

IMPLEMENTATION OF A DECISION SUPPORT SYSTEM FOR ACIDITY CORRECTIONS IN THE FRAMEWORK OF PRECISION OENOLOGY

George A. COJOCARU, Arina Oana ANTOCE

University of Agronomic Sciences and Veterinary Medicine of Bucharest, Faculty of Horticulture,
Department of Bioengineering of Horti-Viticultural Systems, 59 Mărăști, District 1,
011464 Bucharest, Romania, cojocaru.george@ymail.com

Corresponding author email: aantoce@yahoo.com

Abstract

Acidity corrections are currently performed in the industry in accordance to regulations and necessities. In the precision oenology for these corrections the dosage of the products used for the treatments can be calculated based on the values determined for the must and wine parameters, simplifying in this way the work of the winemaker. The performance and limits of the mathematical equations are evaluated in these paper, both for acidification and deacidification. The equation derived for acidification processes, irrespective of the acid used (tartaric, citric, malic) gives values which correlates well with the data experimentally obtained, making the application of this equation very useful. In the case of the deacidification the equation does not always give results correlated with the experimental data. For instance, the deacidification performed with alkaline salts containing potassium also react with other must/wine compounds than acids, so that the exact dosage to be used cannot be calculated. However, for the deacidification with calcium carbonate, the most used salt for these type o treatments, the equation can be applied with good results.

Key words: acidification, deacidification, decision, equation

INTRODUCTION

Acidity corrections by acidification / deacidification are necessary to give the wine stability and flavor. Such corrections are usually made when grapes are crushed for a better stabilization of potassium hydrogen tartrate during fermentation, microbial stability and flavor. Musts and wines are very complex matrices, so that precise calculation of pH and titratable acidity changes during acidification and after potassium hydrogen tartrate precipitation is very difficult without laborious analysis. For this reason we propose an easier way to calculate these changes in red and white musts prior acidification / deacidification, although not as accurate as the laborious wine analysis of a the above prepared samples would be, but satisfactory for practical purposes. A methodology with even less accurate results was proposed by Moreno et al., 2012. For better results, we modified some equations on the methodology, by taking into account the solubility of potassium hydrogen tartrate

with a correlation proposed by Ratsimba (1990) and previously used by Gerbaud, (1996) in his PhD thesis. Also, it is well known that the main complexing agents for potassium hydrogen tartrate precipitations are phenolic compounds and proteins, but potassium hydrogen tartrate can be inhibited by ionic reactions between potassium and sulphate. Potassium hydrogen tartrate precipitation changes the must titratable acidity and pH and is less affected by complexing agents in white musts than in reds, where to the presence of phenolic compounds is in greater quantities (Balakian, 1968). In white wines the titratable acidity after cold stabilization of musts was found to drop about twice as much than in red wines. The proposed methodology is less laborious, but still needs some routine analyses such the determination of pH, titratable acidity of musts and buffer capacity.

MATERIALS AND METHODS

Raw materials: White must of 'Feteasca regala' and red must of 'Dornfelder' from the

experimental vineyard of USAMV Bucharest were used for the study.

Treatments. For *acidification* treatments tartaric, malic and citric acid were applied in doses of 6.86 meq/l for the white must and 5.78 meq/l for the red must. For *deacidification*, the salts used for treatments were alkaline salts of CaCO₃, KHCO₃ and K₂CO₃, in doses of 14.82 meq/l for the white must and 10.55 meq/l for the red must.

For a better representation of results three stages of experiment were considered:

Stage 0. Determination of musts characteristics before acidification / deacidification is performed. The principal physico-chemical characteristics that are analyzed are: titratable acidity (TA, meq/l), pH, buffer capacity (β_{HCl} , meq/l / β_{NaOH} , meq/l). From buffer capacity can be computed: the alkalinity of ash (AA, meq/l) and the value for the hypothetical monoprotic acid dissociation constant pK_v, presented hereafter.

Stage 1. Determination and calculation of the acidification / deacidification effect on musts parameters (titratable acidity, pH, buffer capacity and alkalinity of ash) using the milliequivalent-for-milliequivalent basis. Two simulations are performed by computation of initial parameters and compared with the determined values obtained by physico-chemical analyses. The first one is a new model of simulation, while the second one is a model suggested by Moreno et al., 2012).

Stage 2. Determination and calculation of the potassium hydrogen tartrate precipitation effect on musts parameters (titratable acidity, pH, buffer capacity and alkalinity of ash) using the milliequivalent-for-milliequivalent basis and its solubility in musts in accordance with the temperature. For this stage, both musts were cold stabilized at 0°C for 2 weeks. Both simulations were performed on each must.

Methods of analyses and equipments: pH was determined with an Hanna pH 212 (OIV, 2009b). *Total titratable acidity* (TA) was determined with TitroLine easy Schott Instruments until the end point of titration at pH 7.0 was reached (OIV, 2009a), while the *buffer capacity* (β) was determined with the

same equipment by titration with HCl 0.1 N or NaOH 0.1 N, using 20 ml of must until 1 pH unit was dropped or raised, respectively. The calculation of buffer capacity was done using the mathematical relations presented hereafter. The *alkalinity of the ash* (AA) was calculated based on titratable acidity and buffer capacity, in accordance to the mathematical relations presented hereafter.

Calculations: In order to achieve practical goals, it will be considered that a single monoprotic acid HV is present in the must. For this case acid dissociation constant can be easily calculated based on the laboratory determinations of pH, total titratable acidity (TA) (Moreno et al., 2012). Thus, the equilibrium reaction can be represented as: $HV \leftrightarrow H^+ + V^-$.

As shown in this chemical equilibrium, the acids present in musts are partly dissociated. Anions formed in this reaction are neutralized by cations [M⁺] from the must leading to electrochemical neutrality. Thus, the following relations, can be established (Moreno et al., 2012):

$[V^-] = [M^+] = AA$ and $[HV] = TA$, where:
 [V⁻] - anions from musts; [M⁺] - cations from musts (alkali metals); AA - ash alkalinity; [HV] - undissociated acid from must; TA - total titratable acidity of the must;

In accordance to the Mass Action Law and Henderson-Hasselbalch equation (Țârdea, 2007; Usseglio Tomasset, 1992; Moreno et al., 2012), the value of acid dissociation constant (K_v) of the above equilibrium, can be calculated as:

$$K_v = \frac{[V^-] \times [H^+]}{[HV]}, \text{ where:}$$

$$pK_v = pH - \log_{10} \frac{[V^-]}{[HV]} = pH - \log_{10} \frac{[AA]}{[TA]}$$

Because the alkalinity of the ash (AA) determination is very laborious, it can be indirectly calculated by taking into account the buffer capacity and by applying the following equation (Țârdea, 2007; Usseglio Tomasset, 1992; Moreno et al., 2012):

$$\beta = \frac{L}{|\Delta pH|} = \ln(10) \times \frac{TA \times AA}{TA + AA}, \text{ where:}$$

$$\beta, \text{ meq/l} = \frac{V \times N \times F \times 1000}{|\Delta pH| \times S}, \text{ where:}$$

$$AA = \frac{\beta \times TA}{\ln(10) \times TA - \beta}, \text{ where:}$$

L – weight equivalent of a strong acid or base (HCl / NaOH) which changes the pH with one unit of one liter of must. $|\Delta pH| = pH_f - pH_i$; pH_i – initial value of pH, before titration; pH_f – final value of pH after titration; V - ml of acid or base (HCl 0.1 N/ NaOH 0.1 N) used for titration of musts; N – normality of solution NaOH / HCl (0.1 N); F – NaOH / HCl 0.1 N correction factor; 1000 – value that reports the result to a liter; S – quantity of the sample used in analysis, (20 ml); TA - total titratable acidity in meq/l, determined by physico-chemical analysis; AA – alkalinity of ash in meq/l, calculated indirectly from physico-chemical analysis of β ;

According to Henderson-Hasselbalch equation, pK_v value for hypothetical monoprotic acid in musts (equivalent to the combination of each acid present) and pH value can be calculated (Moreno et al., 2012):

$$pK_v = pH - \log_{10} \frac{[AA]}{[TA]}, \text{ where:}$$

$$pH = pK_v + \log_{10} \frac{[AA]}{[TA]}$$

After acidity corrections are performed, precipitation phenomena of potassium hydrogen tartrate and / or calcium tartrate will occur, due to the abundance of potassium and / or calcium ions and low saturation point of these salts in musts, mostly at lower temperatures. Of greater interest for calculation of changes in titratable acidity, pH, alkalinity of ash and buffer capacity is the solubility of potassium hydrogen tartrate in hydro-alcoholic solutions at different temperatures. Although, there are tables which give the solubility of potassium hydrogen tartrate in hydro-alcoholic solutions (Berg et al., 1958; Ratsimba, 1990), Ratsimba (1990) proposes an equation which correlates the potassium hydrogen tartrate solubility in hydro-alcoholic solutions with temperature and alcoholic concentrations (Gerbaud, 1996):

$$C_{KHT}, g/l = a_0 + a_1 \times a_v + a_2 \times a_v^2$$

Standard deviation of equation is 0.01 g/l.

where:

$$a_0 = 143.3747 - 1.14947 \times T + 2.319 \times 10^{-3} \times T^2$$

$$a_1 = -15.08854 + 0.114296 \times T - 2.182 \times 10^{-4} \times T^2$$

$$a_2 = 1.10444 - 8.01748 \times 10^{-3} \times T + 1.46 \times 10^{-5} \times T^2$$

C_{KHT} – solubility of potassium hydrogen tartrate, g/l;

a_v – alcoholic concentration of liquid;

T – absolute temperature, °K, where:

$$T^{\circ}K = (273.15 + T^{\circ}C);$$

$$C_{KHT}, meq/l = \frac{C_{KHT}, g/l \times 1000}{188,177 g/mol}$$

RESULTS AND DISCUSSIONS

Effect of acidification:

Stage 1. Immediate effects of acidification on alkalinity of ash, titratable acidity and pH can be computed for both, red and white musts by following relations:

$$AA_1 = AA_0$$

$$TA_1 = TA_0 + HA$$

$$pH_1 = pK_v + \log_{10} \left(\frac{AA_1}{TA_1} \right)$$

where:

HA – the quantity of acid added in meq/l;

Buffer capacity results of proposed mathematical model are very accurate, correlating well with the determined values of treated musts in the case of all acids used in the experiment (Figure 1.a.). The suggested model of Moreno *et al.*, 2012 is not so precise due to the overestimation of titratable acidity from figure 1.b. and 2.b. stage 1.

In this stage (1) alkalinity of ash remains the same as in the initial determination (Figure 1.c. and figure 2.c.). Both musts behaved similarly in stage 1.

The pH of both musts in stage 1 can be calculated using Moreno *et al.*, 2012 equation with accurate results (Fig. 1.d. – white must; Fig. 2.d. – red musts;). Slight differences in pH can be observed for both musts analyzed, due to the different dissociation constants of the three acids applied. At this stage, the mathematical models used does not take into account the pK_a 's of different acids.

Stage 2. This stage is more complex than the first one and shows that the restoration of ionic equilibrium occurs differently for each type of musts matrix. In the red musts the phenolic compounds can inhibit potassium hydrogen tartrate precipitation by complexes formed with approximately 50%. Effects of hydrogen tartrate precipitation on alkalinity of ash (AA), titratable acidity (TA) and pH can be calculated depending on the type of must, white or red, using the equations presented further.

White musts equations:

$$AA_2 = AA_1 - \frac{1}{2} \times (AA_1 - C_{KHT})$$

$$TA_2 = TA_1 - 2 \times (AA_1 - C_{KHT})$$

$$pH_2 = pKv + \log_{10} \left(\frac{AA_2}{TA_2 + C_{KHT} + (AA_1 - C_{KHT})} \right)$$

In the case of white musts that are cold stabilized (stage 2.), the buffer capacity can be accurately calculated using the relation described by Usseglio Tomasset (1992), only if the values for TA and AA are accurately predicted.

We showed that the titratable acidity can be predicted with good results (Figure 1.b. and 2.b.), while the Moreno et al., 2012 model overestimates this parameter.

Alkalinity of ash is also important for buffer capacity prediction, as well as the titratable acidity and its prediction, which is well estimated by both models used for simulation.

The pH simulation on white must was predicted very close to the determined value for all samples, irrespective of the acid used for correction. Due to the different pKa's of acids, the pH of these samples behaved only slightly differently (Figure 1.d.).

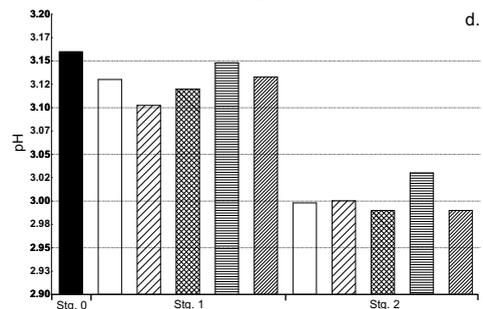
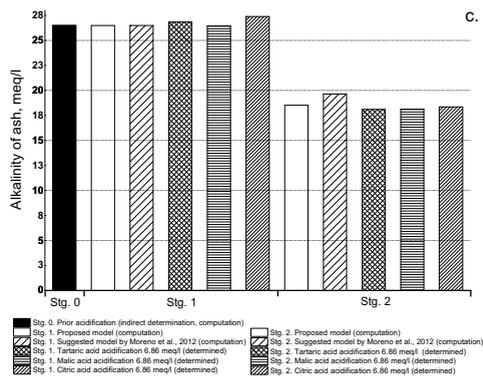
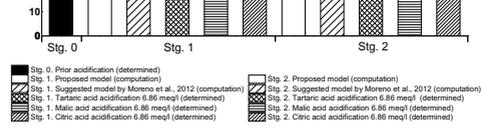
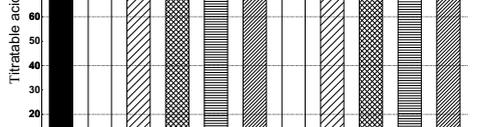
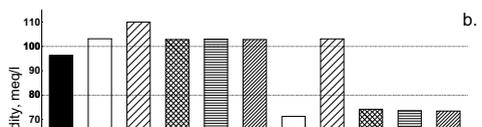
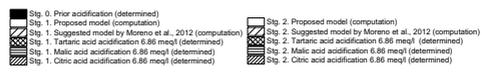
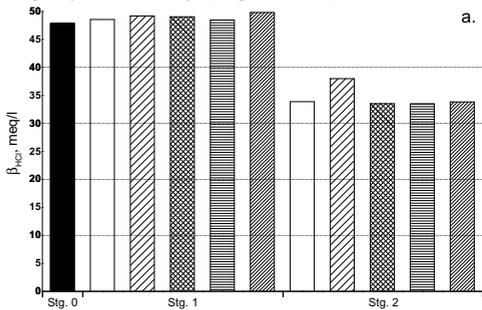


Figure 1. Effect of acidification with tartaric, malic and citric acid on white must buffer capacity, titratable acidity, ash alkalinity and pH (determined and computed values).

Red musts:

$$AA_2 = AA_1 - \frac{1}{4} \times (AA_1 - C_{KHT})$$

$$TA_2 = TA_1 - (AA_1 - C_{KHT})$$

$$pH_2 = pKv + \log_{10} \left(\frac{AA_2}{TA_2 + C_{KHT} + \frac{1}{2} \times (AA_1 - C_{KHT})} \right)$$

Red must behaved differently comparing to white must mainly due to the greater concentration of phenolic compounds.

Regarding buffer capacity of red acidified and cold stabilized musts (stage 2) the predicted values with both models are very close to the determined values (Figure 2.a.)

As in the case of white musts, in this case too, the titratable acidity is predicted accurately with proposed model and overestimated by the Moreno et al., 2012 model (Figure 2.b. and 1.b.).

Alkalinity of ash is slightly lower than determined values by physico-chemical analysis. Suggested model by Moreno et al., 2012 underestimates this parameter (Figure 2.c.).

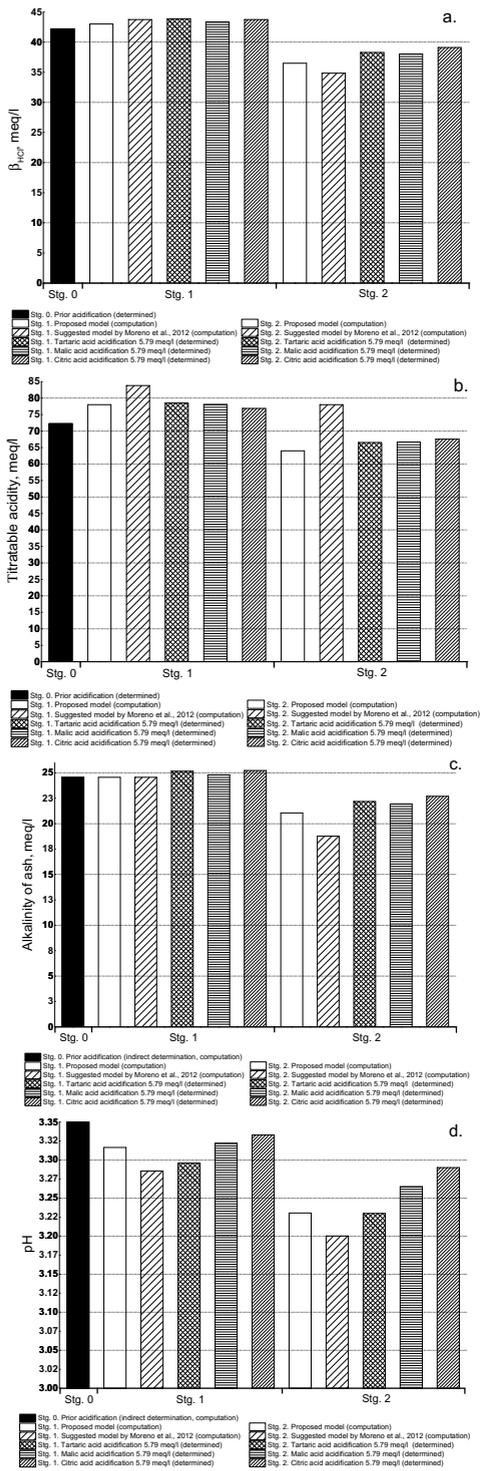


Figure 2. Effect of acidification with tartaric, malic and citric acid on red must buffer capacity, titratable acidity, ash alkalinity and pH (determined and computed values).

The pH of red wines can be predicted with good results using proposed model. Differences are higher than those obtained on white must (Figure 2.d. and Figure 1.d.) and all acids behaved slightly differently from one to another due to the pKa's and must matrix.

Effect of deacidification:

Stage 1. Immediate effects of deacidification on alkalinity of ash, titratable acidity and pH can be computed for both, red and white musts by following relations:

$$AA_1 = AA_0 + A^-$$

$$TA_1 = TA_0 - A^-$$

$$pH_1 = pK_V + \log_{10} \left(\frac{AA_1}{TA_1} \right)$$

Buffer capacity can be satisfactorily calculated using the equation proposed by Usseglio Tomasset (1992), for both red and white musts. Its variation in the experiment is due to the titratable acidity and alkalinity of ash predictions. If the titratable acidity and alkalinity of ash are well predicted, the calculated buffer capacity is similar to the determined values (Figure 3.a. and 4.a).

In the stage 1, titratable acidity and alkalinity of ash are well correlated to the determined results for both of musts used (Figure 3.b., 3.c. and 4.b., 4.c.).

Stage 2. As in the case of acidification, phenolic compounds form complexes with potassium hydrogen tartrate and increase its solubility by approximate 50%. The effects of hydrogen tartrate precipitation after cold stabilization on buffer capacity, AA, TA and pH can be calculated depending on the type of must, white or red by following relations:

White musts:

$$AA_2 = AA_1 - \Delta TA - \frac{1}{2} \times (AA_1 - \Delta TA - C_{KHT})$$

$$TA_2 = TA_1 - (AA_1 - C_{KHT})$$

$$pH_2 = pK_V + \log_{10} \left(\frac{AA_2 + \frac{1}{2} \times (AA_1 - C_{KHT})}{TA_2 + \frac{1}{2} \times (AA_1 - C_{KHT})} \right)$$

where:

$$\Delta TA = TA_1 - TA_2$$

Due to the overestimation of titratable acidity and alkalinity of ash in cold stabilized must (Figure 3.a, 3.b., 3.c.) the buffer capacity in stage 2 of white must is much greater using Moreno et al., 2012 model. As opposed, our proposed mathematical model gives for this

parameter well correlated results in stage 2 (Figure 3.a, 3.b., 3.c.).

In white must, the pH calculated with both mathematical models in stage 2 give results with some differences, depending on the salt used for deacidification. The larger difference appears in the case of potassium alkaline salts, may be due to the reactions involved in must matrix (Figure 3.d.).

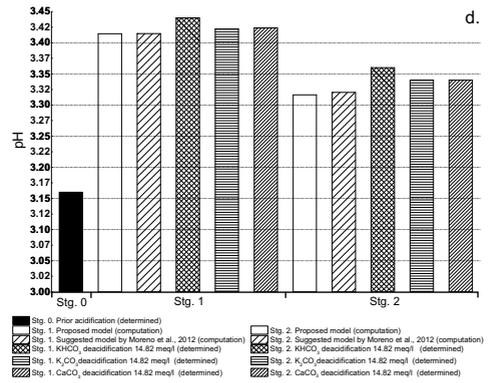
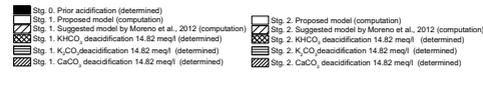
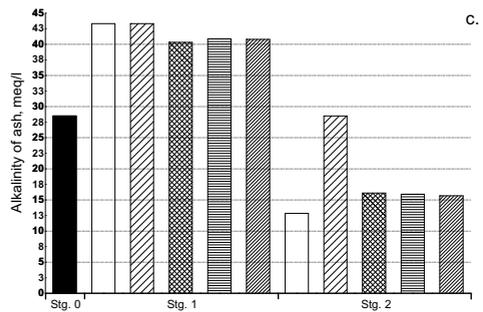
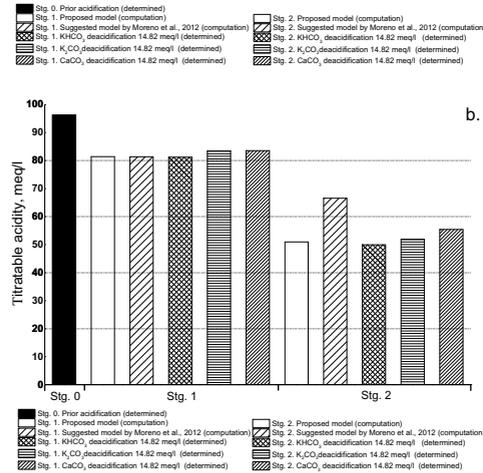
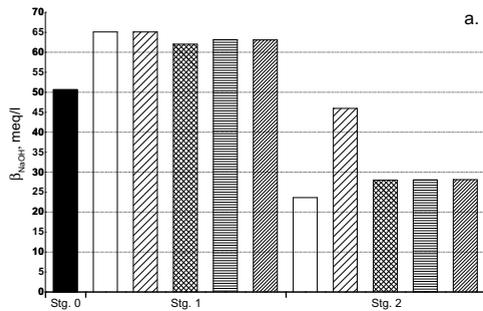


Figure 3. Effect of deacidification with potassium hydrogen carbonate, potassium carbonate and calcium carbonate on white must buffer capacity, titratable acidity, ash alkalinity and pH (determined and computed values).

Red musts:

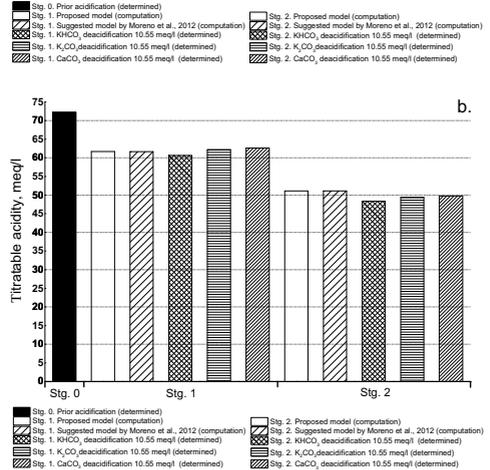
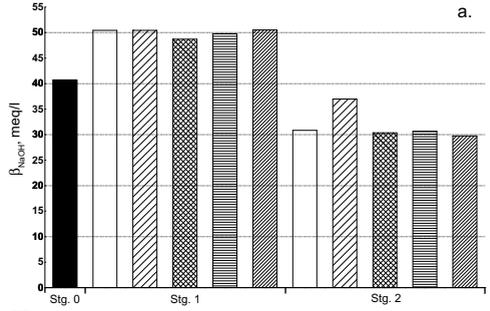
$$AA_2 = AA_1 - \Delta TA - \frac{1}{2} \times (AA_1 - \Delta TA - C_{KHT})$$

$$TA_2 = TA_1 - \frac{1}{2} \times (AA_1 - C_{KHT})$$

$$pH_2 = pKv + \log_{10} \left(\frac{AA_2 + \frac{1}{2} \times (AA_1 - C_{KHT})}{TA_2 + \frac{1}{2} \times (AA_1 - C_{KHT})} \right)$$

where:

$$\Delta TA = TA_1 - TA_2$$



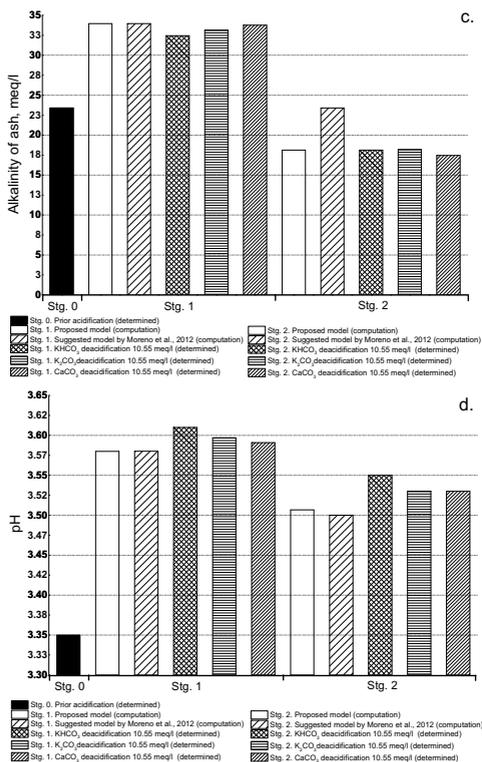


Figure 4. Effect of deacidification with potassium hydrogen carbonate, potassium carbonate and calcium carbonate on red must buffer capacity, titratable acidity, ash alkalinity and pH (determined and computed values).

Analyzing the buffer capacity in stage 2 of red must, a similar behavior of overestimation as in white musts can be observed in the case of Moreno et al., 2012 model due to the overestimation of alkalinity of ash (Figure 4.a., 4.c.).

Titratable acidity is well correlated in stage 2 irrespective of the mathematical models used (Figure 4.b.).

The pH of the red deacidified must is slightly higher in the analyzed samples than the results obtained by simulations (Figure 4.d.), probably due to the potassium reaction with another anions as the sulphate.

CONCLUSIONS

The presented results may be encouraging to be used as a decision support system in wine industry for acidity corrections and for its simplicity of computation.

The proposed model can give oenologists a quick estimation of the dose of acid or alkaline salt to be used in some musts for acidification or deacidification, respectively. Simulation models describe well the changes of must parameters after acid or alkaline salt addition.

To be on the safe side and avoid any dose overestimation or underestimation of the chemical used for the treatment, it is advisable to prepare a laboratory sample first, check the final parameters of the corrected wine and only then proceed to the industrial scale treatment.

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