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Acidification of musts in warm regions with tartaric acid and calcium sulfate at industrial scale

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Abstract. Acidification of musts is necessary in warm areas where high temperatures during ripening accelerate breathing combustion of tartaric acid and, in particular, malic acid in the berries. L(+) tartaric acid, L(-) or D,L malic acid and lactic acids are the only chemical acidifiers authorized by the OIV and European Community regulations. The use of calcium sulfate (gypsum: $CaSO_4{\cdot}2H_2O$) is also authorized in the European Community as a complementary acidifier in generous and generous liquor wines from Spain (a practice known as plastering), provided that the residual sulfate content in the wine does not exceed 2.5 g/L expressed as potassium sulfate. However, this practice is not yet approved by OIV. To predict the effect on pH of different acidifiers, several chemical modeling approaches have been described in the literature, in particular a simplified model where the acidity of wine is considered to be due to a monoprotic acid. The aim of this work is to verify this model at pilot and industrial scale in the acidification of musts with tartaric and calcium sulfate, added either individually and in combination, using doses up to 3 g/L and to study the modifications that these practices produce on the compositions of the resulting wines. This work supplies useful information to study this practice in OIV in order to consider its approval.

1. Introduction

The acidification of musts has the objective of reducing their pH to suitable values in order to inhibit bacterial activity, stabilize the color and improve the sensorial characteristics of the resulting wines. The intensity of the acidic taste of wines is directly related to the pH and its length with the buffering power [1]. Acidification of musts is necessary in warm areas where high temperatures during ripening accelerate breathing combustion of tartaric acid and, in particular, malic acid in the berries [2]. L(+)-tartaric acid has traditionally been the only acidification agent used to date but the latest regulations of the European Union also authorize the use of L-malic acid, D,L-malic acid and lactic acid [3,4]. The maximum authorized doses are 1.5 g/L in grape juice and 2.5 g/L in wine, expressed as tartaric acid. The use of calcium sulfate (gypsum: $CaSO_4{\cdot}2H_2O$) is also authorized as a complementary acidifier in generous and generous liquor wines from Spain (a practice known as plastering) provided that the residual sulfate content in the wine does not exceed 2.5 g/L expressed as potassium sulfate. Calcium sulfate is also authorized in the United States for the production of wines aged under yeast veil but residual sulfate cannot exceed 2 g/L [5]. Plastering is a practice that has its roots in history [6] and this approach has traditionally been used in Sherry [7–9] and Port winemaking [10]. More recently, Gómez et al. [11] recommended a combined acidification with 2 g/L of gypsum and sufficient tartaric acid to achieve a pH of 3.25. In this way, the necessary dose of tartaric acid does not exceed 1.5 g/L, the maximum authorized level, and the final concentration of sulfates is lower than 2.5 g/L. Moreover, Casas [12] proposed a semiempirical method to calculate the doses of gypsum and tartaric acid required to reduce the pH of the musts to 3.40.

Several chemical modeling approaches have been described in the literature with the aim of predicting the effect of acidification on pH and the general acid-base properties and ionic strength in white and red wines. Boulton [13] proposed a simple model in which the pH is expressed as a function of the titratable acidity, the potassium and sodium contents and the tartrate to malate ratio. Moreno and Peinado [14] updated and improved the model proposed by Usseglio-Tomasset [15] and developed a model simple and easy to apply. In this model the acidity of wine is considered to be due to a monoprotic acid. The dissociation of the acid can be represented as follows:

$$HA \leftrightarrow A^- + H^+ \tag{1}$$

The acidity constant would be

$$K_V = \frac{[A^-][H^+]}{HA} \tag{2}$$

and

$$pK_V = pH - log\frac{[A^-]}{[HA]} \tag{3}$$

which can be written as

$$pK_V = pH - log\frac{[AA]}{[TA]} \tag{4}$$

where TA is total acidity and AA is ash alkalinity.

The buffering power of the must depends on the concentration of the various ionic forms of tartaric acid in accordance with the following expression:

$$\pi = Buffering\ Power = \frac{dAc}{dpH} = 2.303\frac{[HA][A^-]}{[HA]+[A^-]} \tag{5}$$

which can be simplified as

$$\pi = Buffering\ Power = \frac{dAc}{dpH} = 2.303\frac{[TA][AA]}{[TA]+[AA]} \tag{6}$$

Buffering power can be easily determined in the laboratory and allows the calculation of AA:

$$AA = \frac{\pi \times TA}{2.303 \times TA - \pi} \tag{7}$$

All of these approximations can be applied since the variation of pH is considered to be infinitesimal.

The effect on pH of adding X meq/L of tartaric acid can be predicted by considering that

$$TA_f = TA_i + 2X \tag{8}$$

and

$$AA_f = AA_i \tag{9}$$

where the subscripts "*i*" and "*f*" denote initial and final, respectively.

In this way, the final pH value can be calculated as:

$$pH_f = pK_V + log\frac{AA_f}{TA_f} = pK_V + log\frac{AA_i}{TA_i + 2X} \tag{10}$$

After the addition of tartaric acid a precipitation of X meq/L of potassium bitartrate will occur and AA and TA will be modified as follows:

$$AA_f = AA_i - X \tag{11}$$

and

$$TA_f = TA_i + 2X - X = TA_i + X. \tag{12}$$

And the final pH would be calculated as:

$$pH = pK_V + log\frac{AA_f}{TA_f} = pK_V + log\frac{AA_i - X}{TA_i + X} \tag{13}$$

In this model it is considered that the medium is saturated in tartrate and, as a consequence, the addition of tartaric acid as an acidifying agent will introduce the common ion HT^- and this will precipitate naturally or during cold stabilization as potassium bitartrate. In this way, one can consider that all of the HT^- added will precipitate as potassium bitartrate and this does not contribute to the titratable acidity [14].

The effect of $CaSO_4$ in grape must is based on the displacement of the ionic equilibrium produced by the Ca^{2+} ion. The equilibria of two salts with limited solubility are involved in this case, namely $CaSO_4$ ($K_{SP} = 6.1 \times 10^{-5}$) and calcium tartrate [$Ca(C_4H_4O_6)$, hereafter CaT] ($K_{SP} = 7.7 \times 10^{-7}$). $CaSO_4$ dissolves up to the solubility products of the $CaSO_4$ and CaT. As the latter species is much less soluble than the former, the precipitation of CaT occurs. However, on decreasing the concentration of one of the ionic forms of tartaric acid (hereafter H_2T), a redistribution of the other occurs and, in accordance with the dissociation constants of this acid ($K_1 = 1.04 \times 10^{-3}$; $K_2 = 4.55 \times 10^{-5}$) and to replace the removed tartrate ion (hereafter T^{2-}), a proportion of the bitartrate ion (thereafter HT^-) is dissociated and this in turn is replaced by another tartrate from the dissociation of H_2T. The different ionic reactions considered are as follows:

$$T^{2-} + Ca^{2+} \leftrightarrow CaT\downarrow$$
$$HT^- \leftrightarrow T^{2-} + H^+$$
$$H_2T \leftrightarrow HT^- + H^+$$

which gives rise to the following global reaction:

$$Ca^{2+} + H_2T \rightarrow CaT\downarrow + 2H^+ \tag{14}$$

The release of these two protons leads to a decrease in the pH of the must.

The addition of Y meq/L of $CaSO_4$ removes Y meq/L of tartrate and AA and TA will also decrease to the same extent. Therefore,

$$AA_f = AA_i - Y \tag{15}$$

$$TA_f = TA_i - Y \tag{16}$$

The buffering power will be affected differently depending on whether the acidification is carried out with gypsum or tartaric acid. The increase in the fraction [HA] on adding tartaric acid should affect the numerator rather than the denominator in Eq. (6), thus causing an increase in the buffering power. Similarly, the decrease of $[A^-]$ caused by the addition of gypsum will cause a decrease in the buffering power.

The aim of the work described here was to expand on the procedure described by Gomez [11], for the acidification of musts with gypsum and tartaric acid, added either individually and in combination, using doses up to 3 g/L and to study the modifications that these practices produce on the compositions of the resulting wines. At the same time, chemical modeling of the acid-base and precipitation equilibria was carried out to calculate pH values and compare them with the experimental ones in order to predict the final pH achieved with specific doses of tartaric acid and gypsum. Through these studies the traditional practice of plastering will be explained and evidence will be provided to support this process.

Table 1. Acidification with gypsum at pilot scale.

State	**Gypsum dose (g/L)**		**pH**	**Total acidity (g/L H_2T)**	**Calcium (mg/L)**	**Sulphates (g/L K_2SO_4)**	**Potassium (mg/L)**	**Tartaric acid (g/L)**	**Buffering power (meq/L·u pH)**	**TA (meq/L)**	**AA (meq/L)**	**pKv**	**Calculated pH[3]**	**Relative error (%)**
	$CaSO_4$ $2H_2O$	$CaSO_4$												
Before AF[1]	0.00	0.00	3.79	3.67	175	nd[2]	2018	6.385	38.57	48.93	25.46	4.07	3.79	0.10
	1.00	0.79	3.67	3.60	190	nd[2]	2018	5.615	34.74	48.00	22.00	4.01	3.73	1.60
	2.00	1.58	3.53	3.67	200	nd[2]	2018	4.99	32.92	48.93	20.19	3.91	3.59	1.81
	3.00	2.37	3.41	3.60	270	nd[2]	2009	4.44	31.03	48.00	18.73	3.82	3.43	0.68
After AF[1]	0.00	0.00	3.57	3.74	40	0.53	1400	3.97	35.30	49.87	22.13	3.92	3.57	0.08
	1.00	0.79	3.49	3.82	65	1.61	1567	3.865	34.70	50.93	21.40	3.87	3.49	0.04
	2.00	1.58	3.38	4.36	100	2.60	1800	4.08	33.20	58.13	19.17	3.86	3.41	0.84
	3.00	2.37	3.28	4.48	120	3.59	1900	4.09	32.80	59.73	18.70	3.78	3.27	0.39
2 Months after AF[1]	0.00	0.00	3.69	3.56	40	0.50	950	1.98	30.40	47.47	18.29	4.10	3.69	0.12
	1.00	0.79	3.58	3.39	65	1.50	1150	1.85	27.60	45.20	16.31	4.02	3.58	0.10
	2.00	1.58	3.42	3.70	97	2.52	1400	1.86	26.10	49.33	14.71	3.95	3.45	0.75
	3.00	2.37	3.27	3.99	110	3.45	1550	1.91	26.70	53.20	14.82	3.82	3.26	0.28

[1] AF: Alcoholic fermentation; [2] nd: not determined; [3] Calculations carried out according to Eq. (17).

2. Materials and methods

2.1. Description of the winemaking process

The must for pilot scale tests was obtained in a previous harvest in a winery in the Jerez area (Southern Spain) from *VítisVinifera L* cv. Palomino Fino grapes pressed at less than 1.0 bar and without sulphites.

The industrial scale tests were carried out in two different wineries in the harvest 2014. The musts were collected in 22,000 L stainless steel tanks, and acidified after the filling of the tank. Acidified musts were stirred with mechanicals systems and recirculation to ensure a good mixture of the acidifiers. Two tanks with the same acidifier were prepared every day. The musts were settled for a minimum of 18 h, at controlled temperature, and 40,000 L of clear must were transferred to 50,000 L stainless steel tanks and fermented at 20ºC with inoculums of selected ADY *S. cerevisiae*. It should be remarked that harvest 2014 has been very uncommon because the unusual mild summer produced musts with low pH, what needed lower doses of acidifiers than usual.

2.2. Sample preparation

Samples before fermentation were taken of settled clear musts. Samples after fermentation were taken fifteen days after the end of alcoholic fermentation. An additional sampling was carried out 2 months after the end of fermentation. All samples were centrifuged and filtered through 8 μm membrane before analysis and the fermented ones were also ultrasound degassed to remove CO_2. All tests and analysis were performed in duplicate and average values are given in the tables.

2.3. Analytical methods

The pH, total acidity, potassium, calcium and sulphates were analysed by the official European Union analysis methods [16]. Buffering power was determined by titration until pH = 3 with 0.1N of HCl. The results are expressed in meq/L pH unit. Tartaric acid was determined by colorimetric method [17].

2.4. Equipment

pH-meter: Metrohm 780 pH Meter. Atomic absorption spectrophotometer: Perkin-Elmer Model Analyst 100. Multiparametric: I.S.E. Group Miura One 15.

2.5. Reagents

All laboratory reagents were of analytical grade. The water for the preparation of solutions and controls was bi-distilled. Gypsum and tartaric acid were food quality. Gypsum and tartaric acid were added directly to the must and stirred until they were dissolved.

2.6. Sensorial analysis

Sensorial analysis of samples was made two months after fermentations and carried out by the tasters' panel of Jerez-Xérèz-Sherry Regulator Council, trained with ISO 8586:2012 criteria [18]. The tasters tried to find differences only in acidity among the samples and ordered them according to the intensity of the acid taste.

2.7. Statistical treatment of data and modelling

The nonparametric data were analyzed by studying the variance for unequal sample size, using the H Kruskal and Wallis and Friedman tests. The initial processing of data, as well as the modelling were performed using Microsoft Excel 2013® (for further details, see reference [19]). Statistical analyses were performed using Statgraphics Centurion version 2.16.04 (StatPoint Technologies, USA).

3. Results and discussion

3.1. Acidifier behavior of gypsum at pilot scale

As can be seen from the results in Table 1, the addition of gypsum reduces the pH of the must before fermentation by a magnitude that is directly related to the dose, which for 3 g/L is 0.12 units/g on average. The total acidity does not increase because new H^+ ions are not created and the tartaric acid concentration and buffering power decrease due to CaT precipitation. The calcium concentration increases markedly due to the addition of $CaSO_4{\cdot}2H_2O$ and the potassium concentration does not change. After fermentation, a significant KHT precipitation had occurred due to the formation of ethanol, as shown by the decreases in tartaric acid and potassium concentrations. These decreases are directly related to initial pH due to the relationship between % TH^- and pH. However, it is necessary to take in account the fact that the pH would decrease or increase depending on whether this pH is lower or high than the pH at which the TH^- ion reaches its maximum concentration (see Fig. 1). At the same time, the reduction in pH and increase in total acidity observed can be justified by the fact that the formation of new acids during fermentation [20] is greater than the reduction produced by KHT precipitation. Two months after fermentation an additional KHT precipitation led to increases in pH values and reductions in total acidity, both by a magnitude that is in relation

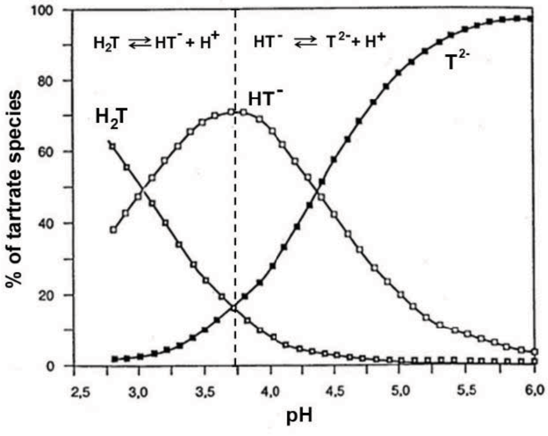

Figure 1. Variation with pH of H_2T, HT^- and T^{2-} concentrations in wine.

Table 2. Acidification with tartaric acid at pilot scale.

State	H_2T Dose (g/L)	pH	Total acidity (g/L H_2T)	Calcium (mg/L)	Sulphates (g/L K_2SO_4)	Potassium (mg/L)	Tartaric acid(g/L)	Buffering power (meq/ L·u pH)	TA (meq/L)	AA (meq/L)	pKv	Calculated pH[3]	Relative error (%)
Before AF[1]	0	3.79	3.67	175	nd	2018	6.385	38.57	48.93	25.46	4.07	3.79	0.10
	1	3.58	4.57	135	nd	1933	6.74	43.72	60.93	27.58	3.92	3.60	0.53
	2	3.43	5.47	150	nd	1766	7.19	47.8	72.93	29.01	3.83	3.41	0.57
	3	3.29	6.60	155	nd	1666	7.53	54.57	88.00	32.43	3.72	3.28	0.36
	4.05	3.24	7.65	165	nd	1566	8.115	60.98	102.00	35.76	3.70	3.15	2.63
After AF[1]	0	3.57	3.74	40	0.53	1400	3.97	35.30	49.87	22.13	3.92	3.57	0.08
	1	3.42	4.25	55	0.54	1267	4.3	37.30	56.67	22.68	3.82	3.36	1.84
	2	3.31	4.81	60	0.44	1134	4.815	39.40	64.13	23.33	3.75	3.22	2.63
	3	3.17	5.51	70	0.48	1067	5.675	43.70	73.47	25.58	3.63	3.12	1.52
	4.05	3.13	6.40	90	0.49	1033	6.155	48.90	85.33	28.27	3.61	3.00	4.06
2 months after AF[1]	0	3.69	3.56	40	0.50	950	1.98	30.40	47.47	18.29	4.10	3.69	0.12
	1	3.51	3.84	45	0.53	950	2.54	31.20	51.20	18.42	3.95	3.43	2.23
	2	3.37	4.22	55	0.47	800	2.79	31.10	56.27	17.77	3.87	3.26	3.33
	3	3.21	5.07	60	0.47	700	3.35	36.50	67.60	20.70	3.72	3.12	2.91
	4.05	3.09	5.90	65	0.48	650	3.97	40.00	78.67	22.29	3.64	3.00	3.03

[1]AF: Alcoholic fermentation; [2]nd: not determined; [3]Calculations carried out according to Eq. (18).

to the initial pH. Finally, calcium concentrations dropped from high initial values of around 200 mg/L to more suitable final values of around 100 mg/L.

As far as pH modeling is concerned, the addition of gypsum leads to decreases in AA and TA due to precipitation of CaT and the considerations: $AA_f = AA_i - Y$ and $TA_f = TA_i - Y$, were taken into account. Therefore, the chemical model used to predict the pH values for the addition of gypsum alone [14] is

$$pH = pK_V + log\frac{AA_f}{TA_f} = pK_V + log\frac{AA_i - Y}{TA_i - Y} \tag{17}$$

where Y is the dose of $CaSO_4$ in meq/L.

As can be seen from the results in Table 1, this model provides a very good prediction of experimental pH values during all of the studied fermentation steps. The fitting is very good and the relative errors are below 2%. Hence, in this case, the theory is in good agreement with pilot scale experimental results.

3.2. Acidifier behavior of tartaric acid at pilot scale

The addition of tartaric acid also reduces the pH of must in relation to the dose. For a dose of 3 g/L the pH is reduced by 0.17 units/g on average with consequent increases in total acidity and buffering power (Table 2). The tartaric acid concentrations do not increase at the same rate as a result of KHT precipitation induced by the addition of H_2T. After fermentation, a significant KHT precipitation occurs and this leads to a reduction in the total acidity of wines by a magnitude that is related to the dose of H_2T used, despite the formation of new acids. Two months later, KHT precipitation continues and there is a consequent increase in pH and reductions in total acidity, tartaric acid, potassium concentrations and buffering power.

With respect to the pH modeling, Eq. (18) is employed in this case. TA, AA and pKv were calculated in a similar way to the previous case. As discussed above, this model takes into consideration acidification plus precipitation of bitartrate; hence, these assumptions can be translated into the model in the following terms: a decrease in AA and an increase in TA, according to the amount of tartaric acid added (X meq/L). Equation employed is:

$$pH = pK_V + log\frac{AA_f}{TA_f} = pK_V + log\frac{AA_i - X}{TA_i + X} \tag{18}$$

where X is the dose of tartaric acid in meq/L [13].

As can be seen from the results in Table 2, good agreement is again observed between experimental and calculated pH values. In general, the relative errors are very low (less than 3%) and this can be considered to be a very good result.

3.3. Acidifier behavior of mixed gypsum and tartaric acid at pilot scale

The fact that all final pH values before fermentation are the same for all samples means that changes in all of the parameters depend on the doses of gypsum and tartaric acid used in each case (Table 3). After fermentation, the pH values were the same in all wines and this finding can be explained because the addition of gypsum reduces the buffering power, which leads to a variation in pH and compensates for the KHT precipitation. In contrast to the situation described in previous sections, the pH continues to decrease two months later because the low pH values are close to the pKa1 of tartaric acid (3.01) and this increases the evolution of the pH values. In any case, this fact favors the acidifying effect of gypsum.

The chemical models that have appeared in the literature to date [14] are very useful to predict pH values at different stages of the fermentation process of musts and wines at pilot scale in cases where only one acidifier is used. However, the simultaneous addition of two acidifiers in combination leads to a different situation that is certainly more complex to model.

In our case, different doses of gypsum were added and tartaric acid was added to provide a decrease in pH to approximately 3.25. Hence, it can be seen from the results in Table 3 that the higher the amount of gypsum present, the lower the amount of tartaric acid, and vice versa. The model was built in a similar way to those in the two previous cases. The parameters employed were TA, AA and pK_v, which are based on the analytical measurements. According to the results in Table 3, TA and AA decrease in all cases, but at a higher rate prior to fermentation, while pK_v remains almost constant. The chemical model employed is shown in Eq. (19) [19]:

$$pH = pK_V + log\frac{AA_f}{TA_f} = pK_V + log\frac{AA_i + Y - X}{TA_i + X} \tag{19}$$

With respect to the model, it should be noted that this is not a direct combination of Eqs. (17) and (18), as one might expect, and the changes mainly concern the denominator, where the contribution of Y meq/L of gypsum has been removed. Considering the numerator, the simple combination gives rise to some trends in the relative error values obtained that are not mathematically acceptable and also lead to some infinite errors (negative value) due to the nature of the data. For these reasons, some empirical changes (mathematical signs) were included in the final model (Eq. (19)) in order to avoid these problems. With respect to the denominator, and according to the experimental data (see Table 3), the contribution of gypsum to total acidity is almost negligible, as this factor is principally due to the addition of tartaric acid ($TA_{sample} \approx TA_{blank} + H_2T$ dose, in g/L). It can be concluded from the results obtained with Eq. (19) that, in general, the relative errors are rather good, i.e., below 6%, with only two main exceptions for the highest doses of tartaric acid; this fact can be justified because the pH values are very close to pK_{a1}, which could be considered as a critical point in the acid dissociation equilibria (Fig. 1). Therefore, the model presented here, despite its simplicity, seems to be of great interest for the prediction and control of pH after combining the addition of gypsum and tartaric acid at pilot scale, regardless of the fermentation stage.

It would be possible to enhance the model but this would certainly involve a more complex and/or more empirical approach, such as a probabilistic one [21].

Table 3. Acidification with gypsum and tartaric acid at pilot scale.

State	Gypsum dose (g/L)		H_2T dose (g/L)	pH	Total acidity (g/L H_2T)	Calcium (mg/L)	Sulphates (g/L K_2SO_4)	Potassium (mg/L)	Tartaric acid (g/L)	Buffering power (meq/ L·u pH)	TA (meq/L)	AA (meq/L)	pKv	Calculated pH[3]	Relative error (%)
	$CaSO_4$ 2 H_2O	$CaSO_4$													
Before AF[1]	0.00	0.00	0	3.79	3.67	175	nd	2018	6.385	38.57	48.93	25.46	4.07	3.79	0.10
	1.00	0.79	3.22	3.25	6.82	245	nd	1919	8.045	53.75	90.93	31.40	3.71	3.21	1.09
	2.00	1.58	2.45	3.24	5.92	270	nd	2000	7.18	48.57	78.93	28.78	3.68	3.26	0.67
	3.00	2.37	1.3	3.24	4.87	425	nd	2027	6.19	40.71	64.93	24.29	3.67	3.39	4.59
After AF[1]	0.00	0.00	0	3.57	3.74	40	0.53	1400	3.97	35.30	49.87	22.13	3.92	3.57	0.08
	1.00	0.79	3.22	3.12	5.85	130	1.55	1234	5.66	43.90	78.00	25.23	3.61	2.88	7.73
	2.00	1.58	2.45	3.13	5.75	190	2.43	1467	5.405	42.30	76.67	24.15	3.63	3.08	1.63
	3.00	2.37	1.3	3.13	5.39	200	3.50	1800	4.835	39.60	71.87	22.60	3.63	3.25	3.77
2 months after AF[1]	0.00	0.00	0	3.69	3.56	40	0.50	950	1.98	30.40	47.47	18.29	4.10	3.69	0.12
	1.00	0.79	3.22	3.08	5.70	115	1.43	850	3.29	37.40	76.00	20.65	3.65	2.68	12.88
	2.00	1.58	2.45	3.08	5.27	152	2.39	1050	3.05	35.50	70.27	19.75	3.63	2.99	2.79
	3.00	2.37	1.3	3.07	4.94	177	3.22	1350	2.56	32.10	65.87	17.68	3.64	3.26	6.21

[1]AF: Alcoholic fermentation; [2]nd: not determined; [3]Calculations carried out according to Eq. (19).

Table 4. Acidification with gypsum and tartaric acid at industrial scale.

STATE	Winery	Sample	Gypsum ($CaSO_4$) dose (g/L)	H_2T dose (g/L)	pH	Total acidity (g/L H_2T)	Buffering power (meq/ L·pH unit)	TA (meq/L)	AA (meq/L)	pK_v	Calculated pH[3]	Relative error (%)
Before AF[1]	1	Tank 4	–	0.2	3.29	4.29	55.2	57.2	41.26	3.43	3.27	0.64
	1	Tank 8	–	0.6	3.14	4.41	78.6	58.8	81.34	3.00	3.09	1.61
	1	Tank 13	1.0	0.4	3.13	4.59	92.3	61.2	116.12	2.85	3.13	0.04
	1	Tank 7	1.0	0.4	3.11	5.00	109.0	66.7	163.17	2.72	3.10	0.15
	2	Tank 2	1	1	3.37	5.08	64.43	67.35	47.86	3.52	3.33	1.03
	2	Tank 3	1	1	3.39	5.2	73.98	68.94	60.15	3.45	3.35	1.04
	2	Tank 7B	1	1.5	3.36	5.6	79.08	74.24	63.89	3.42	3.29	2.18
After AF[1]	1	Tank 4	–	0.2	3.12	5.83	33.30	77.73	17.76	3.76	3.08	1.32
	1	Tank 8	–	0.6	3.16	6.90	58.80	92.00	35.34	3.58	3.09	2.23
	1	Tank 13	1.0	0.4	3.12	6.70	35.30	89.33	18.50	3.80	3.21	2.73
	1	Tank 7	1.0	0.4	3.15	7.10	35.70	94.67	18.54	3.86	3.24	2.72
	2	Tank 2	1	1	3.18	6.19	66.87	82.06	44.93	3.44	3.15	0.86
	2	Tank 3	1	1	3.13	6.10	42.25	80.87	23.73	3.66	3.11	0.70
	2	Tank 7B	1	1.5	3.20	6.00	54.33	79.54	33.54	3.57	3.11	2.72
2 months after AF[1]	1	Tank 4	–	0.2	3.29	6.21	27.6	82.8	14.00	4.06	3.24	1.53
	1	Tank 8[4]	–	0.6	–	–	–	–	–	–	–	–
	1	Tank 13	1.0	0.4	3.18	7.11	27.8	94.8	13.82	4.02	3.29	3.60
	1	Tank 7	1.0	0.4	3.25	6.45	32.0	86.0	16.57	3.97	3.34	2.92
	2	Tank 2	1	1	3.24	6.78	63.16	89.88	39.47	3.60	3.22	0.73
	2	Tank 3	1	1	3.23	6.60	72.94	87.50	49.64	3.48	3.20	0.80
	2	Tank 7B	1	1.5	3.29	6.40	53.37	84.85	31.88	3.71	3.20	2.61

[1]AF: Alcoholic fermentation; [2]nd: not determined; [3]Calculations carried out according to Eq. (19); [4]This tank did not finished the fermentation suitably and was removed.

Table 5. Anova table of the acid scores of the acidified wines.

Sourceof Variance	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between-groups	14.75	4	3.6875	2.08	0.1132
Within-groups	44.25	25	1.77		
Total (Corr.)	59.0	29			

3.4. Acidifier behavior of gypsum and tartaric acid at industrial scale

The study at industrial scale was carried out in two different wineries in the harvest of 2014. In Winery 1, acidifications with only tartaric acid and with the mixture of gypsum and tartaric acid were used, and on the contrary, in Winery 2 all the musts were acidified with gypsum and tartaric acid.

Some analytical parameters measured, along with the calculated pH values and relative errors obtained, are collected in Table 4. The models employed were those mentioned in the previous cases, without modification. As can be seen from the results shown in both tables, the errors in pH predictions were less than 3.9%, what implies an excellent performance of the model, despite the difficulties of applying the described methodology for industrial scale: It is obvious that the control of the behavior of chemical equilibria on an industrial scale is definitively more complicated than on a pilot scale, mainly due to the difference in volume (25 vs. 30,000 L) and the difficulty in achieving complete homogenization of the media after adding gypsum, tartaric acid or both. These facts make the results noteworthy.

3.5. Sensorial analysis

The ANOVA table (Table 5) decomposes the variance of the data into two components: a between-group component and a within-group component. The F-ratio, in this case equal to 2.08, corresponds to the between-group estimate/the within-group estimate ratio. Since the *p*-value of the F-test is greater than or equal to 0.05, statistically there is no significant difference between the acid scores of the samples at the 95.0% confidence level. In other words, the acidification process based on a mixture of gypsum and tartaric acid implies no significant difference in the final product in terms of acid taste with respect to other wines treated with common and usual acidification processes.

4. Conclusion

Considering some discrete aspects of acidification with gypsum or tartaric acid, it has been verified that the addition of gypsum leads to a reduction in pH of 0.12 pH units/g/L without an increase in total acidity and a reduction in the buffering power. Moreover, the addition of tartaric acid reduces the pH by 0.17 pH units/g/L with marked increases in total acidity and buffering power. The addition of gypsum initially produces a significant increase in sulfate and calcium concentrations, although calcium decreases appreciably in the first two months. The addition of tartaric acid leads to a marked reduction in potassium concentrations because of the induced precipitation of KHT. And considering the global acidification processes, the combined addition of gypsum and tartaric acid produces an additive effect when compared to the doses of each one individually and this allows a reduction in the doses of tartaric acid necessary to achieve a pH of enological interest. Consequently, it has been verified that in warm regions it is possible to use both acidifiers in combination to reduce pH accurately. Lower amounts of tartaric acid can be used and the levels required are closer to the legal limits. Chemical modeling in which tartaric acid is considered to be monoprotic has shown excellent pH predictions for the effects of gypsum and tartaric acid in almost all cases. Finally, it has been verified that there is no significant differences in terms of acid taste among wines acidified with different acidifiers. In consequence, it can be concluded that the use of gypsum is still of great interest for must acidification in warm regions, and its use should be approved by the OIV.

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