fermentation

MDPI

Review

Redox Potential and Its Control in Research and Commercial Wine Fermentations

James Nelson [1,*], Roger Boulton [1,2] and André Knoesen [3]

[1] Department of Viticulture and Enology, University of California, Davis, CA 95616, USA; rbboulton@ucdavis.edu
[2] Department of Chemical Engineering, University of California, Davis, CA 95616, USA
[3] Department of Electrical and Computer Engineering, University of California, Davis, CA 95616, USA; aknoesen@ucdavis.edu
* Correspondence: jjnel@ucdavis.edu

Abstract: Redox potential is a solution property that influences specific yeast and bacterial activities and the rate of fermentation completion. There is a need to control it if reproducible fermentation outcomes are to be achieved and reliable conclusions are drawn at both the research and commercial scale of wine fermentation. Desirable outcomes that have been observed so far in wine fermentation include the prevention of sluggish and incomplete fermentations, an enhancement in cell viability, increases in the maintenance rate of non-growing cells, and the avoidance of hydrogen sulfide formation when elemental sulfur is present. Other expected fermentation outcomes include changes in the ratios of glycerol and succinate to ethanol, certain aroma and flavor components, and sulfite formation from sulfate in the juice. The juice composition determines the redox potential's initial value, and the yeast strain's interaction with the changing juice composition determines the pattern of the potential during fermentation. This interaction also establishes the dynamic response of the prevailing redox buffer to disturbances and the ability to control the potential during fermentation. The chemical reaction sequence, entities, and speciation thought to be responsible for establishing the redox potential in juices and wine are described. A quantitative model for control purposes remains elusive. Examples of the role of added iron in juice, different yeast strains, ambient light, and the addition of external hydrogen peroxide on the response of the potential are presented. Recent examples of controlling the redox potential during white wine and red wine fermentation at a commercial scale are presented, and areas for future research are identified.

Keywords: redox potential; autoxidation; oxygen; hydrogen peroxide; tartrate; glutathione; iron; copper; complexes; fermentation; wine

Received: 1 December 2024
Revised: 19 December 2024
Accepted: 28 December 2024
Published: 2 January 2025

Citation: Nelson, J.; Boulton, R.; Knoesen, A. Redox Potential and Its Control in Research and Commercial Wine Fermentations. *Fermentation* **2025**, *11*, 9. https://doi.org/10.3390/fermentation11010009

1. Introduction

In most published descriptions, a solution's redox potential (also referred to as oxidation–reduction potential, ORP, or Eh) has been defined as the tendency of reactive solutes to accept or donate electrons. The Nernst equation is used to relate the ratio of oxidized forms and reduced forms to a measured redox potential when the rate-limiting step of a reaction sequence is known.

The stoichiometric equation for two redox components, A and D, reacting to form their corresponding redox forms, C and B, with a net change of *h* protons and *z* electrons, can be written as follows:

$$aA + bB + hH^+ + ze^- = cC + dD \quad (1)$$

and the potential at equilibrium can be related to their active concentrations and pH by the Nernst equation:

$$E_h = E_{0A/C} - E_{0D/B} = \Delta E_0 - \frac{0.0592}{z}\log\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right) - \frac{0.0592h}{z}pH \quad (2)$$

where E_h is the measured redox potential, and ΔE_0 is the difference between the standard potentials of the two redox couples.

Some researchers have tried to interpret the redox potential measurement (and changes in it) in wine in terms of standard potentials and reversible redox couples [1] and those obtained under current flow due to applied potentials using cyclic voltammetry [2]. Unfortunately, the redox potential of a solution is a dynamic outcome of the forward and backward reactions of the rate-limiting step in the oxidation sequence. The limitations to interpreting redox potential measurements from Equations (1) and (2), using standard potential equations, are that only two redox couples are used to explain the potential, each half-cell equation is assumed to be reversible, and there is a requirement for a reaction mechanism that allows the reaction to occur. If protons are involved in the rate-limiting reaction, or when dissociable ions or complexes are involved, the potential can be pH-dependent [3,4].

In most fermentation media, several alternative redox reactions can compete for electron transfers simultaneously, even for reactions involving dissolved oxygen. Some of these will be interdependent, forming a sequential chain reaction, and others can be slower, thermodynamically favored, but kinetically limited reversals or regenerations. The solution potential of such a mixture will be related to the oxidized and reduced forms of the components in a multi-step reaction sequence, and the rate-limiting step in such a sequence is likely to change during the reaction period.

The rate of oxidation in grape juice or wine is limited by the rate at which oxygen can be activated. This autoxidation sequence begins with binding molecular oxygen to a ferrous–tartrate complex and releasing reactive oxygen species (ROS), primarily hydrogen peroxide. Other reaction products include the formation of ferric–tartrate complexes and oxidized tartaric acid or dihydroxy maleic acid [5]. The regeneration steps involve the return of iron (III) complexes to iron (II) complexes as reduced glutathione (GSH) is converted to oxidized glutathione (GSSG) [6]. This regeneration step allows the cycle to continue until all the oxygen has been consumed. Cuprous–tartrate and cupric–tartrate complexes appear to react in parallel with the iron complexes, but the concentrations of the copper cations (I) and (II) in the complexes depend on both pH and the prevailing potential. Their rate of oxygen activation appears to be faster [7] and additive to that of the iron complexes [8,9]. They also undergo regenerative reactions to reform their copper (I) state, allowing further oxygen activation.

Very few ions and molecules within a mixture, such as grape juice fermentation, play a role in the limiting electron transfer reactions that determine the oxidized and reduced forms that establish the solution redox potential. The redox potential is based on the concentrations of these components and their oxidized products in the juice, the pH and temperature of the fermentation, and concentrations of redox-active components released or taken up as part of the growth and metabolism of the active organisms. Baumberger, who studied the redox potential and the rate of oxygen consumption by yeast suspensions, noted in 1939 that "the problem is one of kinetics as well as potential" [10]. This view is shared by Bokris and Reddy (1970) [11] and Peiffer et al. (1992) [12].

In the case of the two-component, single-step redox reaction, the rate equation of the forward reaction in Equation (1), expressed in terms of the forward and reverse rate constants k_f and k_r, is as follows:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_f[A]^a[B]^b + k_r[C]^c[D]^d \quad (3a)$$

And, for the reverse reaction, it is as follows:

$$\frac{d[C]}{dt} = \frac{d[D]}{dt} = +k_f[A]^a[B]^b - k_r[C]^c[D]^d \quad (3b)$$

Note that, while the rates expected in Equations (3a) and (3b) depend on the concentrations of A, B, C, and D, the mixture potential, E_h, in Equation (2), depends on their ratio. While the protons appear in the charge balance of the overall half-cell reactions, they are not expected to appear in the rate-limiting step of the electron transfer reactions.

The difference between the forward and backward rates determines the speed at which the solution potential moves toward an equilibrium. The electron transfer in proportion to the redox buffer capacity of the mixture will determine the extent of the change in potential during the reaction. The potential only changes when electron transfer takes place between the active species. At equilibrium, these rates become equal:

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d \quad (4)$$

and this can be written as an equilibrium constant, K_{eq}:

$$K_{eq} = \frac{k_f}{kr} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (5)$$

The equilibrium constant will depend on pH if the rate-limiting step of the mechanism directly involves proton(s); i.e., h greater than zero, and independent of pH if h is zero in this simple case. The pH dependency becomes more complicated when anionic ligands or cationic entities play a role and when their metal complexes are involved. The early analysis by Clark (1923) [13] suggests that these secondary pH effects are of minor importance in the pH range 3.0 to 4.0 and for potentials above −200 mV, that is, wine fermentation conditions. The mixture potential throughout a fermentation depends on which redox couple is limiting the electron transfer rate at the time.

While some oxidation–reduction reactions proceed rapidly in solution, "there are many more which proceed slowly or not at all", according to Butler (1964) [3]. In juice and wine fermentation conditions, a slow reaction rate can lead to a slow approach to equilibrium with half-times of tens of seconds to tens of minutes. This slowly drifting potential in response to an oxidative or a reductive disturbance has been confused with drifting or unreliable measurements and the dismissal of the potential as a useful process measurement.

The potential of a redox system is related to the active half-cell reactions that transfer electrons between the oxidized and reduced forms of the couples involved without any external current being applied. In chemical and biochemical systems, many possible half-cell reactions might occur. The redox potential during fermentation is determined by those that are thermodynamically favored and have a kinetic mechanism that allows the reaction between the oxidized and reduced forms to occur. Identifying the reactive couples requires knowledge of the possible mechanisms of the reactions in the medium, some of which are oxidation reactions that involve oxygen activation. In contrast, others are reductive reactions that return oxidized forms to their reduced forms and are linked to the

lower potentials of the electron transfer chain. Most redox reaction mechanisms involve one-electron transfers and two-electron transfers in exceptional cases. For this reason, most half-cell reactions cannot explain the redox potentials observed at the pH, transition metal, and organic acid composition of grape juice and wine. There is presently no quantitative reaction model that can describe the rate-limiting steps of the oxidation and reduction reactions as the fermentation progresses. Such a model would relate the concentrations of oxidized and reduced entities to the value of the solution potential. It would also estimate the response to oxidative disturbances to the composition of the mixture, that is, its redox buffer capacity. The calculation of the buffer capacity of a redox reaction couple can be found elsewhere [14].

Some researchers [15–18] have tried to interpret the values of the redox potential in terms of half-cell reactions involving oxygen, especially for cell growth and fermentations where the rate of oxygen transfer is limiting the growth rate of cells. This leads to a relationship between the redox potential and the logarithm of the dissolved oxygen concentration. Unfortunately, it only applies during logarithmic growth and when the rate of oxygen transfer limits the rate of growth. Others [16,19] have discounted the redox potential as a useful measurement for aerobic cultures and aerated fermentations and prefer the oxygen uptake rate (OUR) measurements instead. In contrast, Harrison (1972) [16] also suggested that the redox potential may be the most suitable measure of metabolic activity in anaerobic cultures, and Dahod (1982) [20] suggested that the redox potential was a more useful control variable than the dissolved oxygen at low oxygen concentrations in penicillin fermentations. Shibai et al., 1974 [21] found that the potential was useful in establishing the end-product formation of *Bacillus subtilis* under aerobic but low-oxygen concentrations. The relationship between the redox potential and dissolved oxygen in broth [22], wastewater [23], and water [24] shows a dependence on the potential with the logarithm of the dissolved oxygen concentration at high oxygen levels, but an independence when the dissolved oxygen levels are close to zero. Attempts to relate the redox potential to the concentration of dissolved oxygen have little meaning in the anaerobic and semi-anaerobic conditions, such as wine fermentations, since these are conditions where the potential is independent of the oxygen concentration. The inability to describe the redox potential in terms of the oxygen concentration in moderately aerated or anaerobic systems is due to the following: (a) only a small fraction of the dissolved oxygen can be activated and contribute to the potential at any time, (b) metal complexes in reduced states are required for this activation to occur, and (c) most chemical reactions and equilibria involving transition metal complexes with anionic ligands will be pH-dependent.

2. Use of Redox Potential in Fermentation Biotechnology

The role of oxygen in the redox reactions within a fermentation medium is likely to differ in "aerobic" and "anaerobic" conditions. In anaerobic fermentations, the nature of the rate-limiting reactions will depend on the presence and concentration of transition metals, even at trace levels (<100 μM), and the corresponding ligands that can form the complex(es) involved in any autoxidation reactions. In the case of ethanol fermentation, the mixture potential and its redox buffering are expected to be different for wine, beer, fruit wine, and saccharified cellulosic fermentations. Unfortunately, few published examples of such measurements exist in these different media.

The importance of these differences becomes significant in determining the effectiveness of control strategies using air, oxygen, or hydrogen peroxide to control the potential during fermentation. Since there are limited applications of the control of the redox potential during fermentations and considerable confusion regarding the role of dissolved oxygen in determining the mixture potential on cellular metabolic effects or fermenta-

tion outcomes, the understanding of redox control during ethanol fermentations remains poorly developed.

A feature of the redox changes observed during these fermentations is that they appear to be linked to active cell growth, even under anaerobic conditions. While the cells may be synthesizing likely reductants such as glutathione during this time, the impact of exported reductive species will meet with the reactivity and redox buffering of the other redox constituents in the medium. The buffering capacity of the redox mixture will be different at different potential values, strongest at the half-cell potentials of the rate-limiting species. Control actions, such as the addition of air, will have different impacts depending on the buffer capacity at the potential to which it is applied. This changing, non-linear medium response makes applying proportional and integral actions problematic, so on–off control actions with timed pulses are currently the preferred approach.

2.1. Relationships Between Microbial Growth and Solution Redox Potential

Table 1 summarizes significant, early examples of redox potential being measured in relation to microbial activity. The earliest example is due to Gillespie in 1920 [25], according to Hewitt (1950) [15], who appears to have introduced the term "redox potential". Subsequent studies of microbial growth and the changes in extracellular redox potential were Hewitt's studies in 1930 and those of Wood et al. (1935) [26], Yudkin (1935) [27], Ward (1938) [28] (according to Hewitt, 1950), and others, reviewed by Tizzano (1946) [29]. Hewitt demonstrated that the redox potential declined rapidly during the logarithmic phase of growth. A turning point in the potential coincided with the cessation of growth under continuously aerated and aerobic conditions for certain *Streptococci* and *Corynebacterium diphtheria*. He also noted that, with organisms that could produce hydrogen peroxide, the potential typically recovered back to starting levels after cell growth had ceased. Wood et al. (1935) [26] studied the changes in the redox potential of growing *Bacillus megatherium* and found the growth optimal in the 0 to −50 mV range at a pH of 7.2. Yudkin (1935) [27] investigated the changes in solution potential during the growth of a strict aerobe, *Bacillus alkaligenes*, a strict anaerobe, *Clostridium sporogenes*, and a facultative anaerobe, *Bacterium (Escherichia) coli*. Longsworth and MacInnes (1936) [30] showed that the lowest value of the redox potential occurred shortly after the peak rate of acid formation with *Lactobacillus acidophilus* under anaerobic conditions. Ward (1938) [28] studied the effects of different types of redox probes and agitation on the aerobic growth of *Escherichia coli* at a pH of 6.9. The starting potential of +350 mV fell to −200 mV within 24 h. He demonstrated that adding potassium ferricyanide strengthened the "poising" (i.e., redox potential buffering) of the medium potential, causing the turning point to increase to +40 mV. Quispel (1947) [31] noted that the development of an *Azotobacter* strain was related to the redox potential of the medium and needed to be above +220 mV for growth in aerobic conditions. In wine fermentations, Schanderl (1948) [32] considered that, for optimal development, wine yeast and bacteria needed to be in specific ranges of pH and redox potential. In a 1970 review, Jacob provided examples of the relationship between dissolved oxygen and the redox potential during growth with the anaerobic bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and a facultative anaerobe (*Proteus vulgaris*) [33]. More recently, De Graef et al. (1999) [34] suggested that internal $NADH/NAD^+$ ratios are related to the external redox potential and are correlated with cellular adaption in *Escherichia coli*. We believe that the same is true of *Saccharomyces cerevisiae* (and probably all other fermentation organisms), providing the link between the control of the external redox potential during wine fermentation and internal metabolic changes in response to it. The increase in viability and maintenance rates of non-growing, fermenting cells has also been observed [35]. We expect changes in the internal $NADH/NAD^+$ ratios to result in elevated glycerol and succinic acid levels at the

expense of ethanol when the potential is controlled using air. These changes have recently been reported by Duncan et al. (2024) [36] when oxygen was delivered throughout a wine fermentation. Similar results are expected in wine fermentations where the redox potential has been controlled by adding air or hydrogen peroxide.

Table 1. Relationship between microbial growth and solution redox potential.

Microorganism	Reference	Year
Streptococci	Hewitt [15]	1950
Corynebacterium diphtheria	Hewitt [15]	1950
Bacillus megatherium	Wood et al. [26]	1935
Bacillus alkaligenes	Yudkin [27]	1935
Clostridium sporogenes	Yudkin [27]	1935
Bacterium (Escherichia) coli	Yudkin [27]	1935
Lactobacillus acidophilus	Longsworth and MacInnes [30]	1936
Escherichia coli	Ward [28]	1938
Azotobacter	Quispel [31]	1947
Bacillus subtilis	Jacob [33]	1970
Staphylococcus aureus	Jacob [33]	1970
Proteus vulgaris	Jacob [33]	1970
Escherichia coli	De Graef et al. [34]	1999

2.2. Relationships Between Solution Redox Potential and Fermentation Outcomes

Despite the differing views on the suitability of the redox potential as a process variable in biochemical systems, there are several studies (Table 2) where the control of the redox potential significantly changed the behavior of microorganisms and the extent and/or composition of the fermentation products [21,37–45]. The extension of monitoring the redox potential in the growth of cultures to that in fermentations was pioneered by Hongo (1958) [37]. It was reiterated that the redox potential was beneficial in anaerobic and aerated systems. A limiting potential for the growth of bacteria was considered, concluding that a low potential condition was required before anaerobic bacteria could grow. This work appears to be the first to suggest a link between the external potential and the potential within the cells, and the ethanol and lactic acid fermentations are examples of this. It was noted that maintaining a high potential in wine fermentation is associated with a lower ethanol yield.

Tengerdy [22] investigated the relationship between the redox potential and aeration rates while producing 2-keto-gulonic acid (KGA) by a mutant *Pseudomonas* strain. These fermentations began at 0 mV and fell to −300 to −400 mV before returning to 0 mV at the of the fermentation. There was little effect on the shape and values of the potential curves during these fermentations due to the aeration rates. He also reported the effect of the potential on the byproduct formation during the continuous fermentation of the same system. The formation of KGA began after the potential had fallen to −400 mV [38].

Hongo's group also demonstrated that, in the glutamic acid, valine, and lactic acid fermentations [40–42], the product formation was altered when the redox potential was manipulated. The influence of redox potential on the formation of higher alcohol concentrations during sake fermentation was also reported by Kawahara et al. (1967) [39]. The results reported by Shibai et al. (1974) [21] show that *Bacillus subtilis* formed lactic acid at −220 mV, 2,3-butylene glycol at −195 mV, and acetoin at −160 mV as the main fermentation products and is close to the byproduct formation observed in the malolactic fermentation in wine.

Table 2. Relationships between solution redox potential and fermentation outcomes.

Fermentation Outcome	Reference	Year
Growth, ethanol	Hongo [37]	1958
2-keto-gluonic acid	Tengerdy [38]	1961
Glutamic acid	Hongo et al. [40]	1972
Valine	Hongo et al. [41]	1972
Lactic acid	Hongo et al. [42]	1972
Higher alcohols	Kawahara et al. [39]	1967
Lactic acid	Shibai et al. [21]	1974
2,3-butylene glycol	Shibai et al. [21]	1974
Acetoin	Shibai et al. [21]	1974
Glutamic acid	Izishaki et al. [43]	1974
Leucine	Akashi et al. [44]	1978
Amino acid (lysine)	Radjai et al. [45]	1985
Amino acids	Kwong and Rao [46]	1991
Xylitol	Chung and Lee [47]	1986
Xylitol	Kastner [48]	2003
Citric acid	Berovic [49]	2000
1,3 propanediol	Du et al. [50]	2007
Volatile sulfur components	Devai and De Laune [51]	1995

Izashaki et al. (1974) [43] monitored the dissolved oxygen and redox potential during a submerged, aerobic, glutamic acid fermentation by *Brevibacterium flavum*. The potential ranged from +100 to +250 mV, and they considered the potential useful at low and constant dissolved oxygen concentrations. Akashi et al. (1978) [44] used the redox potential to classify the medium conditions for leucine production in low oxygen and anaerobic fermentations with *Brevibacterium lactofermentum*. They found that the yield of leucine from glucose was highest when the potential was at −200 to −220 mV, outside of the dissolved oxygen measurement range. In the amino acid fermentations by *Corynebacterium glutamicum*, with low oxygen concentrations, the total amino acid yield was increased by 50% when an adaptive scheme controlled the agitation to hold the potential constant [45]. They reported optimal lysine production at potentials between −210 and −230 mV, optimal homoserine and valine yields at −255 to −275 mV, and optimal leucine formation at −300 mV and below at pH 7.0.

Kwong and Rao (1991) [46] employed redox control of the agitation speed for optimal amino acid production by *Corynebacterium glutamicum* at potentials between +100 and −100 mV at pH 7.2. They found that oxygen should be limited during the growth phase and made available during the non-growing phase of their fermentations. Chung and Lee (1986) [47] monitored the redox potential, dissolved oxygen, and xylose fermentation by non-growing cells of *Pachysolen tannophilus*. They used the minimum in the potential to indicate when the growth had ceased. The highest yields of xylitol and ethanol were found at potentials between −150 and 0 mV. Kastner (2003) [48] found that the optimal formation of xylitol by *Candida tropicalis* occurred at a medium potential of −100 mV. The ethanol to xylitol ratio changed between −50 and −100 mV, favoring xylitol. Berovic (2000) [49] reported, for *Aspergillus niger* in the citric acid fermentation, the control of the redox potential between +80 to +280 mV using agitator speed and aeration to control the potential at scales from 10 to 1000 L. Du et al. (2007) [50] employed a controlled redox potential growth medium to isolate mutants of *Klebsiella pneumoniae* with an enhanced capacity for 1,3 propanediol production when grown on glycerol. They used potentials in the range −190, −280, and −320 mV at pH 7.0 to achieve this selection pressure.

The formation of volatile sulfur components (VSCs) was related to the prevailing redox potential in the marshland soil suspensions by Devai and De Laune (1995) [51]. They

found that, for potentials above −50 mV, the rate of hydrogen sulfide formation was less than a tenth that of the lower potential conditions. A similar effect of less formation at potentials above 0 mV was shown for methanethiol, carbonyl sulfide, dimethyl disulfide, and carbon disulfide.

2.3. Application of Redox Potential to Fermentation Control Systems

The redox potential has been proposed as a state variable for the control of fermentation conditions [45,50,52–58] and the emphasis of these studies has been on the control of the redox potential in aerobic and semi-aerobic conditions usually to deliver optimal fermentation product outcomes.

The redox potential has also been used as a measurement variable for the control of aerated, anaerobic, and denitrifying water treatment systems [59–68]. Kim and Hao (2001) [69] employed a combination of pH and redox potential measurements to control the oscillation of an anaerobic–anoxic reactor system to promote both nitrification and denitrification outcomes under different conditions. The oscillations ranged from −200 to +400 mV at pH 7.2 to 7.6. Beard and Guenzi (1983) [70] showed that the concentrations of volatile sulfur compounds could be lowered by controlling the redox potential to 0 mV and above by bubbling oxygen gas. They noted that potentials of −100 mV and above were previously considered to be needed to prevent hydrogen sulfide; their results showed that, at 0 mV, both hydrogen sulfide and methanethiol formation were prevented. The redox potential has also been used as the control variable in preventing sulfide formation in waste slurry treatment by applying ozone [56]. They lowered the H_2S emission by more than 99%, maintaining the potential at −80 mV.

By controlling the potential at −150 mV in a pH 7 medium, changes in the genetic expression of *Saccharomyces cerevisiae* under very-high-gravity fermentation conditions (initial glucose > 250 g/L) have been demonstrated by Liu et al. (2013) [71]. Lin et al. (2010) [72] concluded that the potential had to be maintained at −150 mV (pH~7) if very-high-gravity fermentations were to finish. Liu et al. (2016) found that complete glucose consumption occurred when the potential was held at −50 mV rather than at −100 or −150 mV [73]. (While buffered at pH~7, these model media do not appear to contain glutathione or other redox components such as transition metals and organic acid ligands like those found in grape juice and are not expected to be strongly buffered in redox terms).

De Graeff et al. (1999) [34] suggested a link between the external redox potential and the internal redox potential of *Escherichia coli* growing on glucose, which determined the ratio of NADH to NAD^+ within these cells. Riondet et al. (2000) [74] showed that the carbon and electron flows were also altered due to the external redox potential in the same organism. Unfortunately, most current metabolic models of glycolysis and yeast growth do not yet consider the pH and redox potential of the external medium and do not estimate the ratios of NAD^+/NADH and $NADP^+$/NADPH, which would be related to the cytoplasmic redox potential and known byproduct formation.

3. Redox Potentials in Grape Juice and Wine Fermentation

Schanderl (1948) [32] suggested that the redox potential was more important than the pH regarding wine quality. An early review of the role of the redox potential in brewing and winemaking is due to Graff (1950) [75], who attributes the first use of the term in winemaking to Geloso (1931) [76]. Graff summarizes the early descriptions of the redox potential in wine due to two redox systems: a fast reversible reaction and a slow reaction of a declining potential that determines the developments during aging. These systems were investigated using rapid and slow redox titrations, and their apparent standard potentials were estimated. The involvement of iron and copper ions and tartaric acid oxidation were

known to play a role. Among the earliest measurements of the potential pattern during a wine fermentation is that by Joslyn (1949) [77], who reported a minimum in the potential at about the midpoint and a slow return at the end of fermentation. Joslyn and Lukton (1956) [78] demonstrated the influence of the redox potential on the formation of iron and copper cases (colloidal hazes) due to its effect on their oxidation states. They found that tannin and sulfur dioxide did not play any role as reduction components of the potential. They also found a fall in the redox potential of 200 mV after the first few hours of sunlight exposure in clear glass bottles.

Several authors [77,79,80] note that the redox potential declines slowly during wine aging when oxygen exposure is limited, such as in barrels or bottles. The role of glutathione as the component driving the potential lower during anaerobic cell growth was proposed by early investigators of how cells could alter their environment [15]. The rate-limiting reaction is expected to change throughout yeast growth and the non-growing stage of wine fermentation. This is reflected in the potential changes during the fermentation. Schanderl (1959) [81] reported that sulfite-resistant wine yeast contained up to three times as much glutathione as more sensitive strains.

In electrochemistry, the relationship space between the equilibrium redox potential and the pH of a solution can be displayed as a Pourbaix diagram [3]. The diagrams for iron and, separately, copper show the effects of both E_h and pH on the speciation of metal cations, such as Fe(II)/Fe(III) and Cu(I)/Cu)(II) [82]. The diagram for sulfur shows the inorganic reactants in solutions such as sulfate, sulfite, elemental sulfur, and hydrogen sulfide [82]. We are unaware of any Pourbaix diagrams that describe iron– and copper–tartrate and –glutathione complexes that would show the speciation and equilibrium states in juices, wine fermentation, and wines, but their development should be possible. In such an equilibrium diagram, specifying the redox potential and the pH would provide the speciation and oxidation states of species expected in the redox systems of wine fermentations.

In grape juice (and wine), the autoxidation of tartaric acid and the related electron transfer chain has recently been described by Coleman et al. (2022) [6]. The reactive entities appear to be the complexes Fe(II)–Tartrate/Fe(III)–Tartrate, which are the high potential oxidative couple that activates oxygen to hydrogen peroxide. It does not involve the Fe(II)/Fe(III) ions in their free forms. This autoxidation reaction of tartaric acid in the presence of reduced iron and air was noted by Fenton in 1894 [83], but seems to have been overlooked due to the speed of the hydrogen peroxide reaction that bears his name. The present oxidation mechanism is based on the earlier contributions of Ribéreau-Gayon (1933) [8], Rodopulo (1951) [9], and Baraud (1954) [84] formulated into a reaction mechanism that involves the one electron transfer from the Fe(II) in the complex and the other from the tartrate ligand [5]. The likely low-potential reductive couples are the reduced and oxidized forms of glutathione (GSH/GSSG) and their related iron and copper complexes. These are responsible for the return of the Fe(III) complexes to their Fe(II) complex state before further oxygen binding, activation, and oxidation can occur. The Cu(I)-ligand/Cu(II)-ligand couples, involving tartrate and GSH/GSSG as ligands, form a parallel redox system that can activate oxygen and which may facilitate the rate of reaction between Fe(III) and GSH. These copper–tartrate complexes contribute to the redox buffering in the 0 to 100 mV region. The upper potential in juices without oxygen activation is between +250 and +350 mV, while the minimum level, observed during maximum yeast growth, is between −100 and −200 mV. (Wines that have completed fermentation return to potentials between 0 and +200 mV at different rates, depending on their composition). The redox potential of a juice will move between these limits depending on its transition metal content, the availability of any dissolved oxygen, its initial glutathione content, and any increase in it due to yeast metabolism during fermentation [85]. A comprehensive study of this formation by major

strains of wine yeasts would be valuable for the understanding of redox potential in juices, fermentations, and wines. The glutathione concentration in several grape cultivars has been reported [86], but a more comprehensive mapping that might help understand its climate and vineyard practices on its accumulation in berries is needed.

In this redox reactive system, the presence of low levels of dissolved oxygen (circa 0.6 mg/L of oxygen for 1 mg/L iron) results in the formation of hydrogen peroxide, which raises the potential quickly to between +400 and +450 mV in a short-lived peak. Such peaks typically rise as much as 100 mV over 15 to 20 min before returning to the medium condition over the next 30 to 45 min [35]. The peaks are thought to be due to the formation of hydrogen peroxide, followed by its reduction, and that of Fe(III), by the oxidation of reduced glutathione within the juice, external to the yeast cells. The peak formation depends on the juice's iron content, which is all in its reduced Fe(II) state. This results in the oxidation of glutathione in the presence of Cu(II) [87] at the base of the electron chain and the return of the potential to the initial level. It appears that it is the ratio of Fe(II)–tartrate to Fe(III)–tartrate, those of Cu(I) to Cu(II) complexes, and reduced glutathione to oxidized glutathione that establishes the redox potential in juices and wine, as well as throughout the wine fermentation. These ratios of the rate-limiting entities in this reaction chain contribute to the mixture's potential and their concentrations that provide the buffering or resistance to change in the potential during wine fermentation. The changes in redox potential during the fermentation are due to changes in the oxidized and reduced forms of the rate-limiting reaction within this chain, and the limiting reaction is expected to be changing throughout the fermentation.

In other fermentation media containing traces of iron or copper, there will be a need for associated ligands, usually dissociated forms of organic acids (citrate, malate, ascorbate, lipoate, etc.), to form the required complexes capable of activating oxygen and producing hydrogen peroxide. This initiation step also involves a limited amount of oxygen. In wine, this metal complex mechanism can only consume stoichiometric quantities of oxygen before the reduced state of the Fe(II)–tartrate complex is depleted. Any additional oxygen cannot be bound and activated until the Fe(III) species return to their Fe(II) forms. In the absence of such metal complexes, it is impossible to promote oxygen activation to raise the redox potential. The ability to use additions of air or oxygen in a control loop will depend on the oxidation state of the transition metal complexes required for the autoxidation reaction. As such, the return of the Fe(II) complexes to their Fe(II) state is required before further oxygen can be consumed and more hydrogen peroxide can be produced. Low levels of glutathione, particularly its Cu- and Fe- complexes, seem to be a source of variation in returning the iron complexes to their reduced form. This determines the speed at which the potential returns to its initial value.

The transition metal concentrations, pH, organic acids, and glutathione are the significant factors that establish the redox potential and responsiveness during the anaerobic ethanol fermentations that produce cider, perry, beer, sake, and fuel ethanol. The difference between the potential curves in these fermentations will depend on the iron-activated autoxidation and the organic ligands involved since they do not contain tartaric acid. It is also important to note that these reactions and the resulting potentials are independent of the dihydroxy phenol components or tannin fractions, and white wine fermentation redox patterns are like those of red wine when temperature is considered.

3.1. Influence of Dissolved Oxygen Concentration and pH on Redox Potential in Wine

Data for wines indicate that there is no significant relationship between wine redox potentials and their dissolved oxygen concentration or pH value [77,88] in line with the view that it is transition-metal-complex-based and no protons are involved (h = 0, in

Equation (2)) in the rate-limiting redox reactions. The concentration of the activated oxygen is involved in the oxidation reaction sequence and the establishment of the redox potential. Most of the dissolved oxygen in wine is unreactive since the iron complexes are saturated by 0.6 mg/L of dissolved oxygen.

3.2. Influence of the Redox Potential on Sensory Characteristics

Early investigators [8,32,77,80,81] considered the redox potential to influence the sensory perception of wines. Schanderl describes the chemical development of "mousiness" in wines with high redox potentials, typically above +200 mV and above, and describes creating this outcome by adding hydrogen peroxide in bench trials. He considered that +100 mV was an ideal potential for the taste and aroma of wines from the Mosel region, with different values for sparkling wines and wines from the Rheingau, in part due to their higher extract. Ribéreau-Gayon considered that wines presented their optimal bouquet due to long-term aging under reducing conditions and low redox potentials. He also attributed the enhancement in the aroma of wine after the malolactic fermentation to the decline in the potential that it brings. Joslyn [77] notes that, even a month after wine is bottled, the redox potential has not returned to its long-term potential in the absence of air. Ribéreau-Gayon and Peynaud [80] note that the development of the bouquet is linked to the progressive decline in the redox potential after the disappearance of dissolved oxygen.

Today, the concentrations of secondary metabolic products are expected to be modified by conducting wine fermentations at controlled potentials. These include glycerol and succinate, higher alcohols, and acetate esters. Similarly, the redox potential of wine delivered to the tongue may provide sensory sensations due to protein folding or receptor configurations that molecular or ionic entities cannot explain.

There do not appear to be any reports in the past 50 years of sensory evaluations of wine conducted under controlled redox potentials. Given the rapid redox response in wines exposed to air and the speed of the initial autoxidation, the redox potential at the time of assessment would seem to provide significant sources of variation between wines and in the perceptions and judgments of their sensations, flavor, and mouthfeel components.

3.3. Role of Redox Potential in Wine Fermentations

Early measurements of the redox potential during wine fermentation include those by Schanderl (1948) [32], Joslyn (1949) [77], and Ribéreau-Gayon (1950) [89]. Joslyn measured the fall in potential during a white wine fermentation at a temperature of 20 °C. The minimum redox potential occurred at the time of the peak fermentation rate, at around 9° Brix in this case, and close to the halfway point of the fermentation, when the cessation of yeast growth is expected. Schanderl (1959) [81] measured the redox potential and CO_2 evolution during small-volume wine fermentations and found that fermentations in which the potential was lowered initially, using added ascorbic acid, displayed longer lag times than those without the addition. He showed the potential changes due to the ethanol and malolactic fermentations and the response to aeration and sulfite additions during the subsequent aging of the wine. He noted that yeast strains differed in their response to the redox conditions in the juice [81].

Changes in the redox potential of +150 mV due to periodic aeration occur during fermentations, as described by Ribéreau-Gayon and Peynaud (1961) [80]. They found that these spikes took 7 to 14 h to return to their starting values. They also describe a trial in which a fermentation with continuous aeration reached its minimum redox potential rate four days earlier than the unaerated reference, indicating the earlier completion of the fermentation. In all of these examples, the interpretation in the winemaking community has been that these outcomes were caused by the dissolved oxygen when, now, they appear

to be due to the prevailing redox potentials, only modified by the small fraction of oxygen activated at that time.

Rankine (1963) [90] measured the redox potential and H_2S formation during bench-scale fermentations in which elemental sulfur was added as a treatment. He showed that the maximum rate of H_2S production corresponded to the minimum in the redox potential and provided the first experimental evidence of the influence of extracellular redox potential on H_2S formation. He noted that "yeasts differed in their power to produce hydrogen sulfide during fermentation". Nevertheless, it now seems this is due to their action on the solution potential, which, in turn, favors the external chemical reaction forming hydrogen sulfide.

Kukec et al. (2002) [91] and Berovic et al. (2003) [92] measured the redox potential during the fermentation of a Sauvignon Blanc and a Cabernet Sauvignon, respectively, at different fermentation temperatures. The warmer fermentation temperatures led to lower minima in the redox potential, with a temperature sensitivity of approximately −20 mV per °C increase. This has implications for the higher temperatures in the skin cap during red wine fermentations, which are related to lower redox potentials than those measured in the juice. A 5 °C higher cap temperature can establish a redox potential of 100 mV lower. This is expected to enhance the formation of sulfides, thiols, and sulfites in the cap during red wine fermentations.

Ribéreau-Gayon and Peynaud [80] also reported faster rates and the earlier completion of aerated wine fermentations, especially in the early stages of yeast growth. It now appears that anecdotal reports related to aeration and added oxygen during wine fermentations may well be effects more accurately described as being caused by the redox potential and the cell's metabolic response(s) to it. As such, the redox response of a wine fermentation will be (a) dependent on trace levels of oxygen but essentially independent of the concentration of dissolved oxygen; (b) iron-dependent, that is, iron available as Fe(II)–tartrate complexes in its reduced state; (c) dependent on glutathione complexes for returning Fe(III) forms back to Fe(II) forms; and (d) time-dependent, due to a delay in the return to Fe(II)–tartrate before further oxygen binding and activation can occur.

3.4. The Role of Redox Potential in the Malolactic Fermentation

The growth and viability of lactic acid and malolactic bacteria, the completion of malate utilization fermentation, and changes in the formation of 2,3 butanediol, acetoin, and diacetyl are outcomes associated with the control of the solution redox potential that deserve more investigation. Ribéreau-Gayon and Peynaud [80] describe the work of Charpentie (1961) [93] in which the malate utilization was measured in a defined medium with MLF bacteria. The initial and final redox potentials were measured in continuously aerated (450 and 470 mV), once-aerated (460 and 260 mV), and anaerobic (260 and 270 mV) fermentation treatments. The malate utilizations at pH 3.83, after twelve days, were 1.5 g/L, 1.5 g/L, and 0.8 g/L, respectively. At similar conditions but at pH 3.45, the utilizations were 1.5 g/L, 1.2 g/L, and 0.13 g/L, respectively. This suggests that the growth and/or malate utilization at redox potentials beginning at 450 and 460 mV are significantly faster than those observed in most commercial wine conditions, usually less than 300, often 200, and occasionally 100 mV. It is important to recognize that this synthetic culture medium probably did not include any glutathione, which might be why the initial potential was unusually high. Regardless, there is considerable research needed into the role of the redox potential in the initiation and duration of the malolactic fermentation.

One of the few reports that include the monitoring of the redox potential during a malolactic fermentation in white wine was conducted by Nielson and Reicheliue (1999) [94]. In their bench-top fermentors, the potential began at 250 mV and fell to a minimum of 150 mV before returning to 200 mV in the anaerobic condition, with the potential minimum

coinciding with the cessation of growth shortly after the depletion of malate. The pattern differed in the semi-aerobic conditions or if 1 g/L of citric acid was added. The potential began at 260 mV and rose to a maximum of 330 mV before falling to a minimum of 270 mV when the malate was depleted. These authors also monitored the concentration of the other byproducts, such as acetic acid, diacetyl, acetoin, and 2,3 butanediol, which differed little in wine at these potentials. Ribéreau-Gayon and Peynaud also refer to a research colleague who considered the redox potential to be the most critical factor in developing bacteria and malolactic fermentation [80].

3.5. The Control of Redox Potentials During Wine Fermentations

The work of Rankine (1963) [90] suggests that H_2S formation during wine fermentation, when elemental sulfur was present in the juice, might be related to the redox potential. It showed that the peak in H_2S formation occurred at the same time as the maximum fermentation rate and the minimum in the redox potential, +50 mV (SHE). The measurement of redox potentials during wine fermentation was revived by Kucek et al. (2002) [91]. They showed the redox potential patterns during Cabernet Sauvignon fermentations at three temperatures, and Berovic et al. (2003) [92] reported similar studies in Sauvignon Blanc fermentations. In each case, the minimum in the redox potential coincided with the maximum fermentation rate and the cessation of cell growth. The effect of temperature was to lower the minimum of the potential curve at warmer conditions.

Killeen et al. (2018) [35] described the redox potential as the process variable that could be controlled by adding air during wine fermentations. This work was performed in triplicate 200 L red wine fermentations and demonstrated the control of the potential at 0 mV by only adding air pulses in a feedback control loop. The corresponding density curves displayed an earlier completion of the fermentation, and modeling pointed to this being due to faster maintenance rates and higher cell viability.

The successful control of the redox potential in large commercial wine fermentors demonstrates that wall-mounted probes are sensitive and responsive and do not appear influenced by the radial and vertical concentration gradients of the significant fermentation components (glucose, fructose, and ethanol). The control of redox potential to prevent H_2S formation in the presence of elemental sulfur has now also been demonstrated in replicated trials of Chardonnay fermentation [95]. Future studies might address the formation of reductants such as sulfite, cysteine, and glutathione using different strains and redox potential setpoints.

4. Monitoring and Control of Redox Potentials in Research Fermentations

Several unanswered questions remain regarding the effects of the controlled redox potential on the fermentation outcomes, other than the speed and extent of completion. These include what determines the present value and the magnitude of changes in the redox potential during fermentation. These are related to the role of the yeast strain, the growing and non-growing stages of fermentation, and the production and export of reduced glutathione. Other aspects involve juice composition and the responsiveness to added oxygen, which requires active complexes of iron and copper in their reduced form.

Figure 1 shows the redox potential patterns during 1 L defined medium fermentations with different yeast strains [96]. This indicates that different yeast strains respond to and have varying abilities to modify the extracellular redox potential as they grow during fermentation. This appears to be the first time such differences have been observed with wine yeast strains. The redox potential pattern during growth and fermentation has previously been used to differentiate species of lactic acid bacteria [97–100]. Future studies

might investigate the application of the redox potential pattern during wine fermentation to characterize yeast and similar studies might be initiated for MLF bacteria.

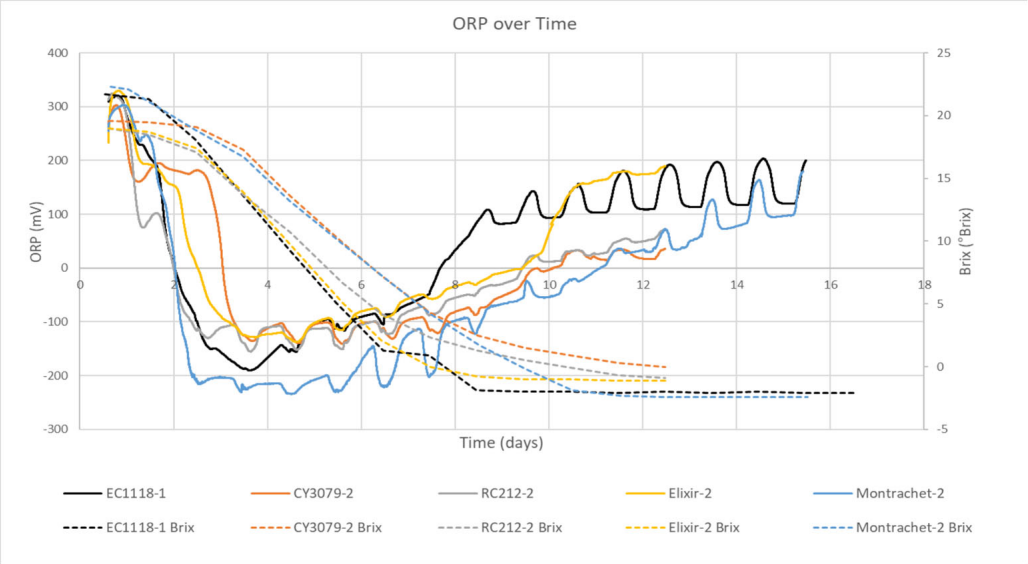


Figure 1. The density and redox potential curves of 5 yeast strains in a defined wine-like medium, in glass fermentors. Fermentations were performed at different times. Reproduced with permission from author [96].

4.1. Influence of Yeast Strain and Ambient Light on the Redox Potential During Wine Fermentation

Figure 1 shows the density and redox potential curves for five yeast strains in the same reconstituted juice. These were conducted in 1 L glass benchtop fermentors in a lab with extensive natural daylight. Daily oscillations in the redox potential for the strains EC1118 and Montrachet appear at different times during the fermentation. They are likely due to the photoactivation of redox reactions involving riboflavin and methionine or S-methyl methionine.

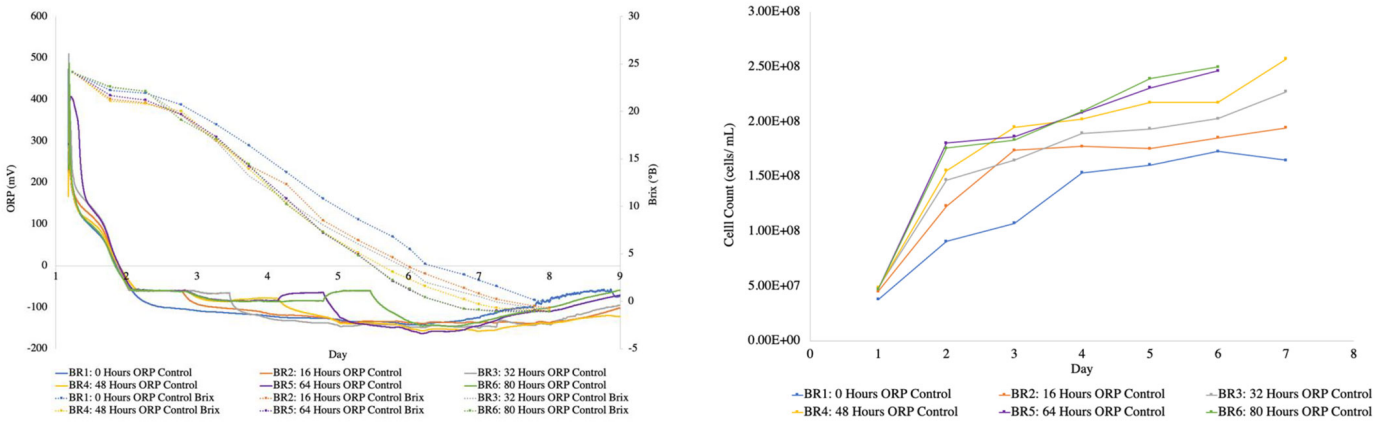
This light activation is associated with visible wavelengths in the 340 to 440 nm range, not UV wavelengths. Sunlight has previously been shown to alter the redox potential of bottled table wines [78] and in sparkling wines [101] by up to a 150 mV decline within 6 h. The oscillations in Figure 1 indicate increases and decreases expected from repeated daily light intensity exposure on clear glass fermentors. The difference in the time of their appearance and absence in other strains points to the compositional aspects associated with cellular-exporting redox-active components at different times and to various degrees. Wine yeast is known to produce significantly different concentrations of riboflavin during fermentation. Facassetti et al. (2017) [102] compared 15 yeast strains and found a two-fold range in riboflavin formation. Light excitation at 350 nm causes riboflavin to fluoresce; this property highlights its light-activated redox reactivity. While this ambient light effect was unexpected, its impact on the redox potential during daylight hours has widespread implications for the reproducibility of published research conclusions developed in glass fermentation vessels.

The major dynamic feature of these curves is the significant fall in potential between one to three days, with all strains showing a decrease of at least 350 mV and some, Montrachet and EC1118, closer to 450 mV. The time of the minimum value, or plateauing, appears to be a significant point. It is postulated that all these strains release glutathione during this period and stop when their growth or metabolism changes for other reasons. The order of this fall in potential is Montrachet, EC1118, RC212, Elixir, and CY3079. EC1118 and Montrachet

finished on day 8 and day 10, respectively, while RC212, Elixir, and CY3079 reached zero Brix after day 12. The depth of the curves appears to indicate the extent to which the yeast has released glutathione into the medium, with an order of Montrachet, EC1118, RC212, Elixir, and CY3079. It is important to note that this medium has no glutathione.

4.2. Influence of the Time of Control Action on Fermentation Outcomes

Figure 2A,B show the impact of controlling the redox potential at −60 mV for different durations during the fermentation of a juice from concentrate, 23 C, EC1118. The earliest completion is when the potential is controlled at −60 mV until zero Brix is reached after 5.5 days. This also has the fastest cell growth rate and the highest final cell mass (2.B). The uncontrolled fermentation is the last to reach zero Brix after 6.25 days, has the slowest growth rate, and has the lowest final cell mass. The difference in final cell mass is 60% higher when the potential is applied throughout the fermentation. The additional cell mass development is most obvious after the first day of growth. All other controlled redox potential durations fall between these extremes, with improved fermentation performance related to when the control was applied.



(**A**) (**B**)

Figure 2. The effect of the duration of a controlled potential of −50 mV on the density and potential curves (**A**) and cell mass growth (**B**). Reproduced with permission from author [103].

The effect of controlling redox potential is greatest at the beginning of growth (Figure 2B) and appears to last throughout these fermentations, even after the control is released in the non-growing stage of the fermentation (Figure 2A). The decline in potential is essentially the same during the first two days, and this is a juice from concentrate that is expected to contain some level of reduced glutathione.

4.3. Influence of Potential Set Point on Fermentation Outcomes

Figure 3A,B show the effect of different redox potential setpoints for the controlled potential, −30, −60, −90 mV, and uncontrolled, in a juice from concentrate, 23 °C, EC1118. The order of completion is from the highest potential set at −30 mV to the uncontrolled case. The time to zero Brix for the −30 mV case is 3.7 days, while the uncontrolled case reached this after 5.2 days. The higher potential set points significantly enhance the fermentation (Figure 3A), and growth rates and final cell mass (Figure 3B) compared to the uncontrolled case. The final cell mass is more than twice that of the uncontrolled case.

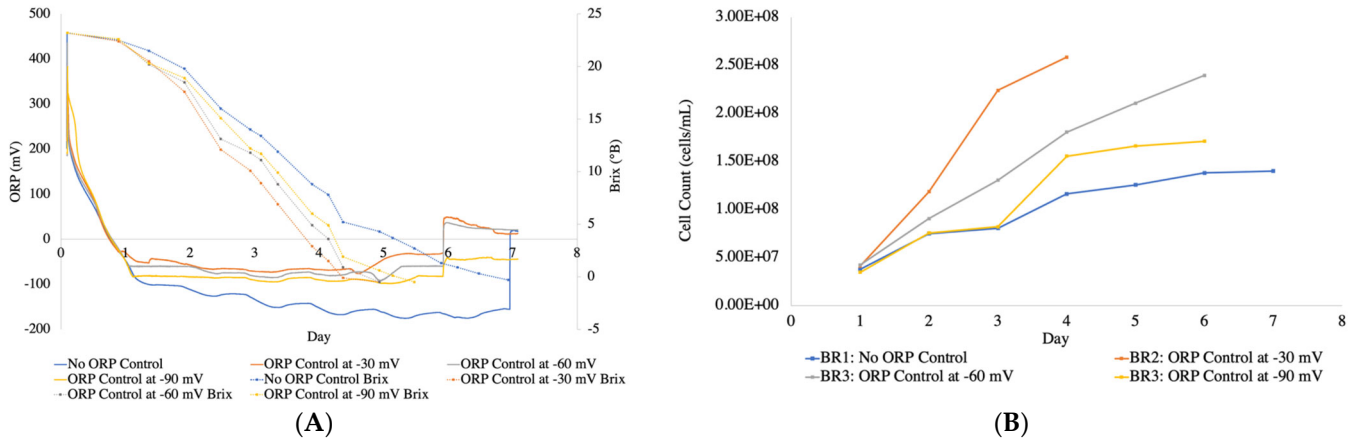


Figure 3. The effect of the setpoint potential (−30, −60, and −90 mV) on the density and potential curves (**A**) and the growth of cell mass (**B**). Reproduced with permission from author [103].

5. Monitoring and Control of Redox Potentials in Commercial Wine Fermentations

The work of Killeen et al. (2018) [35] was extended to commercial volumes 10 KL of Cabernet Sauvignon [104] and has recently been demonstrated with a 140 KL Sauvignon Blanc fermentation, (Figure 4) and a 10 KL Cabernet Sauvignon fermentation, Figure 5.

The ability to control the redox potential at −40 mV at three scales (100 L, 1.5 KL, and 10 KL) in commercial Cabernet Sauvignon fermentation has been demonstrated previously [104]. In the largest of these fermentation volumes, air was delivered in bursts of 120 s, and the frequency of addition was highest at the peak fermentation rate, as might be expected.

The initial setpoint potential for control was −40 mV for this 140 KL Sauvignon Blanc fermentation at 12 °C. The setpoint was changed to −40 mV after 52 h and lowered again to −100 mV once zero Brix was reached. This is the largest demonstration of the ability to control the potential in commercial wine fermentation. It was accomplished using a single redox probe mounted to the wall of the tank, and compressed air was delivered via an open-hole tube into the center of the tank at the base.

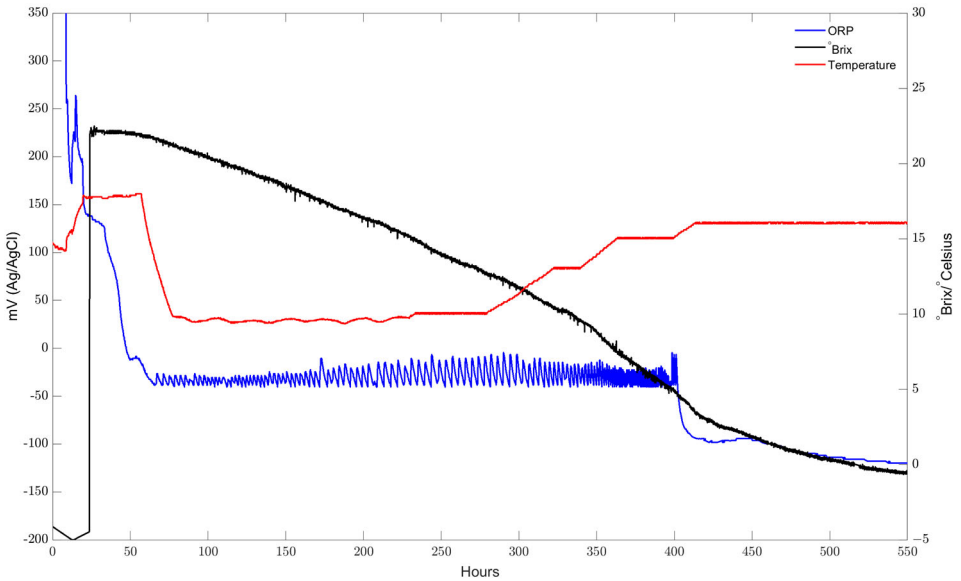


Figure 4. Controlled redox potential at scale, 140 KL Sauvignon Blanc wine fermentation at the Delegat Winery in 2024.

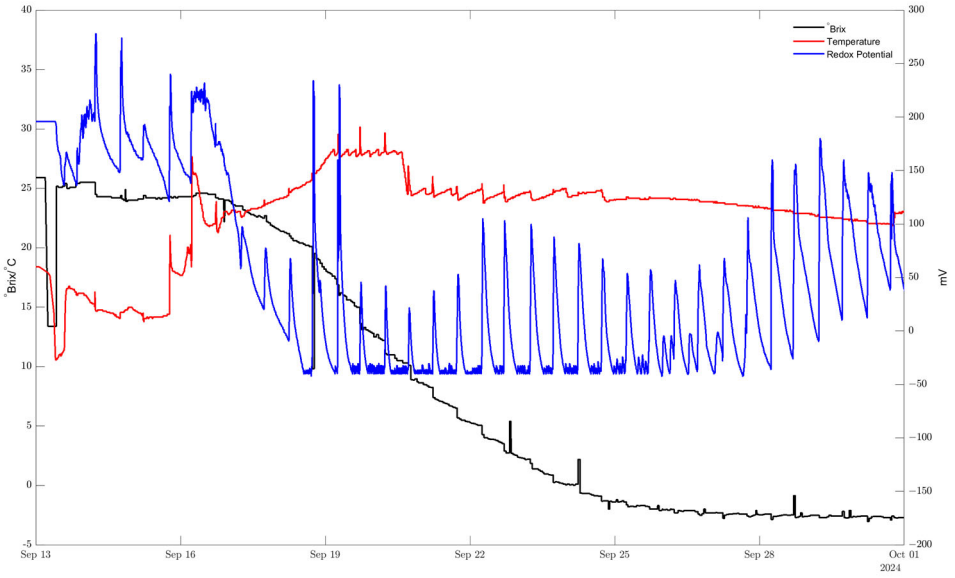


Figure 5. Monitoring of density, juice and skin cap temperatures, and juice redox potential in a 40 KL Cabernet Sauvignon fermentation at the Opus One Winery in 2024.

Figure 5 shows the ability to control the redox potential in a commercial red wine fermentation at −40 mV, using a single open tube for air additions and using short intervals (less than 60 s). In this example, the setpoint is −40 mV for a 140 KL fermentation volume and juice temperatures between 24.5 and 28 °C with a twice-daily automated mixing operation. The peaks in potential observed in response to each air addition range from 75 to 125 mV, and the frequency of addition is shown at the base of the graph. They indicate the amount of hydrogen peroxide formed due to the concentration of the iron–tartrate complex in the reduced state, in proportion to the prevailing redox buffer capacity. The two high spikes during the primary fermentation are when the air addition coincides with a pump-over operation.

There has been no indication that these full-scale trials have any undesirable sensory effects due to the control action and generally display the faster completion of the tailing stage of the fermentation.

6. Recent Research into Control of Redox Potential During Wine Fermentations

6.1. Effect of Iron Salt Addition

During our studies with different juices, there have been cases where the redox potential was less responsive to adding air. The hypothesis was that these juices were low in iron concentration and unable to develop sufficient hydrogen peroxide when oxygen was available. Figure 6 shows an example of such a fermentation where the addition of oxygen had only a limited impact on the redox potential. Air was continuously delivered to this fermentation on a 50% duty cycle; however, the redox potential fell from +125 mV at inoculation to −60 mV one day later. The addition of 1 mg/L $FeSO_4$ resulted in an increase of 100 mV in the measured redox potential. In an identical juice with no air addition (Figure 6), the same $FeSO_4$ addition showed no impact on the redox potential.

This fermentation demonstrates a possible limitation of iron or reduced glutathione in this juice. If the juice is low in total iron, adding a ferrous salt would provide a one-time generation of hydrogen peroxide related to the concentration of iron in the Fe(II) tartrate form as shown in Figure 6. The decline in the potential back to −50 mV indicates that the hydrogen peroxide has been consumed. However, if the addition of air continues, the redox response is not repeated, suggesting that the Fe(III) entities have not returned to their Fe(II)

forms to react again with the available oxygen. This one-time change indicates insufficient glutathione in the reduced form to return the iron to its reactive state. This suggests that both are needed for responsive control by air additions, and, if either is deficient, the action to control the redox potential will be limited.

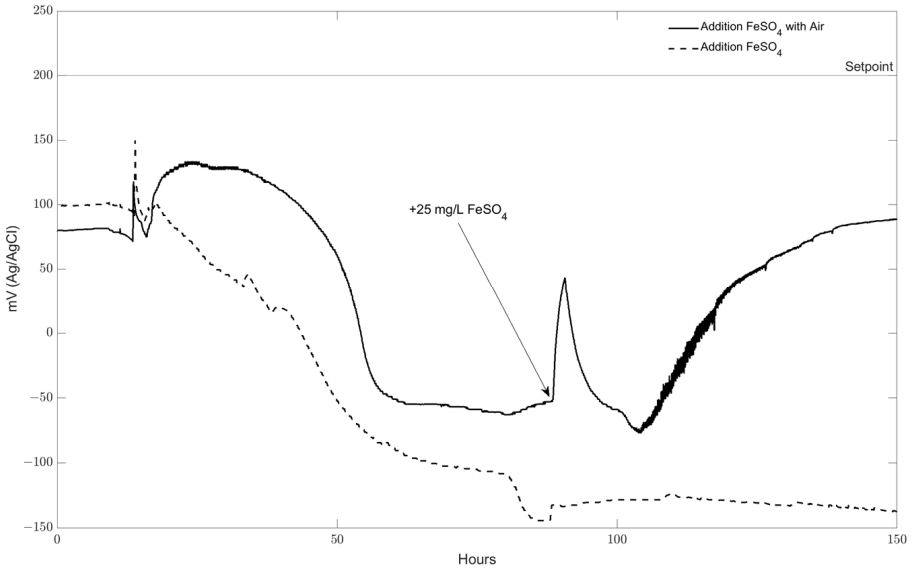


Figure 6. The effect of added ferrous sulfate on the redox potential during a wine fermentation at 20 °C EC1118 yeast strain.

Unfortunately, there is very little known about the glutathione in juices, with only one report of the glutathione concentration in different cultivars [86] and none where iron and glutathione concentrations have been reported for the same juice. It is not known how common these iron and glutathione limitations are across juices; however, some vineyard blocks are expected to show different responses to air addition, different responses to control actions, and correspondingly different fermentation outcomes.

The observation that the redox potentials of some juices respond only limitedly to controlled oxygen additions motivates the consideration of control strategies that bypass the need for iron in the Fe(II) state to initiate peroxide formation and control action.

6.2. Application of Hydrogen Peroxide for Control of the Redox Potential

As an alternative to air additions, hydrogen peroxide has been added to aerobic fermentation as reported previously [105]; however, this was not to modify or control the redox potential of the fermentation. Since the first product that results from the activation of oxygen by the iron(II)–tartrate complexes in grape juice is hydrogen peroxide, the direct addition of it would remove the dependence on, and possible limitation of, the reduced iron complex concentrations and the pH dependence of the oxygen activation reaction.

Figure 7 shows the control of the redox potential in 200 L red wine fermentation with a dilute hydrogen peroxide solution delivered via a peristaltic pump. The redox potential was successfully maintained at −40 mV throughout the fermentation at 25 C. This appears to be the first demonstration of controlled hydrogen peroxide additions to maintain a set point potential during wine fermentation (Nelson 2022, unpublished data). Note that, while the potential rises approximately +100 mV due to the addition, when a pump-over operation coincides with the addition, the rise is approximately +200 mV. In both cases the potential declines back to −40 mV due to the action of reduced glutathione in the juice, typically within 30 min.

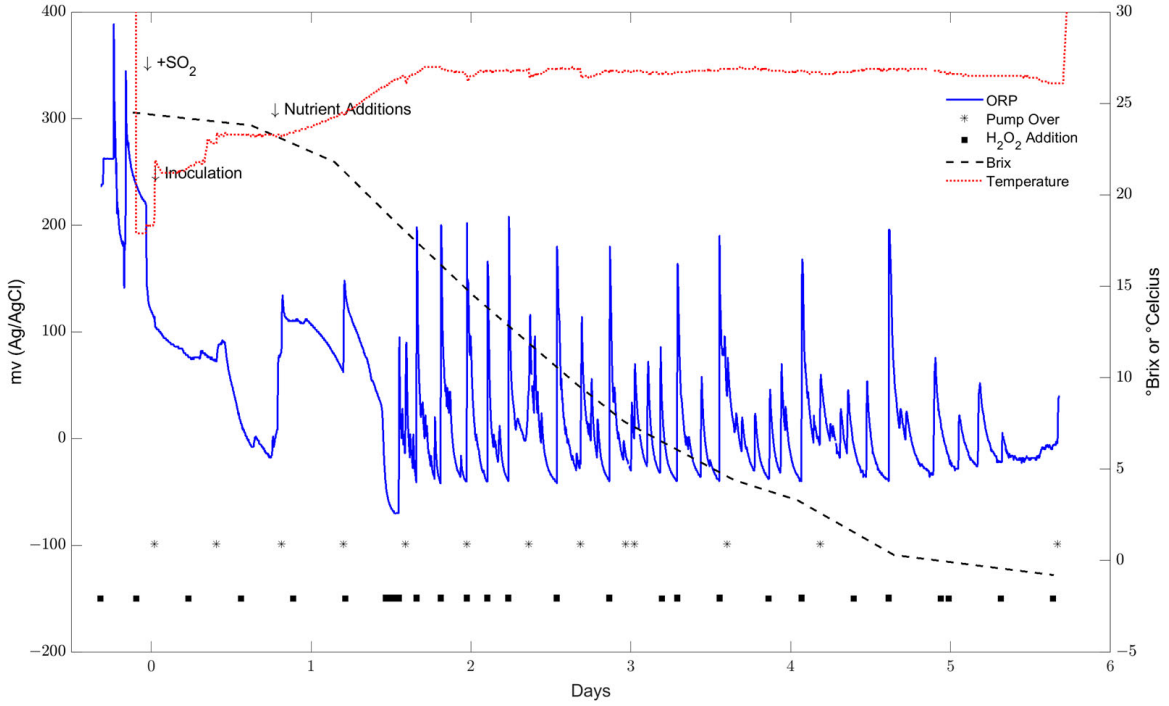


Figure 7. Redox potential is controlled at −40 °C by adding a dilute hydrogen peroxide solution in wine fermentation at 26 °C. Laffort B0213 yeast.

7. Future Directions for the Understanding of Controlled Redox Potential to Research and Commercial Wine Fermentations

Applying a controlled redox potential to ensure reproducible fermentation outcomes in research and commercial winemaking raises questions about several prior conclusions regarding juice composition, yeast and bacterial metabolism and properties, and the physical, chemical, and biochemical aspects of wine fermentations. The precision introduced by the control of the redox potential during wine fermentation is likely to drive changes in some commercial fermentation practices that affect the cap temperature of red wine fermentations and the delivery and mixing of added air in all fermentations.

There is a more complete understanding of redox potentials and the redox reactions in grape juice and wine. The knowledge of the behavior of reactive mixtures made up of several redox couples competing for the preferred electron transfers is meager at best. The usual application of Nernstian couples at equilibrium seems to have little application when the fastest reaction rates determine the short-term outcomes, often at the expense of thermodynamically preferred but slow reactions in such mixtures. The changing nature of a chain reaction sequence and a need for regeneration reactions if the initial reaction continue to make such simplistic interpretations unhelpful.

Below are several topics that might be considered in future research on the effects of the redox potential during wine fermentations, as well as long-term aging and sensory interactions.

7.1. Juice Composition of Redox-Active Components

There is a need for the development of specific panels of juice composition aimed at a better understanding of these redox active components. This would include the concentrations of iron, copper, and other transition metals, as well as glutathione in its reduced and oxidized forms and other possible reducing components. Estimating the extent of complex formation and concentrations of the redox reactive species is likely. Nevertheless, we cannot predict the redox potential of unreactive mixtures, let alone of redox reactive media such as those found during wine fermentations.

7.2. Influence of Medium Composition, Yeast Strain, and Redox Potential

The redox potential of the medium should be considered a stress factor, like temperature, pH, ethanol concentration, and osmotic pressure, and, so, future research might be directed towards investigating the metabolic and genetic expression of yeast and bacterial strains during wine fermentations. Studies in controlled redox potential media are needed to re-evaluate previous findings regarding yeast strain differences in nutrient requirements, growth rate, cell yield, maintenance, cell viability (or fermentation activity), and proton and ionic transport systems.

7.3. Sulfite Formation During Fermentation

Future studies might quantify the effect of the controlled redox potential on sulfite formation and its capture as the aldehyde sulfonate during ethanol fermentation. This adduct typically accounts for more than half of the total sulfur dioxide found in commercial wine. Applying a controlled redox potential is a promising possibility to lower the amount of the sulfite formed during fermentation, the amount of the acetaldehyde-bisulfite adduct developed, and the total sulfur dioxide in the finished wine.

The next step would be to search for controlled potentials that can suppress sulfite formation and its subsequent trapping of acetaldehyde during wine fermentation. This could lead to lower total sulfur dioxide levels in finished wines and less acetaldehyde, which can be released when the free sulfur dioxide declines during aging or long-term storage.

The sulfate reduction metabolism in yeast and its relationship to the external redox potential might provide new information regarding gene expression and sulfite and sulfide formation. Wine strains have been classified as low- and high-sulfite producers [106]. However, the outcomes observed still differ between synthetic and natural grape juice, suggesting a medium property or compositional aspect to the conclusions of the genetic selection studies [107]. The redox potential of the fermentation medium might be one of those factors.

7.4. Hydrogen Sulfide Formation During Fermentation

The recent demonstration of suppressing H_2S formation from elemental sulfur simply by controlling the redox potential during fermentation is a significant winemaking solution to an age-old problem [95]. This result of elemental sulfur added to Chardonnay juice needs to be extended to larger commercial volumes and across the range of commercial wine yeast strains. In the case of red wine fermentations, where elemental sulfur residues can remain attached to grape skins and pulp, the higher temperatures developed in the skin cap make the redox potential in the cap lower than in the juice and, hence, more likely to allow the formation of hydrogen sulfide. The practical solution in this case is to consider the control of the cap temperature independently from that of the juice.

7.5. Glutathione and Cysteine Formation During Yeast and Bacterial Growth

Yeast strains are expected to differ in their response to, and impact on, the redox potential during growth and fermentation. Future research should investigate their ability to lower the redox potential during growth and the effect on their glutathione synthesis and release. While sulfide and sulfite formation have generally been considered essential by-products of yeast metabolism, renewed attention might be directed to understanding the role of the redox potential in forming these components due to the yeast's glutathione and sulfur metabolism. The environmental and compositional factors in the juice that influence the glutathione formation by the wine yeast and bacteria also need to be quantified.

7.6. Glycerol to Ethanol Ratios in Wine Fermentation

The inability to modify the glycerol-to-ethanol ratios by genetic modifications suggests that these are dynamically linked reactions involved in the regeneration of NAD^+ that are part of the internal redox equilibria involved in glycolysis. A similar view of the formation of succinate and higher alcohols in parallel with ethanol formation appears to be part of the collection of reactions aimed at maintaining internal redox potential to favor the rate of the acetaldehyde to ethanol step. The current genetic and metabolic understanding of these capabilities in yeast might provide insights into the sensing, signaling, and response due to the redox potential in the juice during wine fermentation. Since this review was prepared, a recent study [36] of the effect of air exposure/aeration on the significant secondary components shows that glycerol and succinate are formed at higher concentrations at the expense of ethanol.

7.7. Bacterial Growth, Malate Utilization, and Malolactic Fermentation

Since controlled redox conditions during ethanol fermentation now exist, revisiting the redox environment of a concurrent malolactic fermentation and applying the controlled redox potential to the fermentation conditions would seem to be important research initiatives for improving the duration and completion of malolactic fermentation in wine.

The closest examples of the redox potential during the growth of lactic acid bacteria have been studied in milk fermentation [97–100]. Larsen et al. [100] followed the potential changes during the growth of 10 lactic acid bacteria in sterilized skim milk *Leuconostoc mesenteroides*, a similar organism to the more common MLF bacteria in wine developed from +300 to −240; independent of air exposure, all indicate starting potentials of +250 to +300 mV and falls of between −225 and +60 mV depending on the strain.

The common feature of many bacterial strains is a preferred starting potential from +200 to +300 mV. This might be the case in some wines, but it is likely not in others. Investigations into the starting or controlled potential might provide insights into the faster initiation, completion, and successful malolactic fermentation in wines. The control of the redox potential would be a natural follow-on from these studies when optimal set point potentials have been identified. Attention might also be directed to the practice of concurrent yeast and bacterial fermentations at controlled potentials, which might provide more reliable and reproducible outcomes for both.

7.8. Control of Unwanted Microorganisms

The growth, survival, and byproduct formation of organisms such as Brettanomyces, Acetobacter, and others are expected to display characteristics that are a function of the prevailing redox potential of their environment. Like other areas of fermentation microbiology, they have generally been described in terms of aerobic or anaerobic metabolism rather than an understanding of the reactions involved in establishing the redox potential. They have commonly been investigated in terms of their nutrients, pH, and temperature requirements for growth when it is now apparent that the redox potential may play a role in these outcomes. Future research might focus on the response of these organisms to the potential required for their growth and that developed during the aging and conservation of wines after ethanol fermentation.

7.9. Influence on Sensory Impact Components and Sensory Perception

Schanderl (1948) [32] and (1959) [81], Joslyn (1949) [77], and Ribéreau-Gayon and Peynaud (1964) [80] all believed that there was an optimal range of redox conditions for the sensory evaluation of a wine, generally below 100 mV. They also shared that the slow, desirable aging reactions are due to ongoing redox reactions that result in a progressive

decline in the potential of bottled wines once the initial exposure to oxygen has been consumed and further intake has been limited by the closure. The character has been called a "bottle bouquet" and takes several years to develop. The nature and chemistry of these anaerobic redox reactions deserve further investigation.

A final frontier that is now possible to approach is the reproducible investigation of the role of the redox potential on the delivery and headspace presence of sensory impact components, primarily VSCs. It is understood that the binding of thiols and disulfides can form different complexes with the copper in its (I) and (II) oxidation states. The headspace concentrations of these components are directly related to the free, unbound forms in the solution. Due to its redox reactivity, the ratio of these oxidation states will vary considerably as a function of the prevailing redox potential in the wine.

Some believe that some oral sensations associated with tasting wine, such as mouthfeel, bitterness, and "minerality", might be partly related to the prevailing redox potential while the wine is in the mouth. The current understanding of taste receptors, substrate binding, and three-dimensional protein structures may be influenced by the potential within the liquid at the wine–saliva–tongue–receptor interface. Future research might explore such phenomena using well-controlled redox conditions.

Drifting and variable redox potentials have been occurring in all previous fermentation and winemaking trials and the sensory valuation of them. The control of the redox potential should become a standard experimental requirement for all fermentation research, just as those of the temperature of medium pH are currently.

7.10. Alternative Strategies for the Control of the Redox Potential During Fermentation

The role of temperature on the redox potential during fermentation [91,92] implies that alternative methods to prevent high temperatures of the skin cap during red wine fermentations are needed if hydrogen sulfide formation is to be prevented. Current practices that involve pump-overs, punch-downs, delestage, and periodic aeration are not sufficient to have lasting effects on the potential during red wine fermentation. While these practices can modify the potential momentarily, they cannot be repeated frequently enough and consistently to deliver the outcomes of an automated redox potential control loop.

Some work described above suggests that the redox potential might only need to be controlled during yeast or bacterial growth to deliver the desired outcome. While there is clear evidence that there are positive effects on the viability and maintenance rate of the non-growing cell mass, this may be due to the redox conditions during growth that carry over into the non-growing population. If so, the application of the control of the redox potential may only be required during the growth period. The termination of yeast growth corresponds to the maximum fermentation rate, which is easily estimated from the derivative of the density curve.

8. Conclusions

The nature of the redox potential in grape juice and its behavior during wine fermentations appears unique. Initial potentials of +200 to +300 mV can fall to −100 or −200 mV within a day and can respond to added air within minutes, depending on the iron, copper, and glutathione content of the juice.

Controlling the redox potential has demonstrated outcomes such as earlier-finishing and more complete fermentations, the prevention of hydrogen sulfide formation in the presence of elemental sulfur, increases in the growth rate due to controlled redox potential by air additions, and the recognition of differences between yeast strains in their redox sensitivity and fermentation performance.

An alternative method of controlling the redox potential of wine fermentation, the direct addition of hydrogen peroxide, has been demonstrated. Instead of air addition, this bypasses the need for oxygen activation by an iron–tartrate complex, where iron or reduced glutathione is limited in the fermentation medium.

The full-scale applications of controlling the redox potential in commercial fermentations of Cabernet Sauvignon (10 K and 12 KL) and Sauvignon Blanc (140 KL) have been successfully implemented.

Several research topics have been presented in which the impact of the redox environment on the outcomes is expected. This reactive mixture property of culture media and grape juices may have been an invisible, uncontrolled variable that has led to unexplained reproducibility or variance in the cell growth, survival, and fermentation product outcomes. A clearer understanding of the factors contributing to the redox potential during wine fermentation provides exciting new developments in winemaking and a wide range of related food, beverage, and pharmaceutical fermentations.

Author Contributions: Conceptualization, R.B., A.K. and J.N.; methodology, J.N.; software, J.N.; validation, J.N., R.B. and A.K.; formal analysis, J.N. and R.B.; investigation, J.N. and R.B.; resources, R.B. and A.K.; data curation, J.N.; writing—original draft preparation, R.B. and J.N.; writing—review and editing, R.B., J.N. and A.K.; visualization, J.N.; supervision, A.K.; project administration, A.K. and R.B.; funding acquisition, R.B. and A.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Rodgers University fellowship in Electrical and Computer Engineering (JN) and the Stephen Sinclair Scott Endowment (RB) in Viticulture and Enology at the University of California, Davis, CA, USA.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: The authors gratefully acknowledge the datasets from Delegat's Wine Estate, NZ, Opus One Winery, USA, and the Master of Science theses of Kimberlee Marinelli and Gita Mallya.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Danilewicz, J.C. Mechanism of Autoxidation of Polyphenols and Participation of Sulfite in Wine: Key Role of Iron. *Am. J. Enol. Vitic.* **2011**, *62*, 319–328. [CrossRef]
2. Danilewicz, J.C.; Tunbridge, P.; Kilmartin, P.A. Wine Reduction Potentials: Are These Measured Values Really Reduction Potentials? *J. Agric. Food Chem.* **2019**, *67*, 4145–4153. [CrossRef] [PubMed]
3. Butler, J.N. *Ionic Equilibrium: A Mathematical Approach*; Addison-Wesley Publishing Company: Boston, MA, USA, 1964; ISBN 978-0-201-00730-5.
4. Burgot, J.-L. *Ionic Equilibria in Analytical Chemistry*; Springer Science+Business Media: New York, NY, USA, 2012; ISBN 978-1-4419-8381-7.
5. Coleman, R.E.; Boulton, R.B.; Stuchebrukhov, A.A. Kinetics of Autoxidation of Tartaric Acid in Presence of Iron. *J. Chem. Phys.* **2020**, *153*, 064503. [CrossRef] [PubMed]
6. Coleman, R.E.; Stuchebrukhov, A.A.; Boulton, R.B. The Kinetics of Autoxidation in Wine. In *Recent Advances in Chemical Kinetics*; IntechOpen: London, UK, 2022.
7. Duca, G. *Homogeneous Catalysis with Metal Complexes*; Springer Series in Chemical Physics; Springer: Berlin/Heidelberg, Germany, 2012; Volume 102, ISBN 978-3-642-24628-9.
8. Ribéreau-Gayon, J. *Contribution à L'étude Des Oxydations et Réductions Dans Les Vins: Application à L'étude du Vieillissement et Des Casses*; Delmas: Bordeaux, France, 1933.

9. Rodopulo, A.K. Oxidation of Tartaric Acid in Wine in the Presence of Heavy Metal Salts (Activation of Oxygen by Iron). *Izv. Akad. Nauk. USSR* **1951**, *3*, 115–128.
10. Baumberger, J.P. The Relation Between the Oxidation-Reduction Potential and the Oxygen Consumption Rate of Yeast Cell Suspensions. *Cold Spring Harb. Symp. Quant. Biol.* **1939**, *7*, 195–215. [CrossRef]
11. Bockris, J.O.; Reddy, A.K.N. *Volume 1 Modern Electrochemistry: An Introduction to an Interdisciplinary Area*; Macdonald: London, UK, 1970; Volume 1, ISBN 978-1-4615-7468-2.
12. Peiffer, S.; Klemm, O.; Pecher, K.; Hollerung, R. Redox Measurements in Aqueous Solutions—A Theoretical Approach to Data Interpretation, Based on Electrode Kinetics. *J. Contam. Hydrol.* **1992**, *10*, 1–18. [CrossRef]
13. Clark, W.M.; Cohen, B. Studies on Oxidation-Reduction. II. An Analysis of the Theoretical Relations between Reduction Potentials and pH. *Public Health Rep. (1896–1970)* **1923**, *38*, 666–683. [CrossRef]
14. De Levie, R. Redox Buffer Strength. *J. Chem. Educ.* **1999**, *76*, 574. [CrossRef]
15. Hewitt, L.F. Oxidation-Reduction Potentials in Bacteriology and Biochemistry. *Postgrad Med J.* **1950**, *26*, 552.
16. Harrison, D.E.F. Physiological Effects of Dissolved Oxygen Tension and Redox Potential on Growing Populations of Micro-organisms. *J. Appl. Chem.* **1972**, *22*, 417–440.
17. Ribbons, D.W.; Norris, J.R. (Eds.) *Methods in Microbiology*; Academic Press: London, UK, 1970; ISBN 978-0-08-086028-2.
18. Pirt, S.J. *Principles of Microbe and Cell Cultivation*; Wiley: New York, NY, USA, 1975; ISBN 978-0-470-69038-3.
19. Aiba, S.; Humphrey, A.E.; Millis, N.F. *Biochemical Engineering*, 1st ed.; Academic Press: New York, NY, USA, 1965; ISBN 978-0-12-045052-7.
20. Dahod, S.K. Redox Potential as a Better Substitute for Dissolved Oxygen in Fermentation Process Control. *Biotechnol. Bioeng.* **1982**, *24*, 2123–2125. [CrossRef] [PubMed]
21. Shibai, H.; Ishizaki, A.; Kobayashi, K.; Hirose, Y. Studies on Oxygen Transfer in Submerged Fermentation. XIII. Simultaneous Measurement of Dissolved Oxygen and Oxidation-Reduction Potentials in the Aerobic Culture. *Agric. Biol. Chem.* **1974**, *38*, 2407–2411. [CrossRef]
22. Tengerdy, R.P. Redox Potential Changes in the 2-keto- L -gulonic Acid Fermentation—II. Relationship between Redox Potential and Product Formation. *Biotechnol. Bioeng.* **1961**, *3*, 255–260. [CrossRef]
23. Heduit, A.; Thevenot, D.R. Relation Between Redox Potential and Oxygen Levels in Activated-Sludge Reactors. *Water Sci. Technol.* **1989**, *21*, 947–956. [CrossRef]
24. Marín Galvín, R.; Rodríguez Mellado, J.M.; Ruiz Montoya, M.; Jiménez Gamero, C. Oxidation-Reduction Potential (ORP) in Prepared and Industrially Treated Waters. *Bol. Soc. Chil. Quím.* **2001**, *46*, 387–397. [CrossRef]
25. Gillespie, L.J. Reduction Potentials of Bacterial Culture and of Water Logged Soils. *Soil Sci.* **1920**, *9*, 199–216. [CrossRef]
26. Wood, W.B.; Wood, M.L.; Baldwin, I.L. The Relation of Oxidation-Reduction Potential to the Growth of an Aerobic Microorganism. *J. Bacteriol.* **1935**, *30*, 593–602. [CrossRef]
27. Yudkin, J. The Reduction Potentials of Bacterial Suspensions. *Biochem. J.* **1935**, *29*, 1130–1138. [CrossRef]
28. Ward, W.E. The Apparent Oxidation-Reduction Potentials of Bright Platinum Electrodes in Synthetic Media Cultures of Bacteria. *J. Bacteriol.* **1938**, *36*, 337–355. [CrossRef]
29. Di Tizzano, A. Il Potenziale di Ossido-Riduzione e le sue applicazioni in Batteriologia ed in Igiene. *Experientia* **1946**, *2*, 86–99. [CrossRef]
30. Longsworth, L.G.; MacINNES, D.A. Bacterial Growth at Constant pH: Apparent Oxidation-Reduction Potential, Acid Production, and Population Studies of *Lactobacillus acidophilus* under Anaerobic Conditions. *J. Bacteriol.* **1936**, *32*, 567–585. [CrossRef] [PubMed]
31. Quispel, A. The Influence of the Oxidation-Reduction Potential of the Medium upon the Growth ofAzotobacter Chroococcum. *Antonie Van Leeuwenhoek* **1947**, *13*, 33–43. [CrossRef]
32. Schanderl, H. Oxidation-Reduction Potentials during the Phases of Development of Wine. *Weinbau. Wiss. Beih.* **1948**, *2*, 191–198.
33. Jacob, H.-E. Das Redoxpotential in Bakterienkulturen. *J. Basic Microbiol.* **1971**, *11*, 691–734. [CrossRef]
34. De Graef, M.R.; Alexeeva, S.; Snoep, J.L.; Teixeira De Mattos, M.J. The Steady-State Internal Redox State (NADH/NAD) Reflects the External Redox State and Is Correlated with Catabolic Adaptation in *Escherichia coli*. *J. Bacteriol.* **1999**, *181*, 2351–2357. [CrossRef]
35. Killeen, D.J.; Boulton, R.; Knoesen, A. Advanced Monitoring and Control of Redox Potential in Wine Fermentation. *Am. J. Enol. Vitic.* **2018**, *69*, 394–399. [CrossRef]
36. Duncan, J.D.; Devillers, H.; Camarasa, C.; Setati, M.E.; Divol, B. Oxygen Alters Redox Cofactor Dynamics and Induces Metabolic Shifts in Saccharomyces Cerevisiae during Alcoholic Fermentation. *Food Microbiol.* **2024**, *124*, 104624. [CrossRef]
37. Hongo, M. Application of Oxidation Reduction Potential to Fermentation. *J. Agric. Chem. Soc. Jpn.* **1958**, *32*, A101–A105. [CrossRef]
38. Tengerdy, R.P. Redox Potential Changes in the 2-keto-L-gulonic Acid Fermentation—I. Correlation between Redox Potential and Dissolved-oxygen Concentration. *Biotechnol. Bioeng.* **1961**, *3*, 241–253. [CrossRef]

39. Kawaharada, H.; Hayashida, S.; Hongo, M. The Mechanism of Formation of High Concentration Alcohol in Sake Brewing Part II. *J. Agric. Chem. Soc. Jpn.* **1967**, *41*, 635–639. [CrossRef]
40. Hongo, M.; Ishizaki, A.; Uyeda, M. Studies on Oxidation-Reduction Potentials (ORP) of Microbial Cultures Part I. *Agric. Biol. Chem.* **1972**, *36*, 141–145. [CrossRef]
41. Hongo, M.; Uyeda, M. Studies on Oxidation-Reduction Potentials (ORP) of Microbial Cultures Part II. *Agric. Biol. Chem.* **1972**, *36*, 269–272. [CrossRef]
42. Hongo, M.; Uyeda, M. Studies on Oxidation-Reduction Potentials (ORP) of Microbial Cultures Part III. *Agric. Biol. Chem.* **1972**, *36*, 273–278. [CrossRef]
43. Ishizaki, A.; Shibai, H.; Hirose, Y. Basic Aspects of Electrode Potential Change in Submerged Fermentation. *Agric. Biol. Chem.* **1974**, *38*, 2399–2406. [CrossRef]
44. Akashi, K.; Ikeda, S.; Shibai, H.; Kobayashi, K.; Hirose, Y. Determination of Redox Potential Levels Critical for Cell Respiration and Suitable for L-leucine Production. *Biotech Bioeng.* **1978**, *20*, 27–41. [CrossRef]
45. Radjai, M.; Hatch, R.; Cadman, T. Optimization of Amino-Acid Production by Automatic Self-Tuning Digital-Control of Redox Potential. *Biotechnol. Bioeng.* **1984**, *14*, 569–657.
46. Kwong, S.C.W.; Rao, G. Utility of Culture Redox Potential for Identifying Metabolic State Changes in Amino Acid Fermentation. *Biotechnol. Bioeng.* **1991**, *38*, 1034–1040. [CrossRef]
47. Chung, I.S.; Lee, Y.Y. Effect of Oxygen and Redox Potential on D-Xylose Fermentation by Non-Growing Cells of Pachysolen Tannophilus. *Enzym. Microb. Technol.* **1986**, *8*, 503–507. [CrossRef]
48. Kastner, J.R.; Eiteman, M.A.; Lee, S.A. Effect of Redox Potential on Stationary-Phase Xylitol Fermentations Using Candida Tropicalis. *Appl. Microbiol. Biotechnol.* **2003**, *63*, 96–100. [CrossRef]
49. Berovic, M. Scale-up of Citric Acid Fermentation by Redox Potential Control. *Biotechnol. Bioeng.* **1999**, *64*, 552–557. [CrossRef]
50. Du, C.; Zhang, Y.; Li, Y.; Cao, Z. Novel Redox Potential-Based Screening Strategy for Rapid Isolation of *Klebsiella pneumoniae* Mutants with Enhanced 1,3-Propanediol-Producing Capability. *Appl. Env. Microbiol.* **2007**, *73*, 4515–4521. [CrossRef] [PubMed]
51. Devai, I.; DeLaune, R.D. Formation of Volatile Sulfur Compounds in Salt Marsh Sediment as Influenced by Soil Redox Condition. *Org. Geochem.* **1995**, *23*, 283–287. [CrossRef]
52. Dobson, A.; Bullen, J.J. A Method for the Control of Eh and pH during Bacterial Growth. *J. Gen. Microbiol.* **1964**, *35*, 169–174. [CrossRef] [PubMed]
53. Wimpenny, J.W.T. The Effect ofEh on Regulatory Processes in Facultative Anaerobes. *Biotechnol. Bioeng.* **1969**, *11*, 623–629. [CrossRef] [PubMed]
54. Kjaergaard, L. The Redox Potential: Its Use and Control in Biotechnology. In *Advances in Biochemical Engineering*; Springer: Berlin/Heidelberg, Germany, 1977; Volume 7, pp. 131–150. ISBN 978-3-540-08397-9.
55. Ndegwa, P.M.; Wang, L.; Vaddella, V.K. Potential Strategies for Process Control and Monitoring of Stabilization of Dairy Wastewaters in Batch Aerobic Treatment Systems. *Process Biochem.* **2007**, *42*, 1272–1278. [CrossRef]
56. Hjorth, M.; Pedersen, C.Ø.; Feilberg, A. Redox Potential as a Means to Control the Treatment of Slurry to Lower H_2S Emissions. *Sensors* **2012**, *12*, 5349–5362. [CrossRef]
57. Bonan, C.I.D.G.; Biazi, L.E.; Dionísio, S.R.; Soares, L.B.; Tramontina, R.; Sousa, A.S.; De Oliveira Filho, C.A.; Costa, A.C.; Ienczak, J.L. Redox Potential as a Key Parameter for Monitoring and Optimization of Xylose Fermentation with Yeast Spathaspora Passalidarum under Limited-Oxygen Conditions. *Bioprocess Biosyst. Eng.* **2020**, *43*, 1509–1519. [CrossRef]
58. Kjaergaard, L.; Joergensen, B.B. Redox Potential as a State Variable in Fermentation Systems. *Biotechnol. Bioeng. Symp.* **1979**, *9*, 85–94.
59. Rohlich, G.A. Oxidation-Reduction Potential Measurements in Activated Sludge and Activated Sludge-Sewage Mixtures. *Sew. Work. J.* **1944**, *16*, 540–557.
60. Koch, F.A.; Oldham, W.K. Oxidation-Reduction Potential—A Tool for Monitoring, Control and Optimization of Biological Nutrient Removal Systems. *Water Sci. Technol.* **1985**, *17*, 259–281. [CrossRef]
61. Caulet, P.; Bujon, B.; Philippe, J.P.; Lefevre, F.; Audic, J.M. Upgrading of Wastewater Treatment Plants for Nitrogen Removal: Industrial Application of an Automated Aeration Management Based on ORP Evolution Analysis. *Water Sci. Technol.* **1998**, *37*, 41–47. [CrossRef]
62. Janssen, A.J.H.; Meijer, S.; Bontsema, J.; Lettinga, G. Application of the Redox Potential for Controling a Sulfide Oxidizing Bioreactor. *Biotechnol. Bioeng.* **1998**, *60*, 147–155. [CrossRef]
63. Chang, C.-N.; Ma, Y.-S.; Lo, C.-W. Application of Oxidation–Reduction Potential as a Controlling Parameter in Waste Activated Sludge Hydrolysis. *Chem. Eng. J.* **2002**, *90*, 273–281. [CrossRef]
64. Li, B.; Bishop, P. Oxidation-Reduction Potential (ORP) Regulation of Nutrient Removal in Activated Sludge Wastewater Treatment Plants. *Water Sci. Technol.* **2002**, *46*, 35–39. [CrossRef] [PubMed]
65. Holman, J.B.; Wareham, D.G. Oxidation-Reduction Potential as a Monitoring Tool in a Low Dissolved Oxygen Wastewater Treatment Process. *J. Environ. Eng.* **2003**, *129*, 52–58. [CrossRef]

66. Hood, J.W. Measurement and Control of Sewage Treatment Process Efficiency by Oxidation-Reduction Potential. *Sew. Work. J.* **1948**, *20*, 640–650.
67. Rohlich, G.A. Measurement and Control of Sewage Treatment Process Efficiency by Oxidation-Reduction Potential: A Discussion. *Sew. Work. J.* **1948**, *20*, 650–653.
68. Frosteil, B. Process Control in Anaerobic Wastewater Treatment. *Water Sci. Technol.* **1985**, *17*, 173–189. [CrossRef]
69. Kim, H.; Hao, O.J. pH and Oxidation–Reduction Potential Control Strategy for Optimization of Nitrogen Removal in an Alternating Aerobic–Anoxic System. *Water Environ. Res.* **2001**, *73*, 95–102. [CrossRef]
70. Beard, W.E.; Guenzi, W.D. Volatile Sulfur Compounds From a Redox-controlled-cattle-manure Slurry. *J. Env. Qual.* **1983**, *12*, 113–116. [CrossRef]
71. Liu, C.-G.; Xue, C.; Lin, Y.-H.; Bai, F.-W. Redox Potential Control and Applications in Microaerobic and Anaerobic Fermentations. *Biotechnol. Adv.* **2013**, *31*, 257–265. [CrossRef] [PubMed]
72. Lin, Y.-H.; Chien, W.-S.; Duan, K.-J. Correlations between Reduction–Oxidation Potential Profiles and Growth Patterns of Saccharomyces Cerevisiae during Very-High-Gravity Fermentation. *Process Biochem.* **2010**, *45*, 765–770. [CrossRef]
73. Liu, C.-G.; Hao, X.-M.; Lin, Y.-H.; Bai, F.-W. Redox Potential Driven Aeration during Very-High-Gravity Ethanol Fermentation by Using Flocculating Yeast. *Sci. Rep.* **2016**, *6*, 25763. [CrossRef]
74. Riondet, C.; Cachon, R.; Waché, Y.; Alcaraz, G.; Diviès, C. Extracellular Oxidoreduction Potential Modifies Carbon and Electron Flow in *Escherichia coli*. *J. Bacteriol.* **2000**, *182*, 620–626. [CrossRef]
75. Graff, Y. Le Potentiel D'Oxydo-Reduction. Application Des Notions D'Oxydo-Reduction a La Brasserie et a L'oenologie. *Ann. De La Nutr. Et De L'alimentation* **1950**, *4*, 253–294.
76. Geloso, J. Relation Entre Le Vieillissement Des Vins et Leur Potentiel d'Oxydoreduction. *Ann. De La Brass. Et De La Distill.* **1931**, *29*, 177–193.
77. Joslyn, M.A. Oxidation-Reduction Potentials at Various Stages of Production and Aging. *Ind. Eng. Chem.* **1949**, *41*, 587–592. [CrossRef]
78. Joslyn, M.A.; Lukton, A. Mechanism of Copper Casse Formation in White Table Wine. *I. Relation of Changes in Redox Potetnial to Copper Casse. J. Food Sci.* **1956**, *21*, 384–396. [CrossRef]
79. Schanderl, H. Die Entwicklungsgeschichte des Embryos bei den Rosaceengattungen Prunus, Pirus und Malus. *Der Züchter* **1949**, *19*, 206–210. [CrossRef]
80. Ribéreau-Gayon, J.; Peynaud, E. *Traite d'Oenologie I*; Librairie Polytechnique Beranger: Paris, France, 1964.
81. Schanderl, H. Mikrobiologie Des Mostes Und Weines. In *Handbuch Der Kellerwitschaft II*; Verlag Eugen Ulmer: Stuttgart, Germany, 1959.
82. Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*; National Association of Corrosion Engineers: Houston, TX, USA, 1974; ISBN 978-0-915567-98-0.
83. Fenton, H.J.H. LXXIII.—Oxidation of Tartaric Acid in Presence of Iron. *J. Chem. Soc. Trans.* **1894**, *65*, 899–910. [CrossRef]
84. Baraud, J. Etude Des Derives Naturels de L'Acide Tartrique. Ph.D. Thesis, University of Bordeaux, Bordeaux, France, 1954.
85. Park, S.K.; Boulton, R.B.; Noble, A.C. Formation of Hydrogen Sulfide and Glutathione During Fermentation of White Grape Musts. *Am. J. Enol. Vitic.* **2000**, *51*, 91–97. [CrossRef]
86. Cheynier, V.; Souquet, J.M.; Moutounet, M. Glutathione Content and Glutathione to Hydroxycinnamic Acid Ratio in *Vitis vinifera* Grapes and Musts. *Am. J. Enol. Vitic.* **1989**, *40*, 320–324. [CrossRef]
87. Ngamchuea, K.; Batchelor-McAuley, C.; Compton, R.G. The Copper(II)-Catalyzed Oxidation of Glutathione. *Chem. A Eur. J.* **2016**, *22*, 15937–15944. [CrossRef] [PubMed]
88. Dikanović-Lučan, Ž.; Palić, A. Redox-Potential of Wines from a Croatian Market. *Z Leb. Unters Forch* **1992**, *195*, 133–136. [CrossRef]
89. Jean, R.-G. *Traité D'oenologie, Transformations et Traitements Des Vins*; C. Béranger: Paris, Fance, 1947.
90. Rankine, B.C. Nature, Origin and Prevention of Hydrogen Sulphide Aroma in Wines. *J. Sci. Food Agric.* **1963**, *14*, 79–91. [CrossRef]
91. Kukec, A.; Berovic, M. The Role of On-Line Redox Potential Measurement in Sauvignon Blanc Fermentation. *Food Technol. Biotechnol.* **2002**, *40*, 49–55.
92. Berovic, M.; Mavri, J.; Wondra, M.; Ko, T. Influence of Temperature and Carbon Dioxide on Fermentation of Cabernet Sauvignon Must. *Food Technol. Biotechnol.* **2003**, *41*, 353–359.
93. Charpentie, Y. Contribution a l'Etude Biochimique Des Facteurs de l'Aciditie Des Vins. Ph.D. Thesis, University of Bordeaux, Bordeaux, France, 1954.
94. Nielsen, J.C.; Richelieu, M. Control of Flavor Development in Wine during and after Malolactic Fermentation by *Oenococcus oeni*. *Appl. Env. Microbiol.* **1999**, *65*, 740–745. [CrossRef]
95. Young, S.; Merrell, C.; Arvik, T.; Boulton, R. Redox Control of Chardonnay Fermentation to Limit Conversion of Elemental Sulfur to Hydrogen Sulfide. In Proceedings of the American Society of Enology and Viticulture, Napa, CA, USA, 26–29 June 2023.
96. Mallya, G. Exploring the Use of Redox Potential to Predict Fermentation Outcomes in Relation to Initial Juice Conditions. Master of Science Thesis, University of California, Davis, CA, USA, 2022.

97. Cachon, R.; Jeanson, S.; Aldarf, M.; Divies, C. Characterisation of Lactic Starters Based on Acidification and Reduction Activities. *Lait* **2002**, *82*, 281–288. [CrossRef]
98. Brasca, M.; Morandi, S.; Lodi, R.; Tamburini, A. Redox Potential to Discriminate among Species of Lactic Acid Bacteria: Redox Potential of Lactic Acid Bacteria. *J. Appl. Microbiol.* **2007**, *103*, 1516–1524. [CrossRef]
99. Morandi, S.; Silvetti, T.; Tamburini, A.; Brasca, M. Changes in Oxidation-Reduction Potential during Milk Fermentation by Wild Lactic Acid Bacteria. *J. Dairy Res.* **2016**, *83*, 387–394. [CrossRef] [PubMed]
100. Larsen, N.; Werner, B.B.; Vogensen, F.K.; Jespersen, L. Effect of Dissolved Oxygen on Redox Potential and Milk Acidification by Lactic Acid Bacteria Isolated from a DL-Starter Culture. *J. Dairy Sci.* **2015**, *98*, 1640–1651. [CrossRef] [PubMed]
101. Maujean, A.; Haye, M.; Feuillat, M.; Thomas, J.C.; Petit, D. Contribution à l'étude Des «goûts de Lumière» Dans Le Vin de Champagne. II. Influence de La Lumière Sur Le Potentiel d'oxydoreduction. Corrélation Avec La Teneur En Thiols Du Vin. *Oeno One* **1978**, *12*, 277–290. [CrossRef]
102. Fracassetti, D.; Gabrielli, M.; Encinas, J.; Manara, M.; Pellegrino, I.; Tirelli, A. Approaches to Prevent the Light-Struck Taste in White Wine: Prevention of Light-Struck Taste. *Aust. J. Grape Wine Res.* **2017**, *23*, 329–333. [CrossRef]
103. Marinelli, K.A. The Effects of Oxygenation on Redox Potential and Fermentation Kinetics. Master's Thesis, University of California, Davis, CA, USA, 2022.
104. Nelson, J.; Coleman, R.; Chacón-Rodríguez, L.; Runnebaum, R.; Boulton, R.; Knoesen, A. Advanced Monitoring and Control of Redox Potential in Wine Fermentation across Scales. *Fermentation* **2022**, *9*, 7. [CrossRef]
105. Schlegel, H.G. Aeration without Air: Oxygen Supply by Hydrogen Peroxide. *Biotechnol. Bioeng.* **1977**, *19*, 413–424. [CrossRef]
106. Dott, W.; Heinzel, M.; Truper, H.G. Sulfite Formation by Wine Yeasts: IV. Active Uptake of Sulfate by Low and High Sulfite Producing Wine Yeasts. *Arch. Microbiol.* **1977**, *112*, 283–285. [CrossRef]
107. Agarbati, A.; Canonico, L.; Comitini, F.; Ciani, M. Reduction of Sulfur Compounds through Genetic Improvement of Native Saccharomyces Cerevisiae Useful for Organic and Sulfite-Free Wine. *Foods* **2020**, *9*, 658. [CrossRef]