, which must affect the quality of the resultant wine after long-term storage (Cheynier et al., 1999).These authors also stated that the phenolic concentration was not related to the duration of the treatments since the results did not improve when pre-fermentation maceration time was increased but the effect was more evident when grapes were not completely mature. Alvarez et al. (2006) found an important decrease of the proanthocyanidins, of the mean degree of polymerization (mDP) and of the percentage of epigallocatechin (EGC) and an increase of the percentage of galloylation were reported when cold soak maceration was used. It might be expected that, with the application of these low temperature techniques, which are supposed to help the physical degradation of skin cell walls, the concentration of skin proanthocyanidins would increase in the wines, but these results indicated that the increase in proanthocyanidins is mainly due to an increase in seed proanthocyanidins. These results also agree with those obtained by the study of Busse-Valverde et al. (2010) who showed that proanthocyanidins concentrations in Monsatrell and Cabernet Sauvignon wines are increased with cold treatment and this increase seems to be related to the extraction of seeds proanthocyanidins. The cold Treatment is more effective when it is realized with less mature grapes (Álvarez et al. 2006). This result is according to previous studies for wines of other grape varieties (Couasnon, 1999).

PRE-FERMENTATION HEATING MACERATION

Historically, this type of maceration is coupled to the fermentation in liquid phase. Practically, it is used to quickly handle the entry of large volumes of grape harvest. Technically, this practice is used to extract phenolic compounds, denature alteration enzymes and destruct vegetal aromas of grapes. Many variations of pre-fermentation heating maceration exist:

i) The pre-fermentation heating maceration followed by direct pressing: grapes are heated to 70-75°C. The maceration must last between 6 to15 hours to obtain the same amount of polyphenols as a classical vinification.

ii) The pre-fermentation heating maceration followed by maceration during fermentation: its principle is the same as the first pre-fermentation heating

maceration but heating maceration lasts 2 hours and then the bunch is cooled down.

iii) The thermo-vinification process: this technique consists in bunch heating to 70-75°C for a short duration (30-40 minutes). The bunch is then pressed and cooled. Wines are generally less rich in phenolic compounds comparing to a classical vinification.

iv) The flash release (FR) process: it consists in heating the grapes quickly at high temperature (>95 °C) with biological vapor (i.e., steam produced from the water present in the grape, without dilution) at atmospheric pressure and then placing them under a strong vacuum (pressure closed to 60 hPa) which causes instant vaporization. The vaporization induces weakness in the cells wall and cooling of the treated grapes which favorites the polyphenol extraction. It is generally coupled to fermentation in liquid phase.

In 2000, Berger and Cottereau studied the winemaking of fruity red wines by pre-fermentation maceration under heat. The trials were conducted in the Beaujolais using a pre-fermentation heating to 70°C lasting from 8 to 16 hours. They found that this technique increase significantly the color (+40%) and tannins content (+55%) comparing to traditional Beaujolais vinification. It was also judged that the pre-fermentation technique influenced the wine aromas with red fruits notes.

The influence of bunch heating technique on the phenolic composition of red wines (Pinot noir, Lemberger and Cabernet Franc), regarding those of the control wines, was studied by Netzel et al. (2003), and the results have shown an efficient extraction of anthocyanins (located in the skin of red grapes), flavonols (especially quercetin glycosides accumulate in the skin), resveratrol (stored within the grape cells in the form of glucosides) and total flavan-3-ols (highest concentration in the seeds), while the level of individual monomeric (catechin and epicatechin) and dimeric (proanthocyanidins B1 and B2) flavan-3-ols were similar to or less than the control wine. These results were in accordance with those obtained by Borazan and Bozan (2013). In contrast, the phenolic acids (found in the skin, juice, solid pulp, and seeds) and tyrosol (produced from tyrosine by yeast during fermentation which is the only phenolic compound produced in significant amounts from non-phenolic precursors) did not show these effects.

A preliminary study carried out on flash-release (FR) by Moutounet et al. (2000) showed an increase of 50% in the total phenolic compounds than that observed in the control wines. In 2006, Morel-Salmi et al. applied FR treatment on three grape varieties in different vintage (Grenache, Mourvedre, Carigan), and the results, presented in table 1, showed that FR wines contained larger amounts of flavonols, anthocyanins, catechins and proanthocyanidins (tannins) than the control wines. The average chain length of proanthocyanidins (mean degree of polymerization, mDP) in control and FR wines were almost identical. The FR-treated wines contained higher percentages of galloylated units and lower proportions of epigallocatechin (EGC) units than the control wines (table 1). Again, this presumably reflects the fact that the extraction of tannins from seeds is greater than that of the skins (Morel-Salmi et al., 2006). This study also showed that FR increased total anthocyanins, total polyphenol index (TPI), color intensity (CI) and it lowered sulfite bleaching resistance than in the corresponding control wines. FR increased the tannin-to-anthocyanin ratio. This increase in the ratio T/A allows the conversion of anthocyanins to T-A dimers adducts that show the same color properties as anthocyanin. Formation of T-A adducts increased with the oxygenation, tannin-to-anthocyanin ratio and with FR and heating (Fulcrand et al., 2004).

Table 1. Effect of Flash Release on the Wine Polyphenol and Proanthocyanidin Composition (mg/L) (Morel-Salmi et al., 2006).

		Anthocyanins	Flavonols	Hydroxycinnamic acids	Catechins	Proanthocyanidins	DPm	% gall	% EGC
Grenache 2003	control	106.1 ± 8.6	20.8 ± 1.4	460.8 ± 12.8	85.2 ± 12.8	751.2 ± 46.9	4.00 ± 0.16	3.42 ± 0.16	10.51 ± 0.4
	flash release	110.9 ± 2.1	30.8 ± 1.1	355.7 ± 7.3	143.3 ± 1.9	997.2 ± 59.1	3.3 ± 0.13	4.8 ± 0.3	7.52 ± 0.3
Mourvèdre 2003	control	173.2 ± 4.7	36.1 ± 2.0	47.9 ± 5.8	33.9 ± 1.4	819.5 ± 52.1	4.78 ± 0.18	3.1 ± 0.17	13.9 ± 0.6
	flash release	198.7 ± 1.7	67.9 ± 0.3	26.8 ± 1.4	46.8 ± 3.1	1281.7 ± 308.5	4.5 ± 0.2	4.9 ± 0.3	9.5 ± 0.3
Grenache 2004	control	83.5 ± 0.5	5.4 ± 0.6	316.1 ± 5.4	55.4 ± 2.6	564.1 ± 35.2	3.95 ± 0.13	4.04 ± 0.28	12.1 ± 0.85
	flash release	87.6 ± 0.7	9.4 ± 0.1	270.8 ± 5.7	113.8 ± 3.4	851.5 ± 36.0	3.11 ± 0.06	5.3 ± 0.16	7.5 ± 0.07
Carignan 2004	control	161.4 ± 1.9	13.4 ± 1.2	94.1 ± 3.8	26.0 ± 0.7	308.7 ± 9.2	3.97 ± 0.07	2.08 ± 0.1	19.0 ± 0.66
	flash release	210.3 ± 5.6	27.5 ± 0.7	103.2 ± 2.8	32.3 ± 0.8	356.2 ± 11.2	4.02 ± 0.12	3.0 ± 0.12	17.6 ± 0.2

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CARBONIC MACERATION

Carbonic maceration consists of placing whole grapes in a closed tank under CO_2 atmosphere. The tank is kept at a moderate temperature (20-30°C) for 1-2 weeks. The carbon dioxide gas permeates through the grape skins and begins to stimulate fermentation at an intracellular level. The entire process takes place inside each single, intact berry. Then the juice is run off, the pomace pressed, and the free- run and press wines are usually assembled prior to normal alcoholic and malolactic fermentation (Ribéreau et al., 2006).

The influence of fermentation with carbonic maceration, on the contents of catechins, proanthocyanidins, and anthocyanins in Tinta Miúda red wines, was studied by Sun et al. (2001). They reported that the carbonic maceration wine contained the highest amounts of catechins, oligomeric and polymeric proanthocyanidins comparing to traditional process of winemaking, which might be explained by the fact that the phenolic compounds released from the solid parts of the grape cluster, using the carbonic maceration technique, are well-protected against oxidation or other physicochemical reactions during intracellular fermentation/maceration (Sun et al., 2001). On the other hand, analysis of individual and total anthocyanins by Sun et al. (2001) has shown that the concentrations of total anthocyanins and nearly all individual anthocyanins in the carbonic maceration wine were lower than traditional wine. Moreover, the carbonic maceration wine had less colored density and higher hue than the control wine.

Sun and Spranger (2005) also reported highest procyanidin levels in carbonic maceration Tinta Miúda red wines. It was shown also that carbonic maceration afforded wines with most stability in color density for 26 months' storage. On the opposite, Spranger et al. (2004) detected higher catechins and procyanidin levels in Castelão red wines made by classical techniques. Castillo-Sanchez et al. (2008) also found that procyanidin and catechin levels in traditional wines were much higher than in carbonic maceration wines

While studying the influence of winemaking protocol on the evolution of the anthocyanin content, Castillo-Sanchez et al. (2006) showed also that carbonic maceration led to lower anthocyanin levels and less intense coloration than the conventional pumping over and the rotary vats. They claimed also that during storage, the carbonic maceration wines underwent less color degradation than the others.

Castillo-Sanchez et al. (2008) found that carbonic maceration produced wines with less color density and higher hue than the conventional process of winemaking. These results were in agreement with those obtained by Timberlake and Bridle (1976). Although, the carbonic maceration protocol might have been expected to increase the release of anthocyanins from the grape skin due to the longer overall time spent macerating and fermenting and to the higher temperature used (Lorincz et al., 1998), these effects seem to have been overweighed by the effect of reducing post-crushing fermentation time to 2–3 days, which reduced the duration of intimate contact between skin and must. Similar results were obtained by Spranger et al. (2004) where they detected higher anthocyanin levels in classical fermentation Castelão red wines obtained than in carbonic maceration Castelão red wines.

POST-FERMENTATION RE-HEATING

It is a method consisting in prolonging the fermentative maceration by post-fermentation re-heating to approximately 45°C for 42 hours, in order to complete the liberation of grape skin constituents fulfilled by pre-fermentative and fermentative maceration. Discordant results are reported in literature on the effect of post-fermentation re-heating on red wine quality. A study by Koyama et al. (2007) on the influence of heating at the end of maceration during red winemaking from Cabernet Sauvignon showed that, contrary to expectations, the anthocyanin concentration was

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not increased. Flavonols showed an extraction similar to anthocyanins, while heat treatment decrease the level of proanthocyanidins, their mDP and the galloylation rate (%G). Barra et al. (2005) obtained higher increase in anthocyanin content (+10.7% of malvidin 3-glucoside), in color intensity (+13%) and total sensory score, in Pinot noir wine by heating at the end of maceration than by control vinification. Similar results were reported by Gerbaux et al. (1993). Potential variables, e.g., grape variety, berry maturity, heat conditions and fermentation scale might have affected the results.

MACERATION ENZYMES

The grape skin cell walls formed mainly by polysaccharides (pectins, hemicellulose and cellulose) are limiting barrier that prevent the release of polyphenols into the must during fermentation. Maceration enzymes may help in phenolic extraction and, at the same time, may modify the stability, taste and structure of red wines, because it is not only anthocyanins that are released from skins, but also tannins bound to the cell walls. These may be extracted due to the action of pectinases (polygalacturonase, pectin lyase and pectin esterase activities), hemicellulases and cellulases and the extracted compounds help to stabilize wine color and increase mouth feel sensations (Canal-Llaubères and Pouns, 2002). In the literature, the effect of the addition of enzymes on the phenolic content remains unclear because of some contradictory results.

The effect of enzymes treatment on phenolic composition was tested on a Monastrell wine by Bautista-Ortín et al. (2007) and it was compared to two other enological practices (running-off a part of must and tannins addition). The authors noticed that the addition of enzymes (pectinase + mannanase + glucanase activities) promoted higher values of total phenols (OD280) than in the control wine as also observed by Parley (1997) and Pardo et al. (1999). It seems that the action of the enzyme facilitates a higher extraction of proanthocyanidins from both skin and seeds but without changing their proportion or composition, as compared to control wines (Busse-Valverde et al., 2011). On the opposite, Ducasse et al. (2010) found a higher proanthocyanidin content in Merlot wines treated with enzymes but, surprisingly, not in the percentage of skin-derived proanthocyanidins, but with an increase of seed proanthocyanidins. Regarding anthocyanin concentrations, some authors have reported an increase in the anthocyanin levels (Bautista-Ortin et al., 2005; Kammerer et al., 2005; Romero-Cascales et al., 2012), whereas others have reported a decrease in the anthocyanin levels (Kelebek et al. 2007; Parley et al., 2001; Revilla and Gonzales-Sanjose, 2003;). Borazan and Bozan (2013) studied also the effect of pectolytic enzymes on the phenolic composition of Okozguzo wines. They found that the wines treated by the pectolytic enzyme addition had a lower monomeric flavan-3-ol content than the untreated wines, and that the amount of monomeric anthocyanins extracted did not increase with the addition of enzymes.

This different observations could be due to a different activities present in enzyme commercial preparations.

EFFECT OF YEASTS AND BACTERIA

Yeasts and bacterial metabolism during fermentations produce a large array of metabolites which contribute to the aroma and flavor of wine.

The influence of yeast used for winemaking on phenolic compounds is still poorly understood; but it is known that yeasts interact with polyphenols by 3 mechanisms:

- Adsorption of phenolic compounds on yeast cell wall
- Extraction of phenolic compounds
- Excretion of parietal polysaccharides (mannoproteins) which can interact with tannins for better stabilization and sensorial perception of the wine.

Hayasaka et al. (2007) studied the impact of two different yeasts, *Saccharomyces cerevisiae* (SC) and *Saccharomyces bayanus* (SB) on the phenolic composition of red wine made from the same batch of Cabernet Sauvignon grapes. The color properties and pigment profiles of SC and SB wines were compared at 8 days and 387 days after yeast inoculation. Anthocyanin concentration was found to be lower in SB wines than in SC wines at day 8 and 387, but SB wine exhibited greater wine color density. The anthocyanin concentration did not correlate with wine color density. The levels of pigmented polymers and SO_2 non-bleachable pigments were found to be higher in SB wine at day 387, demonstrating that the formation of stable pyranoanthocyanins and pigmented polymers was enhanced by SB yeast. It was demonstrated that the formation of acetaldehyde-mediated pigments was enhanced by the use of the SB yeast. The compositional analysis suggested that the differences in color properties and pigment profiles of SC and SB wines were largely due to the greater production of acetaldehyde-mediated pigments by the use of SB yeast.

Caridi et al. (2004) studied the effect of two yeasts strains on the phenolic profile of red wine. They reported that the Strain Sc2659, compared to strain Sc1483, produced a wine with significantly higher values of color, color intensity, total polyphenols and monomeric anthocyanins. Also, the content of flavonoids, total anthocyanins, flavans and proanthocyanidins was higher in the wine produced by strain Sc2659, but the differences from the strain Sc1483 were not significant. The levels of non- anthocyanic flavonoids were significantly lower. Therefore, strain Sc2659 protects during winemaking the phenolics and the anthocyanins of the must better than strain Sc1483.

Two commercial yeast strains (Fermirouge and Rhône 2323) were tested during the winemaking process of Monastrell grapes to determine their influence on color and phenolic composition of the resulting wines during alcoholic fermentation and maturation. The results showed that in 2002, the wines did not present great differences but in 2003 higher color intensity and phenolic compounds content were detected when one of the commercial strains was used. The maximum values of monomeric anthocyanins were found when Rhône 2323 (L2) was used. In 2003, differences in hydroxybenzoic acids, flavan-3-ols and total anthocyanins were also found. Rhône 2323 (L2) wines presented the largest concentration of these compounds (Bautista-Ortin et al., 2007).

Yang Sun et al., (2011) studied the effect of six commercial wine yeast strains (BM4x4, RA17, RC212, D254, D21 and GRE) on the profiles of polyphenols in cherry wines. They showed that BM4x4 fermented wine had the highest total phenolics and tannins among the six wines tested, whereas RC212 fermented wine had the highest content of total anthocyanins. Therefore a wide range of concentrations of total anthocyanins, total phenolics and tannins were revealed depending on yeast strains.

Regarding low molecular weight phenolic compounds, it is known that some phenolic acids can inhibit the growth of lactic acid bacteria while others can stimulate malolactic fermentation carried out by *Oenococus oeni*. During this process, hydroxycinnamic acids and their derivatives are the main compounds modified. The decrease in the concentration of *trans*-caftaric and *trans-p*-coutaric acids until disappearance, along with an increase in the corresponding free forms, *trans*-caffeic and *trans-p*-coumaric acids could be linked to lactic acid bacteria metabolism.

It has been described that *Lactobacillus hilgardii* can degrade gallic acid and catechin (Alberto et al., 2004). *Pediococcus pentosaceus* can also reduce the quercetin levels (Locascio et al., 2006). *Oenococcus oeni* was found to be able to metabolize anthocyanins and other phenolics by a glycosidase action producing important wine aroma compounds (De Revel et al., 2005; Bloem et al., 2008).

Bloem et al. (2006) studied the production of vanillin from simple phenols by wine-associated lactic acid bacteria. They found that bacteria were not able to form vanillin from eugenol or vanillic acid. However, they showed that *Oenococcus oeni* could convert ferulic acid to vanillin.

Cabrita et al. (2008) reported that hydroxycinnamic acids and their derivatives were the main compounds modified by malolactic fermentation, independently of the use or not of commercial lactic bacteria. In fact, it seems clear that the decrease in the concentrations of caftaric, coutaric and

fertaric acids, and the increase in the concentrations of caffeic, *p*-coumaric and ferulic acids are linked to lactic acid bacteria metabolism.

REACTION BETWEEN ANTHOCYANINS AND TANNINS: IMPACT OF MICRO-OXYGENATION

Anthocyanins are the most significant components, responsible for the purple-red color of young red wines. They are unstable and participate in reactions during fermentation and maturation to form more complex pigments, which mainly arise from the interaction between anthocyanins and other phenolic compounds, especially flavan-3-ols. Several mechanisms have been proposed and confirmed for the formation of these new pigments:

a) Direct anthocyanin-tannin condensation reactions (A^+-T product). The products are colorless flavenes, which can be oxidized to the corresponding flavylium ions, finally developing into yellow xanthylium salts. These reactions take place during fermentation, and O_2 is required (Liao et al. 1992; Santos-Buelga et al. 1999; Ribéreau-Gayon et al. 2000b).
b) Direct tannin-anthocyanin condensation reactions (T^+-A). The products are colorless, but are rapidly dehydrated into a reddish-orange form. This reaction is stimulated by higher temperatures, and O_2 is not required. It occurs predominantly during bottle aging (Remy et al. 2000; Ribéreau-Gayon et al. 2000b; Hayaska and Kennedy, 2003).
c) Reactions between anthocyanins and flavanols mediated by acetaldehyde to give a resulting product, with an ethyl bond, that can be protonated to form a colored compound. (Timberlake and Bridle, 1976; Francia-Aricha et al., 1997). Acetaldehyde can be derived from ethanol oxidation or from yeast metabolites.
d) Cycloaddition reactions to form pyranoanthocyanin compounds. Anthocyanins react with yeast metabolites or wine oxidation products (e.g. vinyl phenols, acetaldehyde and pyruvic acid). Vitisin-B is the specific compound resulting from ethenol (aldo-enol transformation of acetaldehyde) and malvidin-3-glucoside. Phenylpyranoanthocyanins, carboxypyranoanthocyanins and pyranoanthocyanins are respectively the results of the reaction between anthocyanins and vinylphenols, pyruvic acid and acetaldehyde (Atanasova et al., 2002; Mateus et al., 2003; Fulcrand et al., 2006; Rentzsch et al., 2007).
e) Addition reactions between anthocyanins and oxidized phenolic compounds (i.e. ortho-quinones) (Cheynier, 2006; Guyot et al. 1996).
f) Depolymerization and repolymerization reactions of tannins during wine aging. These transformations can occur in the presence or absence of oxygen; however, the resulting structures will differ, depending on the pathways taken (Vidal and Aagaard, 2008). Oxygen brings about the production of different aldehydes, with acetaldehyde being the most abundant. Subsequently, acetaldehyde can react rapidly with tannin molecules. The resulting products are not as important as are direct C4–C8 and C4–C6 polymerization reactions between procyanidin molecules and are hence less astringent (Ribéreau-Gayon et al., 1983; Tanaka et al., 1994).
g) Copigmentation of anthocyanins. The phenomenon of copigmentation is due to molecular association between anthocyanins (intramolecular copigmentation) or between anthocyanins and other non-colored organic molecules (intermolecular copigmentation). Copigmentation is important in color modification in young red wines, promoting an increase in the maximum absorption wavelength

All of these reactions result in the formation of more stable compounds that stabilize wine color since they partly resist discoloration by SO_2 and provide better color stability at wine pH.

Micro-oxygenation (MOX) is a technique that consists in introducing small and measured amounts of oxygen into wines with the objective of improving wine color, aroma and texture and involves the use of specialized equipment to regulate the oxygen doses applied (Parish et al. 2000; Paul, 2002). The term does not usually include the passive oxygen exposure that occurs during barrel aging nor the range of winemaking practices (such as pumping over and racking) where oxygen exposure may be intentional but is not well measured (Rieger, 2000). An important stipulation of micro-oxygenation is to introduce O_2 into the wine at a rate equal to or slightly less than the wine's ability to consume that, avoiding accumulation of dissolved oxygen (Du Toit et al. 2006). It is for this reason that the success of MOX depends strongly on controlling the rate of oxygen exposure. Typical dosage rates are relatively small, ranging from 2 to 90 mg O_2/L of wine/month (Dykes, 2007). Studies on MOX applications indicate that it can be performed at any time during the winemaking process. However, the best results are achieved when oxygen is added at the end of alcohol fermentation and before beginning malolactic fermentation (Parish et al., 2000; Castellari et al., 1998, González-Sanjosé et al., 2008).

A study conducted by Sánchez-Iglesias et al. (2009) on the effect of MOX on the phenolic fraction of Tempranillo wines during two consecutive vintages, showed significant higher contents of total anthocyanins, pyruvic derivates and polymerization pigments than the control wines, in which most of the pigments belonged to the group of flavanol-anthocyanin (direct and ethyl-bridged) derivatives (Arapitsas et al. 2012). Similar results were observed by (Atanasova et al. 2002) in blended red wine (var. Cabernet Sauvignon and Tannat) with a decrease in the percentage of copigmentation. As regards of chromatic parameters all of the micro-oxygenation wines showed significantly higher values of color intensity and percentage of blue, with a lower percentage of red and yellow than the control wines (Sánchez-Iglesias et al. 2009). These data agree with those already described for the greater anthocyanin drop, together with higher percentages of polymeric anthocyanins and greater contents of pyruvic derivatives (Revilla et al. 2001; Revilla et al. 2002). On the other hand a study carried out by Bastante et al. (2011) on the effects of micro-oxygenation before malolactic fermentation on Cencibel red wines, showed a decrease of the content of flavan-3-ols versus non micro-oxygenation wines. The micro-oxygenation treatment, together with the aforementioned lower content of flavan-3-ols, suggests that the oxygen addition activated the reactions between free anthocyanins and flavan-3-ols. As a consequence, new anthocyanin-derived pigments more stable to pH changes and bisulphite bleaching were formed (Escribano-Bailón et al. 2001). The latter was supported by the increase of percentage of polymerization and the lower value of copigmented anthocyanin (Hermosín-Gutiérrez et al. 2005).

The formation of polyphenolic compounds and pyranoanthocyanins during MOX could be enhanced by the presence of oak. This latter contains high amounts of hydrolyzable tannins such as ellagitannins and gallotannins. These compounds have high gallolated content that is more efficiently oxidized than the majority of the grape-derived phenolic compounds which are non-gallolated (Schmidtke et al., 2011).

BARREL AGING

Aging in wooden barrels is a process used to stabilize the color and enrich the sensorial characteristics of wine. Many compounds are released from wood into the wine; oxygen permeation through the wood favors formation of new anthocyanin and tannins derivates (De Rosso et al., 2009). During barrel aging, the total anthocyanins monoglucosides (the monoglucosides of delphinidin, cyanidin, peonidin, petunidin and malvidin, together with their acetyl and coumaryl derivates) decreased, but the percentage of pigments in the red form increased from 15 to 45%. This

transformation of colorless anthocyanins (free anthocyanins) into the colored form (polymerized compounds) compensates for their loss and leads to the increase in color density (Cano- Lopez et al., 2010). In other hand, a drop in free and total anthocyanins was thus observed, with the concentration of anthocyanins dropping from about 850 mg/L to 400 mg/L within six months (Atanosova et al., 2002). The concentration of direct adducts (T-A^+ or T^+-A) increased after six months in new barrels (Cáno-López et al., 2010). As regards their chromatic characteristics the color intensity (the sum of the yellow, red and blue colors) increased from 8 to 10 and 12 to 16 between 3-6 months after barreling. The percentages of red color was lower than that of the control wine but the percentages of yellow and blue were higher due to pigments resistant to SO_2 discoloration. Such a difference in color density can be observed visually. In South African Pinotage and Shiraz wines, it was found that the origin of the barrel (American, French or Russian) did not affect the difference in color intensity, color hue or total red pigments. The Total phenol content (expressed as optical density at 280nm) increased in barrel aged wines as regards of the control wine due to the extraction of phenolic compounds from oak (phenolic acids, ellagitannins, wood aldehydes) (Gómez-Cordoves et al., 1995).

Several of these positive modifications in wine phenolics occurring during wood aging are due to: (1) the release of ellagitannins from wood to wine. These compounds have 15 OH groups per molecule and are highly reactive toward oxygen penetrating through wood. In the presence of oxygen, the ellagitannins will be more easily oxidized than the majority of grape constituents such as anthocyanins to produce hydrogen peroxide. When hydrogen peroxide reacts with ferrous iron to yield the hydroxyl radical, this highly unstable radical reacts almost immediately. It does not react selectively with anti-oxidants such as phenolics, but instead reacts with all substances present in solution, almost in proportion to their concentration (Gómez-plaza and Cano-López, 2011). Expected products in wine would be the oxidation of alcohol to acetaldehyde (Wildenradt et al., 1974), molecule that is incorporated into red wine phenolic polymers (Drinkine et al., 2007). As a consequence, a modification of red wine color (Timberlake et al., 1976) occurs. The phenolic compounds released from wood may also directly interact with colorant matter of wine giving condensation products bringing to a bathochromic shift of color absorbance (Quideau et al., 2005). (2) Condensation reactions occur between wine phenolics and aldehydes released from oak barrels (Es-Safi et al., 2000; Sousa et al., 2005). In this regard, it has been recently shown that the vanillin, one of the main aldehydes released from oak wood, leads to the formation of an anthocyanin–catechin purple pigment (Sousa et al., 2007). Due to the fact that some acetaldehyde-derived flavanol–anthocyanin polymers are insoluble (Escribano-Bailon et al., 2001), a precipitation of phenolics also occurs. According to several authors, this might explain the losses of astringent material observed as a result of wood aging (Haslam et al., 1980; Vivas et al, 1996). Another mechanism that has to be considered is the adsorption of wine phenolics on wood. In a study performed using a model solution, it has been observed that at least 50% of the resveratrol content can be sorbed by the wood (Barrera-Garcia et al., 2007), indicating that the wood sorption process was selective for the most hydrophobic compound. Different phenolic molecules are involved with the bitterness, astringency and fullness of red wine, but it is mainly the flavanols that are responsible for these tastes and flavors. A very young red wine might be harsh, course, very astringent and even bitter. During aging of red wine in barrels the wine becomes softer and less astringent. It is mainly the acetaldehyde-induced polymerization that contributes to the polymerization of flavanols. The resulting products are not as reactive towards proteins as their constituents. However, direct C4-C8 and C4-C6 polymerization reactions between procyanidin molecules produce products that are more reactive towards proteins and are hence more astringent than those formed from acetaldehyde-induced condensation reactions (Cheynier et al., 1997). In the case of flavanols, where the C6 and C8 positions can be occupied, polymers larger than trimers have been isolated. Both types of reactions produce procyanidins with a limit of 8 or 10 flavan units. The interaction of anthocyanin molecules

with procyanidins can also influence the taste of wine because they can form the terminal subunits, thus preventing further polymerization (Ribéreau-Gayon et al., 2000; Monagas et al., 2005).

AGING ON LEES

The definition of wine lees given by EEC regulation No. 337/79 states that ‘‘wine lees is the residue that forms at the bottom of recipients containing wine, after fermentation, during storage or after authorized treatments, as well as the residue obtained following the filtration or centrifugation of this product” (Pérez-Serradilla and Luque de Castro, 2008). When wine is kept in contact with lees, the yeast covering is naturally and slowly degraded and most nutrient supplies are depleted. This microbiological phenomenon, known as autolysis, is mainly induced through different enzymatic activities of the yeast itself. This degradation in wine enriches this latter with products (polysaccharides, peptides and fatty acids) from different cell parts (Mazauric and Salmon, 2005). The importance of wine lees in the aging technique impact on phenolic compound composition comes from the fact that they can adsorb phenolic compounds and release to wine some compounds, among them enzymes and mannoproteins.

The compounds released can influence the structural integration of the wine in terms of phenols, body, aroma and wine stability (Palomero et al., 2009). Results showed that mannoproteins released during yeast lees autolysis can interact with phenolic compounds, improving the color stability and reducing the wine astringency by decreasing tannin aggregation and precipitation (Feuillat et al., 2000; Poncet-Legrand et al., 2000; Fornairon-Bonnefond et al., 2002).

It has been generally reported that anthocyanins content in wines decreases after contact with lees (Mazauric and Salmon, 2005; Mazauric and Salmon, 2006). This decrease is due to the adsorption of anthocyanins on wine lees. Mazauric and Salmon (2005) showed that this adsorption follows biphasic kinetics: an initial and rapid fixation is followed by a slow, constant and saturating fixation that reaches its maximum after about 1 week. Other authors (Delcroix et al., 1994; Cunier, 1997) explained that anthocyanins decrease during wine aging is due to the degradation of anthocyanins by β-glucosidase enzymes released by yeast lees.

Evolution of red wine anthocyanins with or without aging on lees was studied by Moreno-Arribas et al. (2008), and the results showed that wines aged in the presence of lees, had the highest values of anthocyanins-glucosides (delphinidin-3-glucoside, petunidin-3-glucoside, peonidin-3-glucoside, malvidin-3-glucoside) and anthocyanins-cinnamoylglucosides (delphinidin-3-(6’’-P-coumarylglucoside), malvidin-3-(6’’caffeoylglucoside), malvidin-3-(6’’coumaroylglucoside), than the wines aged without lees. On the other hand, the results showed that the formation of anthocyanin-vinylphenol adducts seems to be favored by yeast and lactic acid bacteria from lees. Similar results were reported by Pozo-Bayón et al. (2004).

One of the disadvantages of aging on lees is that they consume oxygen. Oxygen plays an important role in the stabilization of wine color by enhancing condensation reactions between flavonoids mediated by acetaldehyde and in the cycloaddition reactions between pyruvic acid and anthocyanins. Therefore, the consumption of oxygen can reduce the condensation and polymerization reactions between phenolic compounds and can result in decreasing of wine color. The aging on lees also favors the formation of reduction aromas. It seems that this problem can be resolved by combining the lees and oak aging because oak aging favors the transfer of oxygen into wine.

Hernandez et al. (2006) studied the impact of aging on lees on 38 non-anthocyanin phenolic compounds. They didn’t observe any significant difference in the content of these compounds after 14 months of Aging. They reported an increase in hydroxycinnamic acids during aging on lees in oak barrels and they explained this result by the enzymatic activity of yeast and lactic acid bacteria and the hydro-alcoholysis of oak wood. Same results were obtained by Del Barrio-Galan et al. (2012) when studying the effect of the aging on lees on the low molecular weight phenols of Tempranillo red wine aged in oak barrels.

FILTRATION AND MEMBRANE TECHNIQUES

Wines, after alcoholic and malolactic fermentations, are a complex medium and need to be clarified and stabilized. Stabilization could be divided into physico-chemical and microbiological stabilization. The microbiological stabilization is ensured by filtration techniques while the physico-chemical stabilization is achieved through fining process, cold stabilization and addition of stabilizers agents. The filtration methods used in wine industry could be divided into 2 groups:

i) Precoat filtrations using exogenic additives as diatomaceous earth, perlite and cellulose
ii) Filtrations using filtering media as membranes and pads

All filtrations methods have an incidence on the chemical and organoleptic composition of wines (Serrano, 1998). For precoat filtrations, the impact depends on the permeability of the diatomaceous earth. Polyphenols loss in precoat filtrations is noticed through adsorption of the compounds in the exogenic additives.

Polyphenols losses were more studied in cross-flow microfiltration because it was shown that these compounds with polysaccharides are the main responsible of membrane fouling. At the beginning, several authors (Poirier et al., 1985, Belleville et al., 1990 and 1992) have reported that the colloidal deposit on ceramic membranes has an intense red color and therefore they pointed out the implication of polyphenols in membrane fouling. The involvement of wine polyphenols in the membrane fouling was been identified by washing the fouled membrane with acidified methanol. Significant increases in permeability were obtained. This fact can be attributed to the elimination of the layers of phenolic compounds because the other wine constituents are insoluble in this solvent (Cameira Dos Santos, 1995). According to Czekaj et al. (2000) and El Rayess et al. (2011; 2012), an increase in polyphenol concentration in wine leads to a decrease of membrane permeability and thus to an increase of membrane fouling.

Researchers have also demonstrated that membrane materials exhibit different fouling behaviors with wine compounds. Ulbricht et al. (2009) showed that polysaccharides and polyphenols adsorption occurs more on polar (hydrophilic) polyethersulfone (PES) membranes that on non-polar (hydrophobic) polypropylene membranes. In fact, Polyphenols are amphipathic molecules with hydrophobic aromatic rings and hydrophilic phenolic hydroxyl groups. So their adsorption involves both hydrophobic effects and the formation of hydrogen bonds. El Rayess et al. (2012) have reported that the most plausible mechanism for membrane fouling by tannins is a fast interaction between tannins and the ceramic membrane (adsorption) quickly followed by tannins-tannins interaction leading to aggregates that could block the pores and form a deposit at the top surface of the membrane. Recently, it was shown that cross-flow microfiltration significantly decreased the mean degree of polymerization (mDP) of tannins by 25% and it selectively removed the high polymerized proanthocyanidin. It was also reported that this technique lowered the levels of catechin, dimers and anthocyanins comparing to the control (Oberholster et al., 2013).

The effect of other membrane processes (Reverse osmosis, nanofiltration, electrodialysis,…) on polyphenol content in wine was also studied. Membrane processes including nanofiltration, reverse osmosis, pervaporation and membrane contactor can be used to reduce alcohol in wines. These techniques form alternatives to traditional techniques. There are two methods to reduce alcohol content in wine: i) reduction of sugar concentration of musts; ii) de-alcoholization of wine (Mietton-Peuchot, 2010). The electrodialysis is used for tartaric stabilization while the bipolar membrane electrodialysis serves to acidify or de-acidify the wine.

Gomez-Benitez et al. (2003) showed a negligible impact of electrodialysis on color intensity. Granès et al. (2009) also demonstrated that bipolar membrane electrodialysis had no effect on polyphenol contents in wine. Cottereau et al. (2007) reported that The REDUX® process (association of ultrafiltration and nanofiltration to reduce the sugar concentration of musts) allows the concentration of polyphenols in wines due to volume reduction. In 2011, Bogianchini et al.

evaluated the phenolic profile and the antioxidant activity of commercial dealcoholized wines by reverse osmosis. They found that the reverse osmosis process didn't significantly affect any phenolic acids regardless to their chemical structure and alcoholic degree but the antioxidant activity decreased in average 40% compared to untreated wine. The antioxidant activities and phenolic compounds of these products were monitored for seven months. No significant changes were observed. In 2012, Liguori et al. tested the osmotic distillation for wine de-alcoholization and they tested its effect on wine phenolics. No significant differences in chemical analyses between crude and dealcoholized wine were found. The last observation is in agreement with the results obtained by Gambuti et al. (2011) while studying the influence of partial de-alcoholization by membrane contactor on red wines quality.

FINING AGENTS

Fining is used to clarify and stabilize wines. The purpose of fining is to cause haze-forming particles to combine with additional agents, leading to flocculation, clarity, and stabilization. Fining agents are used to eliminate or reduce undesirable substances in wine. Table 2 summarized the common fining agents, their sources and their applications in enology. Three major mechanisms of action of fining agents include charge-charge (electrical) interaction, bond formation, or absorption/adsorption. Wine components and the type of fining agent determine the mechanism of action. When compounds of opposite charges interact, larger particles form and settle. In the case of bond-formation, chemical bonds (i.e., hydrogen bonds) form between fining agents and wine components. Absorption occurs when compounds are engulfed by the fining agent. Alternatively, when the substance is bound to the agent's surface, the substance is adsorbed.

Table 2. Common fining agents used in winemaking

Fining agent	Source	Purpose of application
Gelatin	Animal Tissue	Removal of tannin and brown polymeric pigments
Isinglass	Fish bladder	Reduce phenolic compounds; add fruitiness to wine
Casein	Milk	Reduce wine haze and tannin content
Egg Albumen	Egg whites	Reduce wine haze and tannin content
Bentonite	Clay, volcanic deposits	Protein removal
Tannin	Wood and grapes seeds	Targets phenolic and proteins compounds
Sparkalloid	Alginate	Clarification and settling aid
Polyvinyl-polypyrrolidone	Synthetic polymer	Reduce polyphenols

Winemakers use several chemical substances (table 2), the choice of which depends on the nature of the wine and the compounds that are going to be eliminated (Gómez-Plaza et al. 2000).

Bentonite is negatively charged clay. The clay consists of complex hydrated aluminum silicate with exchangeable cationic components. Calcium and sodium bentonite are two forms that are commercially available for wine use. The mode of action of bentonite is electrostatic. The flat surface of a hydrated bentonite platelet is negatively charged. Positively charged particles adsorb onto the surface of the bentonite. Bentonite is principally used to remove proteins (protein stabilizer) from

white wine and juice. It also attracts other positively charged compounds such as anthocyanins, other phenolics and nitrogen. Bentonite is not reactive towards small phenolic compounds but binds only large phenolic compounds such as anthocyanins and may also bind phenolic compound complexes with protein (Kalkan Yildirim, 2011)

Egg albumin and Gelatin are positively charged proteins used to remove excess negatively charged tannins from wine (Kalkan Yildirim, 2011). They are most commonly used to reduce the level of astringency and bitterness in the press fraction of wines, with reference to soften red wines (Stankovic et al. 2012). Egg albumen is colloidal in nature and has a positively charged surface that attracts negatively charged tannins in red wines. It is unsuitable for white wines treatment. Whereas, gelatin is primarily used to soften red wines but can also be used to reduce the phenol level and brown color in white juice before fermentation. Gelatin reduces astringency in red wines by lowering tannin levels and tends to remove more, higher molecular weight galloylated proanthocyanidols than lower molecular weight tannins (Sarni-Manchado et al., 1999). After the formation of gelatin-tannin complex, this complex may interact with anthocyanins, causing their removal.

Casein fining preparations are used in particular for the treatment of astringency and for the clarification of white and rosé wines, but are also sometimes used with red wines. Casein is a positively charged protein that flocculates in acidic media such as wine. When added to wine, casein adsorbs and mechanically removes suspended material as it settles. Casein is difficult to mix into the juice/wine as it is relatively insoluble in acidic solutions and should be mixed in water with a pH value above 8 or made alkaline prior to mixing.

Isinglass is a positively charged fining agent derived from the air bladder of a sturgeon. It is available as sheet or flocculated isinglass. Isinglass is used principally in white still and sparkling wines and to clean up the aroma, improve clarity and modify the finish without significantly modifying tannin levels.

Polyvinyl polypyrrolidone (PVPP) is a high molecular weight fining agent made of cross-linked monomer of polyvinlypyrrolidone. It complexes with phenolic and polyphenolic components in wine by adsorption and attracts low molecular weight tannins. It removes bitter compounds and browning precursors in both red and white wines. PVPP is quick acting with no preparation required.

Several studies in the literature treated the impact of fining agents on the phenolic composition of wines. A study done by Stankovic et al. (2012), on the effect of fining agents, on red Pinot noir variety of different ages, showed that fined wines lead to significant reduction of color intensity, ionized anthocyanins, and a low reduction of colorless anthocyanins, relative to unfined wines. Castillo-Sanchez et al. (2006) investigated the impact of PVPP, casein, egg albumin and gelatin on the evolution of anthocyanins and color of Vinhão wines. They found that all fining agents induced loss of color density and anthocyanin content but surprisingly, they noticed that PVPP caused more loss of color than the other fining agents. Several authors also found a decrease in anthocyanin content with fining (Castillo-Sanchez et al., 2008; Cosme et al., 2007; Karamanidou et al., 2011). Cosme et al. (2007) studied the interactions between protein fining agents and proanthocyanidins in white wine. They reported that the monomeric flavanols were significantly depleted by casein, and gelatin with low molecular weight (MW) distribution, and isinglass obtained from fish swim bladder. The degree of polymerization of polymeric proanthocyanidins that remained in the fined wine decreased significantly after addition of protein fining agents except when potassium caseinate was used. Casein and isinglass induced a significant decrease in wine color (A420nm), a decrease in browning potential and a decrease in turbidity. Cosme et al. (2012) focused their research on determining if non-allergenic pea protein or polyvinylpolypyrrolidone (PVPP) are possible alternatives for casein fining. The results indicate that flavonoid and non-flavonoid phenols decreased in the wines treated with potassium caseinate, pea protein, and PVPP. All fining agents decreased wine color. Potassium caseinate was the most effective fining agent for reducing browning potential. When applying the CIELaB chromatic characterization, they found that the value for b*

(yellowness) decreased significantly with all fining agents assayed; however, the decrease was greater in all experiments fined with potassium caseinate, indicating a higher reduction in the yellow intensity of the fined wine. Chroma (C*) is a parameter that indicates the contribution of a*(redness) and b*(yellowness).The value of C* decreased significantly after addition of pea protein, potassium caseinate and formulations of pea protein with PVPP. They found that PVPP could be used alone or in combination with much smaller quantities of casein and still effectively reduce wine oxidation through removal of polyphenols in reduced and oxidized (quinones and quinone methides) forms, which includes simple phenolic acids and flavonoids. Recently in 2013, Oberholster et al. investigated the effect of gelatin and egg albumin on the phenolic composition of Pinotage wine. They found that both gelatin and egg albumin fining decreased the mean degree of polymerization (mDP) of tannin significantly by 26.4% and 25.2%, respectively, compared to the control. Egg albumin treatments significantly decreased the total pigment content compared to control.

CONCLUSION

This chapter reviewed the winemaking techniques which are admitted to affect the phenolic composition of wines. The maceration and the aging remain the most influencing steps while fermentation and filtration slightly impact the polyphenols content.

Despite all the progress made in this sector, some information remain contradictory. Moreover, the effects of some winemaking processes on wine polyphenols composition are still lacking. Therefore, more studies are required to elucidate the real impact of each step during the winemaking of a given wine.

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