

**EVALUATION OF
TARTRATE STABILISATION TECHNOLOGIES
FOR WINE INDUSTRY**

by

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A dissertation submitted for the degree of
Doctor of Philosophy

July 2007



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SUMMARY

In the Australian wine industry, cold stabilisation is a widely used industrial process to prevent tartrate instability in bottled wines. This process involves cooling the wine close to its freezing point for extended periods, thereby inducing tartrate precipitation. However, it has several important disadvantages. Consequently, alternative methods to cold stabilisation have been developed. This includes electro dialysis, nanofiltration and contact processes.

In this study, current knowledge regarding performance and cost of cold stabilisation and alternative technologies for tartrate stabilisation is reviewed. Whilst there have been occasional cost comparisons between cold stabilisation and alternative technologies, existing data is not suitable for properly evaluating the relative economics of the different process options. Therefore, alternative technologies to cold stabilisation, including the Westfalia process, nanofiltration and electro dialysis were compared for both technical and economic performance. Berri Estates Winery was used as the basis for engineering calculations and conceptual cost estimates. This is the first time that such a comprehensive evaluation has been undertaken of a broad range of alternative technologies for tartrate stabilisation during wine production. Product loss was a key cost driver in differentiating tartrate stabilisation processes. Cold stabilisation was found to be the most economic treatment process irrespective of scale or winery size. The Westfalia process and nanofiltration were the next most cost effective options.

Data for economic evaluation and environmental assessment were summarised in a survey form that was circulated to technical experts from Hardy Wine Company, the Australian Wine Research Institute (AWRI) and the University of Adelaide. The purpose of the survey was to obtain the experts' opinions on the merits of the alternative technologies. The results of this survey were used for comparison between current cold stabilisation and alternative technologies, by performing multi-criteria decision analysis (MCDA). This represents an original application of MCDA techniques to decision making in the wine industry. The MCDA analysis identified a strong preference by experts for nanofiltration combined with centrifugation as an alternative to cold stabilisation.

As a consequence, laboratory investigations and field testing of nanofiltration were conducted to obtain new and practical information which was not presently available and relevant to understanding and implementing this process for tartrate stabilisation of wine.

The laboratory experiments were performed with a range of membranes and tartrate unstable wines (i.e. *Semillon*, *Colombard* and *Shiraz*) using a purpose-designed laboratory-scale continuously-stirred batch-test membrane cell. The results showed that a range of commercial nanofiltration membranes with a nominal molecular weight cut-off (MWCO) between 200 and 500 Daltons (Da) were able to achieve tartrate stabilisation of all wines tested. This was achieved at moderate pressures less than 20 bar with a recovery of at least 50 %. It was also observed that seeding of wine following nanofiltration might reduce the holding time required to achieve stability and also enable reductions in the recovery rate to values of less than 50 %.

The field testing was performed at Berri Estates Winery in the Riverland region of South Australia. The testing was performed using an existing commercial membrane system. This membrane system was already used for juice/wine concentration. The nanofiltration membranes had a nominal MWCO of 300 Da. The testing was conducted on *Colombard* and *Shiraz* wines. The field tests confirmed that nanofiltration could successfully tartrate stabilise *Colombard* and *Shiraz* wines at recoveries of 50 %; without seeding; within relatively short holding periods of less than four hours; and at flux rates between 5 and 10 L/m²/h. Crystallisation kinetics were also studied. At low recovery, the crystallisation was initially controlled by diffusion step, then surface integration. However, at high recovery, the crystallisation was controlled solely by surface integration.

Sensory testing (by duo-trio difference tests) produced adverse sensory outcomes when compared with treatment of the same wines by cold stabilisation. Unfortunately, it could not be established whether this problem was inherent to the process or arose from unrelated factors. Setting aside the adverse sensory result, this is the first time that technical feasibility of nanofiltration for tartrate stabilisation has been successfully demonstrated.

Further field testing and sensory evaluation of nano-filtered wines should be carried out to verify the effect of nanofiltration on wines. If the process is successful and favourable, the process design for implementation of a production scale nanofiltration for tartrate stabilisation should then be optimised.

ACKNOWLEDGMENTS

This dissertation is never a sole effort of the author. I am deeply indebted to everyone that has contributed to this dissertation in innumerable ways. Firstly, I would like to thank my principal supervisor, Dr. Chris Colby for his generosity with his time and advice. Without his encouragement and supervision, this project would not have been possible. I would like to acknowledge my co-supervisors: A/Prof. Brian O'Neill, Dr. Chris Ford (School of Agriculture and Wine, The University of Adelaide), Mr. Jim Godden (former Operations Manager, Berri Estates Winery) and Mr. Mark Gishen (former Quality Liaison Manager, The Australian Wine Research Institute (AWRI)) for their invaluable guidance and kind encouragement.

I am grateful to Faculty of Engineering, Computer and Mathematical Science for providing Divisional Scholarship Award and to Hardy Wine Company for providing additional scholarship and in-kind contributions to this project. I also like to acknowledge AWRI for supporting this research. This research also has been funded by Australia's grapegrowers and winemakers through their investment body the Grape and Wine Research and Development Corporation, with matching funds from the Australian government.

I am also thankful to the staff and students in the School of Chemical Engineering for their friendship, assistance and encouragement. Special thanks to Peter Kay, Mary Barrow, Elaine Minerds, Kyleigh Victory and Aning Ayucitra.

I am grateful to all of the personnel at different institutions (especially Berri Estates Winery, AWRI and Hickenbotham Wine Science Winery) who not only provided access to valuable resources throughout my studies but also valuable discussions.

I give my heartfelt thanks to my housemates - Khar Yean Khoo and Alice Zhu for their care and support throughout the years. Thanks to all my friends, you know who you are!

I would like to express my deepest gratitude to Greg Balkwill for everything from technical to emotional support. Thank you for being there for me all the time.

Last but not least, I would like to extend my deepest appreciation to my family. Thank you for believing in me. I would like to dedicate this dissertation to my beloved parents.

LIST OF PUBLICATIONS

Refereed Journal Papers

Low, L., Colby, C. B., O'Neill, B., Ford, C., Godden, J., Gishen, M. (2007). Economic evaluation of alternative technologies of tartrate stabilisation of wines. *Int. J. Food Sci. Technol.* Accepted for Publication.

Refereed Conference Papers

Low, L., Colby, C., O'Neill, B., Ford, C., Godden, J., Gishen, M. (2005). Alternataive Technologies for Tartrate Stabilisation of Wines: Which is Better? In: *Proceedings of the 33rd Australasian Chemical Engineering Conference (CHEMECA 2005)*, Brisbane, 25-28 September 2005, Hardin, M. (ed.). Institution of Engineers, Brisbane, paper no. 130, CDROM ISBN 1-86499-832-6.

Low, L., Colby, C., O'Neill, B., Ford, C., Godden, J. & Gishen, M. (2006). Use of nanofiltration for tartrate stabilisation of wine. In: *Proceedings of the 34th Australasian Chemical Engineering Conference (CHEMECA 2006)*, Auckland, 17-20 September 2006, Patterson, D. & Young, B. (eds.). CCE Conference Management, The University of Auckland, Auckland, paper no. 302, CDROM ISBN 0-86869-110-0.

Low, L., Colby, C., O'Neill, B., Ford, C., Godden, J. & Gishen, M. (2007). Field Testing of Nanofiltration for Tartrate Stabilisation of Wine at Berri Estates Winery. In: *Proceedings of the 35th Australasian Chemical Engineering Conference (CHEMECA 2007)*, Melbourne, 23-26 September 2007, paper no. 120. Accepted for Publication.

Other Non-Refereed Publications

- Low, L., O'Neill, B., Ford, C., Godden, J., Gishen, M. & Colby, C. (2004). Evaluating alternative tartrate stabilisation methods for wine. In: *Proceedings of 12th Australian Wine Industry Technical Conference*, Melbourne, 24 - 29 July 2004, Blair, R., Williams, P. & Pretorius, S. (eds.). Australian Wine Industry Technical Conference Inc., Adelaide, 324-325. ISBN 0-0577870-9-X.
- Colby, C., Low, L., Godden, J., Gishen, M. & O'Neill, B. (2006). Process engineering developments in wine production: Alternative technologies for tartrate stabilisation. In: *ASVO Seminar Proceedings: Maximising the Value – Maximising returns through quality and process efficiency*, Adelaide, 12 October 2006, Allen, M., Cameron, W., Francis, M., Goodman, K. & Wall, G. (eds.). Australian Society of Viticulture and Oenology, Adelaide, 29-33. ISBN 0-9775256-1-9.
- Low, L., Colby, C., O'Neill, B., Ford, C., Godden, J. & Gishen, M. (2007). Poster summary: Field testing of nanofiltration for tartrate stabilisation of wine. In: *Proceedings of 13th Australian Wine Industry Technical Conference*, Adelaide, 29 July – 1 August 2007. *Submitted*.

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