EFFECT OF MIXTURE BENTONITE, GELATIN, ALBUMIN AND PVPP IN FINING FOR CLARIFICATION OF COLOR IN DIFFERENT RED WINES

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Abstract

Fining is a technique used to remove unwanted wine components that affect clarification, astringency, color, bitterness and aroma. Although fining is a useful technique to master, it's an indicator that there may be a problem in vineyard or winemaking (Harbertson, 2008). So, it's important to identify the problem during winemaking process and determining what fining agents are available to solve them. Bentonite fining is a commonly technique used in wine industry as a clarifying technique to remove proteins as potencial source of haze (off-white flakes) in wines (Lambri, Dordoni, Silva, & De-Faveri, 2010). Bentonite interacts with proteins and other molecules. Affinity for protein have shown also animal protein such as gelatin and albumin (F, J, & O, 2009). PVPP (polyvinylpolypyrolidone) reduce the problem of bitterness caused from catechins and potential browning. The effect of fining in color was examined on three samples: two Cabernet wine, one with inherent fermentation and the other with yeast stimulated, and Kallmet wine (autochthonous variety), drain preliminarily. These samples have been treated in four different concentrations of the mixture of these agents (Chiarolet R.Lot-L-371016). This mixture is prepared 4-6 hours before using, diluted in the rapport (1:10) with distillated water. Intensity of color ($A_{420+520}$), hue ($A_{420/520}$) and the optic density in 420 nm, diluted (1:10) with distillated water, were measured before and after fining process. The treatment was last for 2 days. Results suggested that higher concentration doesn't mean a better clarification. Better concentrations were shown a decrease of color intensity and an increase of hue.

Keywords: *bentonite, gelatin, fining, hue, intensity of color*.

Introduction

Fining is a process of a great importance in quality of final product, wine. The main role of these process consist in obtaining a good colour, a clear wine and possibility for a prolonged time of aging. Fining is not an easy process because if it is not done correctly, it can result in loss of colour and different pigments, in loss of stability and in loss of volatile substances. A number of agents are used for finning, but for a better clarification we must to choose them to not change the chemical composition of wine but only remove the undesiderable component that could make the product unstable.

The most commonly used agents are: bentonit, gelatin, egg albumin, casein, isinglass and PVPP (polyvinylpolypyrolidone). They can be used separately and combined with each other but in a defined dosage. For each one of the agents has been known it's effect in enochemical characteristics of wine. Almost a great job is still to do because there are a lot of unknown mechanisem of their activity.

Bentonite is a hydrated aluminium silicate and a member of the smectite class of clays. It commonly contains two forms of mineral, kaolinite and montmorillonite, with the latter being the major form found in the bentonite that is active in wine processing. Both minerals have crystal structures that exist as sheets or layers. Montmorillonite can be subdivided again into two forms, depending on the predominant cation (positively charged ion) found in the inter-laminar regions of the sub-crystalline structure. If this seems a little confusing it will become clearer with a little more explanation (P & V, 2007).

Gelatin is a protein, that is, a polymer of amino acids joined together by peptide bonds. Gelatine is perhaps the most technical of the proteinaceous fining agents, Gelatine is derived from the

hydrolysis of collagen, a triple-helical structural component, from the bones and skins of animals, typically cattle (bovine) or pigs (porcine).

Egg albumin is not suitable for white wines, as high levels of tannins are required for flocculation. Albumin (ovalbumin) is the major protein of many found in egg whites. Egg albumin a medium weight protein and is classically associated with the fining of red wines, due to its noted lack of reactivity towards smaller anthocyanin-tannin complexes and therefore lower color removal. It's not typically used on white wines or on youthful red wines. (Bowyer P. K., 2008)

PVPP (polyvinylpolypyrolidone). This fining agent removes lower molecular weight phenolics, and so is often used to reduce bitterness in wines, particularly white wines which have undergone skin contact. It also can reduce browning, by removing phenolic material that may brown and It has a little effect on astringency. It is produced by the polymeristaion of n-vinyl-pyrrolidone, under prescribed physical and chemical conditions. It is a fine white powder, insoluble in water, alcohol, other organic solvents and acid or alkali. Multiple polyphenol bonding sites means that pvpp is effective at relatively low concentration and has greater affinity for the more polymerized polyphenols (Gopal & Marti, 1999).

Also a number of studies have told us about the role of those agents in different stage of winemaking. So the bentonite does not effect on the aminoacid composition of the grape juice, but reduce only the protein content. The presence of bentonite during fermentations had no effect on the maximum fermentation rate but treating with bentonite and removing it prior to inoculation decreased the maximum fermentation rate. The presence of bentonite, throughout the fermentation had no effect on total fermentation time, but bentonite fining increased overall fermentation time (Weiss & Bisson, 2002).

Other observations have been concluded that doesn't matter also if the treatment is done to must or to wine. So the free terpenols undergo in a lower removal if it is treated the must and after the wine to. The best removal of protein came from treatment of must than from treatment of wine (M, R, A, & D, 2012).

This study has the objective to evaluate the correlation between the dose of fining agent and two parameters like color intensity and hue in different wines with different winemaking process.

Materials and methods

Wines samples

In this experiment have been used two young Cabernet wine, and one Kallmet wine (autochthonous variety) produced in 2011. One of the Cabernet wine was with inherent fermentation and the other stimulated with yeast, grape not dried preliminarily. The Kallmet

wine was produced from fermentation stimulated with yeast and the grape were dried preliminarily the winemaking process. These samples have been treated with the mixture of these fining agents as bentonite, gelatin, egg albumin and PVPP with name Chiarolet R.Lot-L-371016, an Italian product provided by a local supplier for enological products.

Use of mixture fining

The effective dose recommended for these mixtures were 60-100 g/hl. The mixture was prepared 4-6 hours before using, diluted with distillated water improving a 10% solution. From this solution for every sample were carried out this experiment: T1=70 g/hl, T2= 75 g/hl, T3= 80 g/hl and T4= 90 g/hl (Fig.1). The samples of wine treated with fining mixture were 100ml. After 2 days of treatment there was a precipitation in the end of container so we separated the precipitation and analyzed the wine samples.

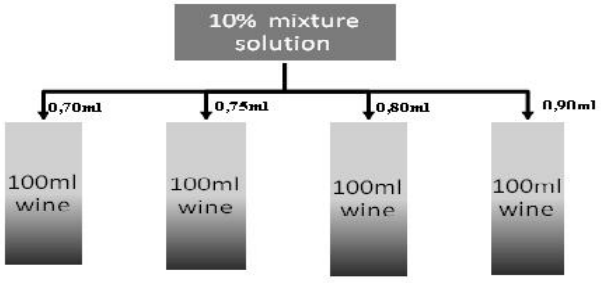

Figura 1 Scheme of the fining experiment

Analyses

Same standard analyzes were done to the samples before fining like pH, determined with a pH-meter, standardized to pH 4.0, 7.0, 10.0 with standard buffer solution. Dry extract, acidity and volatile acidity were determined according to official methods OIV. The alcohol content was determined using an ebulliometer Dujardin-Salleron.

Color intensity and hue were determined after dilution of wine samples with solvent (7g tartaric acid and 35ml NaOH 1N in one 1 liter) in ratio 1:20 and then the absorbance measurements were made in spectrophotometer at 420 nm and 520 nm. The color intensity and hue were calculated as follows:

Color intensity = $(A_{450}+A_{520})*20$

Hue = A_{420}/A_{520}

Results and discussion

Based on Table 1 data the dry extract of Kallmet Dried With Yeast (KDY) is much higher (38,12 g/l) than the other samples of Cabernet Not Dried Not Yeast (CNDNY) and Cabernet Not Dried With Yeast (CNDWY) respectively 31,92 g/l and 31,40 g/l. These wines were young so they were characterized from a high pH that ranged from 3.7 to 3.9 that it related with the presence of acid tartaric in high level. Another parameter that changes evidently from each one sample to the other is the alcohol content.

The KDY samples were characterized from a high alcohol content of 18% v/v in difference with the Cabernet sample that ranged 12.7-12.8 %v/v. These differences came from the drying process where the content of sugar were concentrated till 30°Brix more during drying then in samples of cabernet that were not dried with the initial sugar content 23° Brix. In all samples the fermentation was left until all sugars were converted to alcohol, so they were dried wines.

Table 1 Same standart analyses of wine samples before finning

	Wine samples		
	Kallmet Dried with Yeast	Cabernet Not Dried Not Yeast	Cabernet Not Dried With Yeast
Dry extract g/l	38,12	31,92	31,40
pH	3,96	3,78	3,81
Acidity g/l	5,62	5,83	5,64
Volatile acidity g/l	0,310	0,298	0,227
Alcohol %	18,1	12,7	12,8

During the treatment with different dosage of fining agents changes in color intensity and hue were observed. These changes were observed in comparison with measurement have been made before the treatment. Figure 2 showed the hue of samples before and after treatment with different doses of fining mixture, and from the graph results that the hue of KDY before and after treatment was much higher than hue value from the other samples. The common fact for all three samples was that the hue before treating weren't higher than after fining and values vary from one treatment to another.

Table 2 The influence of different treatment in color intensity and hue of wine samples

	Kallmet Dried with Yeast				
	Before finning	**T1**	**T2**	**T3**	**T4**
Color intensity	14,804	10,2980	9,8	10,3160	10,1740
Hue	0,8620	0,9918	0,9043	1,0046	0,8702

		Cabernet Not Dried Not with Yeast			
Color intensity	17,208	11,8020	11,0200	12,0620	11,1660
Hue	0,6732	0,6127	0,5947	0,6618	0,6561
		Cabernet Not Dried With Yeast			
Color intensity	17,930	12,7500	16,2360	15,1020	14,7920
Hue	0,6291	0,6066	0,6873	0,6739	0,6597

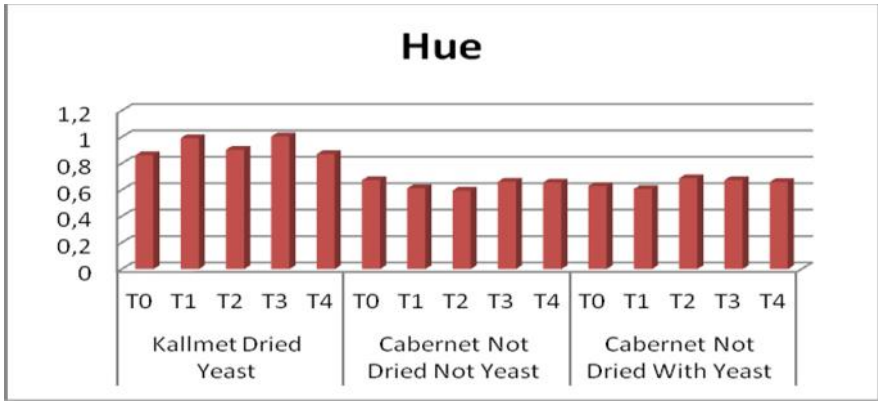

Figura 2 The trend of hue values in all samples

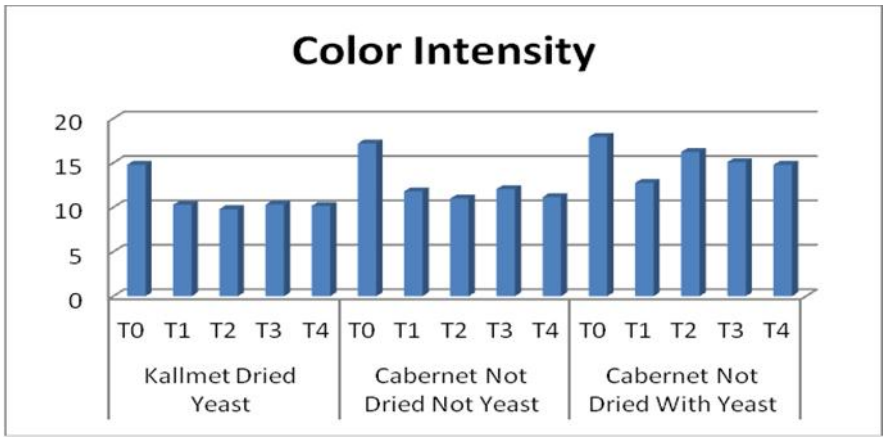

Figura 3 The trend of color intensity values in all samples

From Figure 4 we saw that after fining the hue increased and ranged from 0,8620 before fining in 1,0046 after fining for KDY sample, in CNDNY samples hue undergo in a slight decrease from 0,6732 before fining in 0,6618 after fining and for CNDWY sample, trend is the same as KDY sample with an increase of hue from 0,6291 before fining in 0,6873 after fining. Another thing to considered were the fact that the higher dose of mixture fining doesn't mean the best hue value. For KDY and CNDNY sample the best dose for e better hue was 80g/l and the lower value of hue were obtained from the dose 75g/l fining mixture. The CNDWY sample undergo in a reverse changes, so the better hue value were obtained from dose of 75g/l of fining agent, and a lower value of hue were obtained from dose 70g/l of mixture of fining agent.

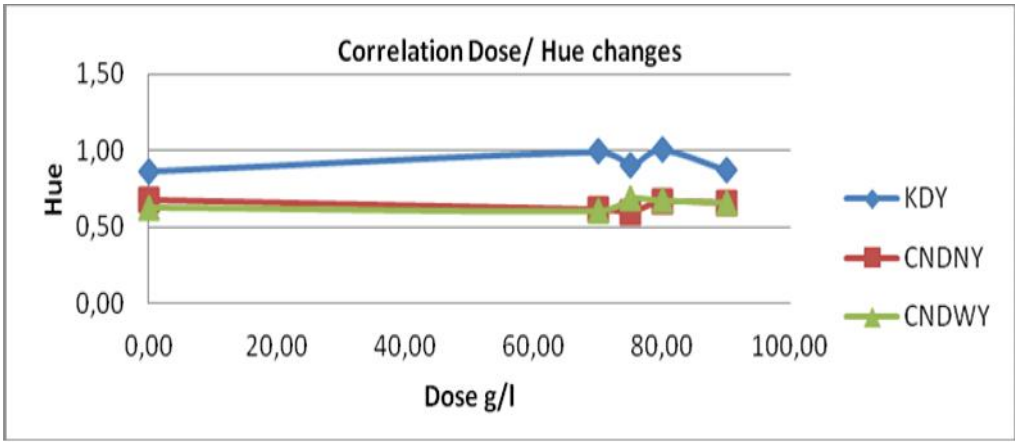

Figura 4. The correlation between the dose of fining agents and the changes of hue value

The results from Figure 3 and 5 showed that the highest value of color intensity before and after fining belong to the sample CNDWY. The color intensity before treatment was much higher than after treatment for all samples. We observed for all samples that color intensity after treatment undergo in decreasing. In different studies this effect were caused from bentonite and gelatin because they change the content of phenolic composition and this is reflected to color intensity. So the bentonite affect ionized anthocyanins decreasing in this way the intensity of red and blue colors but increase the yellow color , which affect the hue of wine and this fact is explained in the Figure 4 where we saw the increased hue after treatment (Stankovic, Jovic, & Zivkovic, 2004) (Balik, 2003).

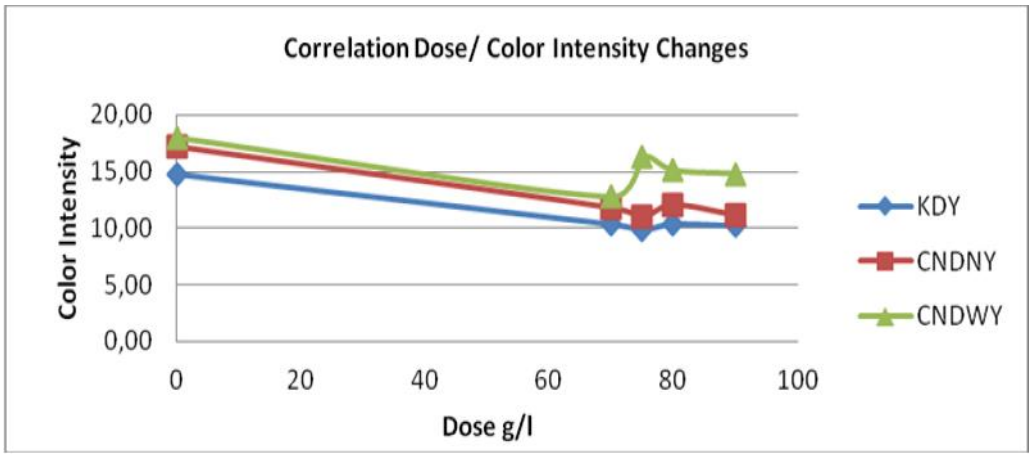

Figura 5 The correlation between the dose of fining agents and the changes of color intensity value

Is to mentioned that different agents affect the decreasing of different proanthocyanidin fraction. So egg albumin used in high concentration reduced the monomeric flavonols and the high concentration of a gelatin and egg albumin together induced a decrease of oligomeric fraction and the reduction of antioxidant activity of red wine (Gonçalves & Jordao, 2009). Other authors had reported that different fining agents can have different impacts on phenolic compounds, even those having similar structures properties, so gelatin with molecular weight higher than 43.0 *k*DA have a great affinity for monomers, oligomers and polymers. While gelatin with molecular weight lower than 43.0 *k*Da and lower than 14.4 kDa affect the oligomers and cause the most color reduction (F, J, & O, 2009).

Conclusions

From data obtained from these research results that the mixture of fining agents had a great role in 2 important parameters like hue and color intensity of wines. Those agents indicate e increase of hue in all samples. This effect was obtained cause from the clarification of wine and in this way the brightness and hue increase. But the quantitative response is not linear so the higher dose doesn't mean a better hue value, for 3 samples the better dose for a better hue value were different.

But for the other parameter, the data showed the reverse effect, so the treatment with the mixture of fining indicates a decrease of color intensity of samples. These results were related with the affinity that these agents bind component that colored the wine, like polyphenols. In this way this

component precipitate in the end of clarification and the color of wine decrease. So the wines were clearer and brightness but less colored.

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