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Verification of the practical suitability of cation exchangers for lowering the pH value in must and wine

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Abstract. Due to climate change, grapes are reaching continuously higher levels of technological maturity. However, this also leads to lower acidity levels and higher pH values in musts and wines. Higher pH values would result in higher risk potential regarding undesirable microorganisms, associated with wine faults. Since 2013, cation exchangers have been allowed for acidification. In addition, yeasts of the genus Lachancea releasing lactic acid during fermentation to lower the pH of the wine. In addition to lowering the pH value, cation exchangers have the advantage of increasing tartaric stability, so that other methods can be avoided. Musts were treated in repeated trials. For comparison, the process was also used in wine. In addition, the lactic acid-producing yeast Lachancea thermotolerans was used. The use of a cation exchanger in must or wine always led to a complete removal of potassium and calcium, and at the same time the pH value dropped in some cases to 2.11. Therefore, only part (20%) of a must or wine may be treated to make the final adjustment. The use of the yeast Lachancea thermotolerans could lead to an increase of up to 6 g/L lactic acid, which resulted in an increase of the total acidity.

1 Introduction

Due to climate change, grapes today often reach very high levels of ripeness even in cooler wine-growing regions. This also leads to lower acidity levels and higher pH values in musts and wines. High pH levels mean a higher risk of undesirable microorganisms that can lead to the formation of volatile acidity and other wine faults. In addition, the antimicrobial activity of SO_2 decreases with increasing pH, so higher amounts must be added for stabilization. In order to lower the pH values, acidification can be can be used to stabilize the product. In addition to tartaric, malic and lactic acid for lowering the pH in the must or wine, also the use of cation exchangers is allowed for this purpose. The classical methods to lower pH prior fermentation are additive treatments whereby the use of cation exchanging membranes are not. Currently, special yeasts of the genus Lachancea are also on the market, producing lactic acid during fermentation and thus also lower the pH value of the wine. To reduce the pH value cation exchangers have the advantage that tartaric stability is increased, so that the addition of metatartaric acid or tartaric stabilization by means of cold contact processes can be omitted. The latter would mean a considerable energy saving for wine-producing operations and additionally a contribution to the reduction of CO_2 emissions. However, due to climate change, resulting decreasing total acidity and increasing pH in must, acidification using cation exchange methods have become more in focus within the last 20 years (Lasanta et al. 2013, Ibeas et al. 2015, Ponce et al. 2018). Cation exchangers are synthetic resins which, for use in must or wine, may consist, for example, of sulfonated styrene-divinylbenzene copolymers. Cations in aqueous solution, such as potassium or calcium, bind to the sulfonic acid groups, which release a hydrogen ion into the solution for each potassium ion. When the capacity of the cation exchanger is used up, it must be reloaded. This can be done with hydrochloric acid or sulfuric acid.

2 Materials and methods

2.1 Experimental winemaking

Musts of Riesling, Pinot Blanc and Sauvignon Blanc as well as a Pinot Noir rosé were fermented and vinified in experimental replicates with pure culture yeast (25 g/h L Lalvin ICV D47TM, Lallemand Inc.). For comparison, the procedure was also used in wine with Riesling and Sauvignon Blanc. In addition, the lactic acid-producing yeast Lachancea thermotolerans (25 g/hL LaktiaTM, Lallemand Inc.) was used for Pinot Blanc and inoculated after 48 h with Saccharomyces cerevisiae (25 g/hL Lalvin ICV D47TM, Lallemand Inc.). The amount of wine that could be treated by ion exchange until it had to be regenerated again with acid and the rinsing volumes required when changing media from water to wine were tested. Commercially available cation exchange materials were Lewatit® S 1568 or Lewatit® S 1668 (Lanxess).

2.2 Analysis

Musts and wines were classically analyzed for parameters such as NOPA, density, malic acid, lactic acid and tartaric acid and pH using FTIR. During the treatment of the products with cation exchangers, the change in pH was constantly monitored using a pH meter. The contents of calcium and potassium were determined by means ofKonelab (Arena 60, Thermo Scientific).

3 Results and Discussion

Using lactic acid-producing strains (Lachancea thermotolerans) pH reduction is made possible. A strain commercialized under the brand name LaktiaTM

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(Lallemand) has already been tested in white winemaking. Pinot blanc (2018) was inoculated with 25 g/hL of LaktiaTM at the beginning of fermentation. Over-inoculation with S. cerevisiae (D47, Lallemand) occurred after 48 hours. As shown in Figure 1, the total acidity increased by almost 6 g/L while at the same time the pH was decreased by about 0.5 units. This is due to the high formation of lactic acid. The wines produced in this way are predestined as blending partners in the form of an "acid reserve", although the reproducibility over several vintages, inoculation rates and overinoculation timing need to be investigated as in the second vintage (2019) the formation of lactic acid was at 6 g/L but pH dropped only by 0.25 units.

The use of a cation exchanger in must or wine always led to a complete removal of potassium and calcium, and at the same time the pH dropped very fast. Figure 2 shows this as an example for the 2020 Pinot Noir Rosé must, in which the pH was lowered to 2.11 in the treated part of the must. Therefore, only a portion of a must or wine, for example 20%, may be treated in order to avoid pH values that are too low. Since protons are introduced into the must by the process, the total treatable acid always increased significantly during application.

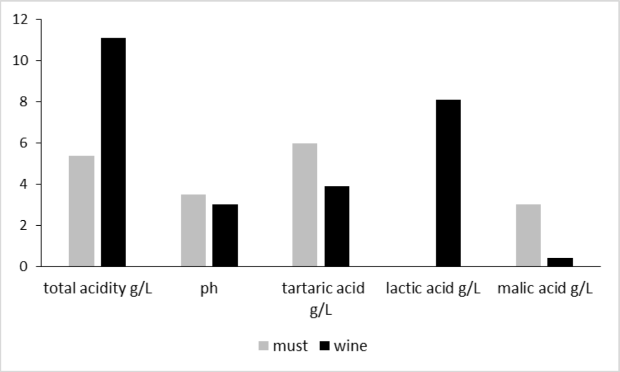

Figure 1. Change in total acidity, pH, tartaric acid, lactic and malic acid after fermentation of Pinot Blanc due to the use of Laktia™.

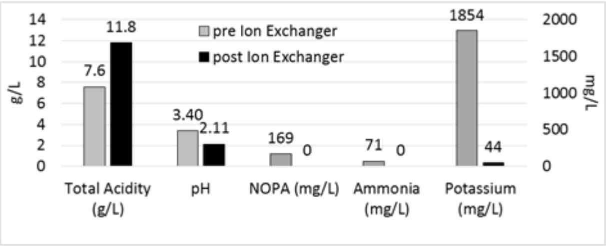

Figure 2. Analytical parameters of Pinot Noir rosé must before and after treatment with cation exchanger.

As Figure 2 further shows, ammonium as well as the yeast utilizable amino acids (NOPA) were also almost completely removed in the treated part. The treatment of a 20% partial quantity therefore leads to 20% lower nitrogen contents in the must, which may have to be compensated by yeast nutrients.

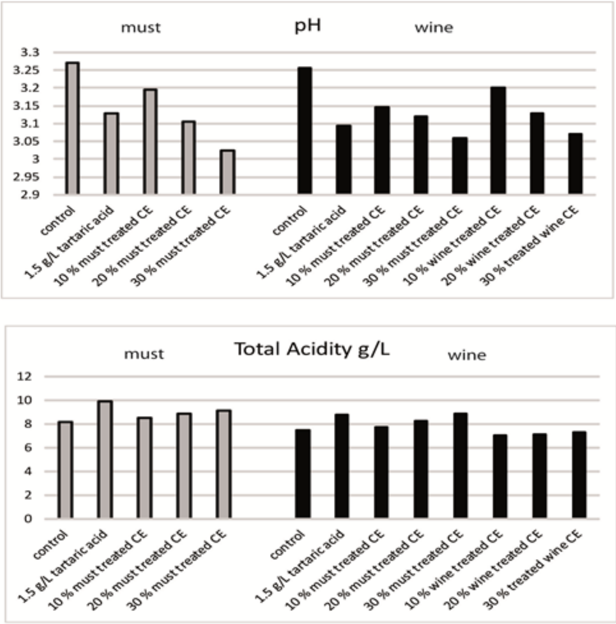

Figure 3. Influence of cation exchangers on total acidity and pH before and after fermentation.

As shown in Figure 3 less tartrate precipitated during fermentation than in the control variant. As less potassium was present in the must after treatment with the ion exchanger: As a result, the total acidity after fermentation was on average only 0.2-0.3 g/L higher than in the control. On the other hand, the addition of tartaric acid led to more tartaric precipitation, so that the total acid decreased more during fermentation than in the control or the ion exchanger-treated variants. After fermentation, the "tartaric acid 1.5 g/L" and "ion exchanger 30%" variants had the same total acidity, with the pH reduction being slightly more effective in the ion exchanger variant.

Treatment at the wine stage had less effect on pH and total acidity, since less potassium could be exchanged for protons due to the tartrate precipitation. Per 10% treated portion, the pH decreased here by only about 0.06 units. Since the total acidity increased by only 0.1 g/L at the same time, the pH could thus be shifted more strongly in relation to the total acidity than by treatment at the must stage. Since the sensory perception of acidity depends primarily on the total acidity, it is to be expected that the variants treated at the wine stage taste less acidic.

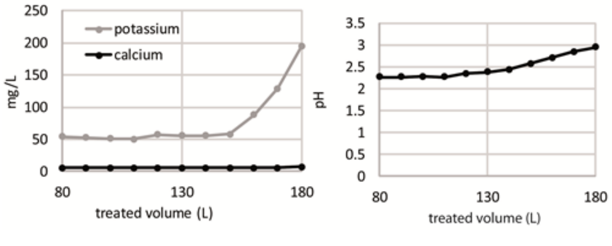

Figure 4. Change in potassium and calcium concentrations (left) and pH value (right) at the ion exchanger outlet as a function of the total volume treated.

Figure 4 is showing the capacity of the resin. If the capacity is exhausted, the ion exchanger must be regenerated with acid. The capacity was tested using the example of an ion exchanger with 8.5 L nominal volume and 6.5 L resin content on the basis of the change in potassium and calcium content, as well as the pH value in the treated wine. Figure 4 (left) shows that the potassium content increased already after 150 L of treated wine, indicating an incipient saturation of the exchanger. The calcium content, on the other hand, initially remained stable, probably because the binding power of calcium ions is greater than that of potassium due to the double charge. The pH of the treated wine began to increase after only 120 L of wine (Fig. 4, right). This parameter, which is easy to measure, is therefore well suited as an early indicator of capacity exhaustion. Regeneration should take place at the latest when the pH in the treated portion rises above 2.8, because otherwise the effect on the pH in the total volume becomes too small. In the present test, this point was reached after 170 L of wine. In practice, larger ion exchangers, for example with a resin content of 25 L, should be used.

4 Conclusion

Treatment of a 10% of the volume witha cation exchanger led to a pH reduction of about 0.1 units in must. The total acidity, which is important for sensory perception, increased by about 0.4 g/L. When the treatment was applied to wine, the effect on pH was somewhat less, but total acidity increased by only 0.1 g/L, which is unlikely to have much effect on sensory perception. It was found that one ion exchanger filled with 25 L of resin in one regeneration cycle was sufficient to treat a maximum total volume of 6500 L (at 10% treated fraction). For larger batches or a higher partial quantity to be treated, the use of correspondingly larger units is recommended. Before use, the water present in the unit must first be displaced by wine or must. It was found that at least twice the cartridge volume must be discarded before the water content in the treated wine is tolerably low. During the final cleaning process, rinsing should be carried out with five times the amount of water in order to avoid microbiological problems. Using lactic acid-producing strains (Lachancea thermotolerans) there is a very promising alternative to lower pH with fermentation and to use these wines for blending.

Acknowledgement

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