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The Effect of Oxygen Dosage Rate on the Chemical and Sensory Changes Occurring During Micro-oxygenation of New Zealand Red Wine

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This thesis is submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Food Science, The University of Auckland, 2007

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ABSTRACT

The technique of micro-oxygenation involves the deliberate addition of continuous, metered amounts of oxygen into a vessel of bulk wine during the maturation period (between the end of fermentation and bottling). The aim of the process is to improve the sensory properties of red wine, particularly the mouthfeel characteristics associated with the various polyphenol constituents. The success of the process appears to depend strongly on the ability to control the rate of oxygen dosage. The effect of dosage rate on the chemical and corresponding sensory changes of a red wine is the central theme of this thesis.

A method of dosing oxygen (at typical micro-oxygenation rates) into small volumes of wine (<100 litres) was developed using a dense polymer membrane diffuser. It was clearly demonstrated that wine could be reliably oxygenated at very low rates using a coiled length of FEP as the diffuser material. Oxygen dosage was regulated by adjusting the oxygen pressure inside the tube. The advantage with a dense polymer diffuser is that no bubbles are generated and the oxygenation efficiency is 100%. The diffuser was fully modeled and characterised for use in the laboratory scale trials detailed in Chapters Four and Six.

The small scale oxygenation equipment was used to conduct a fully replicated experiment to investigate the evolution of a Cabernet Sauvignon wine under four oxygenation treatments at dosage rates of 0, 10, 23 and 36 mg/L/mth. The total period of the trial was 105 days. HPLC analysis indicated that the rate change of low molecular weight polyphenols is directly related to the oxygen dosage rate. The concentration of the majority of the identifiable monomers, most notably the anthocyanins decreased throughout the course of the trial. The rate of decrease was directly related to oxygen dosage rate. Thiolyis results showed an increase in mDP for all treatments over the course of the trial until day 77 when they were observed to decrease for all treatments. The decrease in mDP coincided with an addition of SO₂ which was investigated in a subsequent trial. Spectrophotometric results indicated that the rate of formation of non-bleachable pigments was directly related to the rate of oxygen dosage with significant differences between the high rates (23 and 36 mg/L/mth) and the low rates (0 and 10 mg/L/mth). The trend for all treatments was for increased levels of stable pigments.
The sensory results show that the measured organoleptic temporal development exhibits a similar oscillatory behaviour compared to the anecdotally derived curve presented in figure 1-2. The distinction between the respective phases described in section 1.1.1 was, however less clear. The most significant factor in the model weighting was mouthfeel and astringency which correlates with the observed changes occurring in the wine polyphenols during maturation.

Overall the laboratory scale trial showed that the chemical polyphenol development was directly related to the oxygen dosage rate. The sensory evolution also appeared to be accelerated with higher oxygen dosage rates, although the oscillatory nature of the sensory response given a single linear input indicates a complex underlying mechanism driving the changes.

The effect of SO$_2$ on the development of wine polyphenols with and without oxygen was also investigated. The presence of SO$_2$ was found to have a significant effect on both mDP and the concentration of non-bleachable pigments. mDP was observed to decrease over the six week trial period irrespective of whether oxygen had been added or not. The mDP for the treatments without SO$_2$ increased steadily over the course of the trial. Similarly the formation of non-bleachable pigments was suppressed and even retarded with SO$_2$ present whereas for the treatments without SO$_2$ a steady increase was observed. The implication of these results is that SO$_2$ may have a much larger effect on tannin development than oxygen.

The use of electrochemical micro-oxidation (or ELMOX) was examined ostensibly to determine proof of concept and also compare the performance of glassy carbon and titanium as electrode materials against traditional micro-oxygenation. Notable transformations occurred with titanium showing higher levels of ethanal than the other treatments both chemically and by sensory measure. A greater rate of stable pigment formation was also observed for the titanium compared to the other treatments. The respective dosage rates for the glassy carbon ELMOX and traditional micro-oxygenation treatments were too low to be able to discriminate any significant differences compared to the control wine.
Gross oxygen consumption kinetics was measured using a device developed at the University of Auckland. Autocatalytic behaviour was observed in wines containing, even small quantities of yeast lees. Tightly filtered wines however exhibited first order kinetic behaviour. The result indicates that any residual yeast lees remaining in the wine dominate the consumption of dissolved oxygen effectively decreasing the net availability of oxygen for wine polyphenol reactions.

The computational fluid dynamics (CFD) analysis of the micro-oxygenation system showed that for a typical micro-oxygenation dosage rate there is very little mixing occurring in the tank. Localised flow loops form around the bubble plume and there is only slight lateral dispersion of the bubble column limiting the transport of the dissolved oxygen from the central plume. Despite some limitations in the method the ability to be able to visualise the physical system provides a powerful tool to help in analyzing and subsequently optimising the process.
In memory of
Ian Dykes
1941-2001
ACKNOWLEDGEMENTS

The work described in this thesis would not have been possible without the considerable help from a large number of people.

First and foremost I would like to acknowledge the support of my academic supervisor Dr Paul Kilmartin. Over the period of my research Paul has been fully supportive of my ideas and work giving me technical, logistical and financial assistance when required. Paul has also been a great mentor over the period of my post-graduate studies and someone I am honored and grateful to have as a supervisor.

I was fortunate enough to be awarded an AGMARDT scholarship, and this assisted me greatly in being able to carry out this research. Moreover, the support of the AGMARDT administration team was excellent throughout. Thanks also go to Dr Martin Pour Nikfardjam who was active in getting this project off the ground and for Lincoln University for providing much needed initial support.

Paul Mooney, the winemaker at Mission Estate Wines in the Hawke’s Bay was heavily involved in my own and other research projects at the University of Auckland Wine Science Programme. Paul was a tremendous help through the course of my research either providing wine samples or as a source of insight and pragmatic comment on my work.

I am also extremely grateful to the University of Auckland Statistics department who gave me wise counsel in terms of experimental design and subsequent data analysis. I would like to acknowledge particularly the assistance of Associate Professor Chris Triggs and Dr Marti Anderson for providing me with many useful tools and ideas to examine and better interpret my data. Thanks also for the final chapter go to Professor Peter Hunter who gave me much guidance in terms of converting the equations into working code.

Jan Robinson, the University of Auckland Wine Science Programme Laboratory Manager, gave me significant support throughout the experimental phase of the study, particularly the winemaking and associated tasks over the harvest period.
Acknowledgement should also be made of the sensory panelists who made themselves available for often tedious training and data collection sessions purely on a voluntary basis. Their enthusiasm and dedication was tremendous and is very much appreciated.

Finally I would like to thank my long suffering family for the continued love and support in this endeavor. Particular thanks go to my wife who always managed to put things in perspective when I was not able to. I am also very much looking forward to getting to know my children a little better from now on.
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# NOMENCLATURE

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<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>( a )</td>
<td>specific area (contact area divided by the volume of fluid being aerated) ((1/m))</td>
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<tr>
<td>ANOVA</td>
<td>analysis of variance</td>
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<td>( A-T )</td>
<td>anthocyanin – tannin condensation product</td>
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<tr>
<td>( b )</td>
<td>attribute weighting factor</td>
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<tr>
<td>( c )</td>
<td>response pattern</td>
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<td>standard electrode potential ((V))</td>
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<td>charge ((\text{coulomb}))</td>
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<td>( r )</td>
<td>radius</td>
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R = ideal gas constant - J·mol⁻¹
RDA = redundancy analysis
ROTE = roll on tamper evident
RP-HPLC = reversed phase high performance liquid chromatography
s = fibre length (m)
S = membrane partition coefficient
t = time
T = temperature (K)
T = treatment effect
T - A = tannin – anthocyanin condensation product
TOF = time of flight
UV-VIS = ultra violet - visible
v = velocity (m/s)
v/v = volume per volume
w/v = weight per volume

Greek Symbols

ε = error term in principal response model
φ = diameter (m)
Γ = diffusion coefficient (m²/s)
λ = wavelength (nm)
Λ = Wilks lambda statistic
μ = viscosity (kg/ms)
ω = rotational velocity (rad/s)
ρ = density (kg/m³)
σ = surface tension (N/m)
σ² = variance
Σg = triplet spin state
χ² = chi-squared test statistic

Subscripts

e = cylinder
d = treatment index
e = effective
ext = external
g = gas phase
G = gas phase
GO = bulk gas phase
GI = interfacial gas phase
int = internal
k = attribute index
l = liquid phase
L = liquid phase
LI = interfacial liquid phase
LO = bulk liquid phase
CHAPTER SEVEN

\( a \) = bubble wine interfacial area (m²)
\([A]\) = concentration of reactant A (kg/m³)
\([B]\) = concentration of product B (kg/m³)
\( C \) = bubble force coefficient (dimensionless)
\( c \) = solute concentration (kg/m³)
\( \text{CFD} \) = computational fluid dynamics
\( d \) = bubble diameter (m)
\( e \) = exponential operator
\( \text{E-E} \) = Euler-Euler two phase model
\( \text{E-L} \) = Euler Lagrange two phase model
\( F \) = force (N)
\( g \) = acceleration vector due to gravity (m/s²)
\( \text{GAE} \) = gallic acid equivalent
\( H \) = Henry’s law coefficient (Pa·m³/mol)
\( I \) = identity tensor
\( j \) = mass flux
\( k \) = reaction rate constant
\( K_{L} \) = interphase mass transfer coefficient (m/s)
\( m \) = mass (kg)
\( \text{NTU} \) = nephelometric turbidity units
\( P \) = pressure (Pa)
\( r \) = radius (m)
\( R^2 \) = quality control parameter from regression
\( \text{Re} \) = Reynolds number
\( \text{RMSE} \) = root mean squared error
\( S \) = source and sink terms for the transport equation
\( Sc \) = Schmidt number, \( Sc = \mu / \rho \Gamma \)
\( Sh \) = Sherwood number, \( Sh = k_{L}d / \Gamma \)
\( \text{SSE} \) = sum of square due to error
\( t \) = time (s)
\( u \) = liquid phase velocity vector (m/s)
\( v \) = bubble phase velocity vector (m/s)
\( V \) = volume (m³)

**Greek Symbols**
\( \alpha \) = coefficient in the autocatalytic rate equation
\( \beta \) = coefficient in the autocatalytic rate equation
\( \delta t \) = time increment
\( \varepsilon \) = volume fraction (dimensionless)
\( \xi \) = volume fraction of bubble included in a cell (dimensionless)
\( \phi \) = interphase coupling term (N/m³)
\( \Gamma \) = diffusion coefficient (m²/s)
\( \lambda \) = interpolation factor (dimensionless)
\( \mu \) = viscosity (kg/ms)
\( \omega \) = Lagrangian quantity
\( \Omega \) = Eulerian quantity
\( \rho \) = density (kg/m³)
\( \tau \) = viscous stress tensor (N/m³)
\( \nabla \) = gradient operator (1/m)

**Subscripts**

\( b \) = bubble
\( bub \) = time increment for bubble phase momentum calculation
\( b \rightarrow l \) = bubble to liquid
\( CO_2 \) = carbon dioxide
\( \text{Drag} \) = drag force
\( D \) = sink
\( \text{equivalent} \) = equivalent volume
\( \text{flow} \) = time increment for liquid phase momentum calculation
\( g \) = gas phase
\( L \) = source
\( l \) = liquid phase
\( l \rightarrow b \) = liquid to bubble
\( \text{Lift} \) = lift force
\( P \) = pressure force
\( O_2 \) = oxygen
\( \text{V-M} \) = virtual mass force
\( 0 \) = initial (i.e. at time = 0)

**Superscripts**

\( * \) = interfacial property
\( \kappa \) = iteration counter