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New technologies for tartrate stabilisation – Field testing of nanofiltration

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1 Abstract:

Laboratory and field testing of nanofiltration as an alternative to cold stabilization for achieving tartrate stability was conducted. The laboratory testing was performed with a different commercial membranes and real wines. The results demonstrated that nanofiltration could successfully tartrate stabilise wines. Field testing of nanofiltration was conducted at Berri Estates Winery. Nanofiltration was able to successfully tartrate stabilise Colombard and Shiraz wines. Furthermore, this was achieved; at moderate feed pressures: < 20 bar and recoveries: 50 %; without seeding; within relatively short holding periods: < 3 hr; and at flux rates of between 5 and 10 L/m^2/hr. However, nanofiltration treatment was found to produce adverse sensory outcomes when compared with treatment of the same wines by cold stabilisation. It was not established whether this problem was intrinsic to the process or arose from unrelated factors.

2 Executive summary

Nanofiltration is a membrane process that could be an alternative to cold stabilization for industrial tartrate stabilization of wines. In this process, the potassium bitartate and calcium tartrate salts in a wine are concentrated by membranes to cause their precipitation so they may be removed (as opposed to cooling by cold stabilization to achieve the same outcome). The concentrated wine from a nanofiltration system is called the “retentate” (i.e. as it is “recovered” or retained by the membrane). The precipitated bitartrate and tartrate crystals are separated and removed from the retentate. The clarified retentate is then mixed back with permeate – the component of the wine that passes through the membrane – to reconstitute the wine. As a result of this process, the reconstituted wine should be tartrate stable.

This GWRDC project was initiated as part of a broader project investigating alternative tartrate stabilization processes. The project was undertaken by the Chemical Engineering Department of The University of Adelaide, in collaboration with The Australian Wine Research Institute and the industrial sponsor, Hardy Wine Company. The funding provided by the GWRDC allowed laboratory investigations and field testing of nanofiltration.

The laboratory experiments were performed at The University of Adelaide between March and July, 2006. These experiments were performed with a range of membranes and real wines 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 (MCWO) between 200 and 500 Daltons (Da) were able to achieve tartrate stabilisation of all wines tested. This was achieved at a moderate pressures < 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 undertaken at Berri Estates Winery in the Riverland region of South Australia in September and December, 2006. The testing was performed with an existing commercial membrane system at the Winery. This membrane system was already used for juice concentration and de-alcoholization of wines. The nanofiltration membranes had a nominal MWCO of 300 Daltons (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 %. The holding time required for completion of the crystallisation phase following concentration was between 30 and 150 min depending on the wine and recovery rate. The results suggested that red wines

would require longer holding times than for white wines. The holding time was reduced with increased recovery rate. However, a higher recovery rate may require a longer concentration phase, so net savings in processing time could be neutral. Seeding did not appear to reduce the holding time required.

In the field tests, the NF system was operated in a batch mode. During operation of the nanofiltration system, flux rates of between 5 and 12 L/m^2/hr for Colombard wine, and between 2 and 6 L/m^2/hr for the Shiraz wine, were achieved at feed pressures of approximately 18 bar. With appropriate design, the NF system could be operated as a "single-pass" system. Furthermore, lower operating pressures and/or higher flux rates might also be achievable.

However, sensory testing (by duo-trio difference tests) revealed that nano-filtered wine was significantly different to the raw wine and wine treated by cold stabilisation. Furthermore, these differences were negative. It could not be confirmed whether this problem was intrinsic to the process or arose from unrelated factors:

- Possible oxidation or microbial contamination of nano-filtered wine;
- Dilution of the nano-filtered wine; and/or
- Membrane absorption of flavour and aroma compounds.

This problem and other data produced by the laboratory experiments and the field tests are currently being studied further by a PhD student and the project's Chief Investigator. When this is complete, additional outcomes/findings will be published.

The results of this project have been reported to the project's industrial sponsor, Hardy Wine Company. This will likely decide the immediate prospects for commercial application of nanofiltration technology for tartrate stabilisation by this company. If this proceeds, it is recommended that the following occurs.

1. Reconsideration of estimated process cost estimates based on field testing data;
2. Further field testing and sensory evaluation of nano-filtered wines; and
3. Assuming 1 and 2 are successful and favourable, optimisation of the process design for implementation of a production-scale nanofiltration system for tartrate stabilisation at the targeted winery(ies).

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3 Background

Virtually all commercial wines are stabilised during winemaking to prevent precipitation of potassium bitartate and calcium tartrate crystal deposits (Boulton et al., 1996). These types of crystal deposits in wines are considered undesirable (Dharmadhikari, 2002) and generally do not meet with consumer acceptance (Zoecklein et al., 1995). Uninformed consumers may mistake the deposits for chemical additives, sugar crystals or glass splinters and reject the product (Bott, 1988).

The traditional and currently most extensively used treatment method by the wine industry for tartrate stabilisation is chilling or cold stabilisation (Uitslag et al., 1996). The most basic application of this process is to chill the wine through a heat exchanger to near its freezing point, in the range -4 to 2 °C, store in an insulated vessel for 10 days to three weeks, and clarify the wine whilst still cold (Boulton et al., 1996; Uitslag et al., 1996; Maujean, 1994). The chilling of the wine lowers the temperature to where potassium bitartrate and calcium tartrate salts are less soluble (Uitslag et al., 1996). This induces precipitation of bitartrate and tartrate salts, which slowly deposit on tank walls or as free crystals that settle to the bottom of the tank. Some winemakers also elect to fine with bentonite for removal of protein haze during cold stabilization (Zoecklein, 1988). This is intended to allow bitartrate/tartrate crystals to assist with compaction of the bentonite lees, and thus, minimize the volume of wine occluded in the lees which may subsequently be downgraded in value during recovery.

However, cold stabilisation is considered time consuming and costly (Dhamadhikari, 2002). Low levels of supersaturation lead to poor if any spontaneous nucleation, and thus slow crystallization rates (Rhein and Neradt, 1979). The long period the wine must be held (several days to a week) as a consequence is regarded as inconvenient, especially if cold stabilisation is performed immediately prior to bottling.

Significant amounts of precipitation also occur as a thin crystalline layer on tank walls, which is problematic to remove. Cleaning requirements to remove tartrate deposits from tanks are substantial and disposal to drain often causes effluent treatment and disposal problems.

Refrigeration is required to initially chill the wine and then hold it at low temperature. This places a significant demand on a winery's refrigeration plant. [It has been suggested that up to 70 % of capacity can be associated with meeting the requirements for cold stabilisation.]

Consequently, there is growing interest in alternative tartrate stabilisation strategies. The simplest of these is to use seeding, i.e. add KHT crystals that provide nucleation sites (Dharmadhikari, 2002). This can reduce the stabilisation period to less than a day. However, the cost of the using seed crystals can be significant, and their use does not necessarily eliminate the high refrigeration demand involved with initially chilling the wine.

This has lead to more sophisticated processing strategies designed to maximise energy recovery and reuse seeds (Boulton et al., 1996). Examples include proprietary systems commercialised by Vinipal, Sietz (or the Spica process), Gasquet, Alfal-Laval (Crystal-flow system), Westfalia and Imeca companies (Boulton et al., 1996) as well as Polar System from Della Toffola. These systems usually have the capability of stabilizing wines within 20 to 30 minutes (Boulton et al. 1996) but require additional equipment and are more complex in operation. Boulton et al. (1996) reports higher costs have limited their adoption to less than 200 installations worldwide. Other issues with using these types of systems are how to recover occluded wine from separated seed crystals to minimise product loss, and how to clean, sanitise and/or store seed crystals between processing events to avoid contamination risks.

Electrodialysis is successfully used for tartrate stabilisation in Europe and America and is being trialled or implemented at several wineries in Australia. In this method, electric fields and ion-selective membranes are used to separate tartrate salts from the wine without chilling or precipitation (Escudier et al., 1993). Advantages are claimed to include, inter alia, that wine quality is unaffected (Cameira dos Santos et al., 2000; Bach et al., 1999; Moutounet et al., 1997; Wucherpfennig, 1974); energy requirements are lower (e.g. 0.6 kWh/m3 of wine treated (Wucherpfennig, 1974) and 0.2 to 0.5 kWh/m3 (Moutounet and Escudier, 1991)); and equipment has a smaller footprint and can be automated to reduce labour requirements (Moutounet and Escudier, 1991). According to Moutounet and Escudier (1991), the energy cost required for chilling the wine is threefold more than the unit operating costs of an electrodialysis unit. However, costs of membrane replacement and equipment maintenance currently charged by the equipment supplier appear to be discouraging commercial uptake.

Reverse osmosis or nanofiltration, which concentrates the wine without cooling to induce crystallisation, is another potential tartrate stabilisation technology. The concept of exploiting membrane filtration processes in the wine industry has existed for some time. Membrane technology is already used for other applications, e.g. juice concentration, de-alcoholization. In 1976, Rhein - a Germany inventor has patented the use of reverse osmosis to reduce KHT concentration in wine. Companies like GE Osmonics and OLIVER OGAR ITALIA Spa claim to have developed membrane systems that partially concentrate the tartrate in wine and accelerate the tartrate crystallization process. However, there are

no reports of industrial use to date. The only publicly available data regarding operating performance of the process appears to be a paper by Mannapperuma (2001). Mannapperuma published results of a pilot-scale study to use membranes to stabilize tartrate in wine. In this study, nanofiltration was combined with microfiltration. Nanofiltration was employed to concentrate the wine, inducing precipitation of bitartrate salt crystals. The crystals were removed from the nanofiltration retentate by microfiltration. Permeates from nanofiltration and microfiltration were combined to reconstitute the wine. Mannapperuma (2001) commented on likely cost savings of treatment by nanofiltration, using microfiltration to separate tartrate crystals. It was concluded that such a system could achieve lower treatment costs compared with cold stabilization. However, this study employed highly elevated pressures of up to 60 Bar which would likely make the process uneconomic. There was also no experimental confirmation that tartrate stability was achieved. Nor were sensory effects of the process considered.

Ion exchange already has a history of application in the wine industry for tartrate stabilisation, particularly in America. However, ion exchange may not be considered suitable for some wines where high sodium content is of concern. Furthermore some countries may not regard ion exchange as an acceptable oenological process (e.g. Agreement between Australia and the European Community on Trade in Wine, and Protocol (Australian Treaty Series, 1994)). This could prove problematic where these countries are export destinations for wine product. Ion exchange may also impact wine quality by adsorption of colour and flavour compounds (Boulton et al., 1996; Rankine, 2004). Waste from regeneration of ion exchange resin is highly saline. Separate disposal can be expensive and mixing with other winery waste effluent may increase treatment costs and limit disposal options. These issues appear to have limited wider industry use of the process.

During the past 3 years, Hardy Wine Company has sponsored a research project by a PhD student, Ms Lin Lin Low, in the Chemical Engineering Department at the University of Adelaide. The goal of this project was to investigate process alternatives to cold stabilization for tartrate stabilizing wines at Berri Estates Winery in South Australia. This winery is the largest in the Southern Hemisphere and is solely owned and operated by Hardy Wine Company. Chilling without seeding, or cold stabilization, is presently employed as the sole treatment method for prevention of tartrate instability. Each year approximately 106.5 million litres of wine are cold stabilized. Ion-exchange is not favoured following a previous experience with adverse affects on wine quality and because wine products are exported to Europe, where there are difficulties with commercial acceptance of this process.

As a consequence, Hardy Wine Company wished to identify whether a more cost effective process strategy besides cold stabilization was available for application at Berri Estates Winery. There was particular interest in emerging technologies such as fluidised beds, electrodialysis and nanofiltration.

The first stage of this project included a comparison of the economics or costs of alternative technologies (Low et al. 2007). The engineering calculations and conceptual cost estimates were based on real world data from Berri Estates Winery and equipment manufacturers. Product loss was a key cost driver in differentiating tartrate stabilization processes. Cold stabilization was found to be the most economic treatment process irrespective of scale or winery size. Westfalia process and nanofiltration were the next most cost effective options.

Despite these results, nanofiltration remained of significant interest to Hardy Wine Company as this process had been successfully implemented at Berri Estates Winery for other processing applications including juice concentration and de-alcoholization of wines. Several equipment suppliers were also strongly “spruiking” this technology to the company as a cost-effective alternative to cold stabilization. Therefore, it was decided that experimental studies of nanofiltration were warranted, in particular to collect further information on likely operating parameters and performance. The results could then be used to refine and improve the accuracy of previous cost estimates for commercial decision making.

A successful application was made to the GWRDC for funding to support laboratory and field testing for this purpose.

4 Project Aims and Performance targets

The objectives of this project, as were stated in the GWRDC Project Application, are given below. Also indicated were the performance targets and the proposed and actual timing of project activities that were involved in achieving these objectives.

1. ***Objective:*** *Undertake laboratory experiments to collect data that will establish optimum membrane selection and operating conditions to achieve tartrate stabilisation by nanofiltration.* This objective was to be completed by May 2006. However, a short delay work in achieving the objective was experienced because of problems with construction of testing equipment. Consequently, the experiments were completed by August 2006.
2. ***Objective:*** *Field test nanofiltration for tartrate stabilisation.* Completion of this objective was scheduled for November 2006. However, there were problems with reliably securing tartrate unstable wines at Berri Estates Winery. Consequently, field tests at the winery were concluded in December 2006 and analysis of field test samples were not completed until February 2007.

All of the experiments and field testing undertaken as part of the project were conducted by a PhD student, Ms Lin Lin Low, under the direction of her Principal Supervisor and the Chief Investigator for the GWRDC grant, Dr Chris Colby. All of this work will form part of her thesis, which is yet to be finalised. In this respect, early drafts of her thesis have formed the basis for the majority of information presented in this report, which has been prepared by the Chief Investigator, Dr Colby. Where relevant, the Chief Investigator has included additional analysis, interpretation and comments. A final version of Ms Low's thesis will involve additional detailed information about the laboratory experiments and field testing, and more sophisticated analysis of the results that were obtained, which will be published separately.

5 Laboratory experiments

5.1 Introduction

The laboratory experiments were performed at the University of Adelaide. The performance of various membranes for nanofiltration was compared using real wines and a laboratory-scale continuously-stirred batch-test membrane cell. The following sections briefly present the relevant theory (for interpretation and analysis of results); materials and methods; analytical techniques; results obtained; and concluding remarks and recommendations.

5.2 Relevant theory

5.2.1 Recovery

The recovery during a membrane process refers to volume of permeate recovered from known volume of feed as a percentage. Recovery, r (%), was defined and calculated by the following formula.

$$r = \frac{V_p}{V_{cell,i}} \qquad (5.1)$$

Where V_p is the total volume of permeate passed through the membrane; and $V_{cell,i}$ is the initial volume of wine in the cell.

5.2.2 Permeate flux rate

The permeate flux rate describes the linear velocity of permeate flow through a membrane and is often expressed as the volume of permeate per unit area per unit time. Permeate flux rate, J_V (L/m^2/h), was defined and calculated by the following formula.

$$J_V = \frac{\Delta V_p}{A \times t} \qquad (5.2)$$

Where ΔV_p is volume of permeate (L) during a specified collection time; A was effective membrane area (m^2); and t was time required for the collection of ΔV_p (hr).

5.2.3 Rejection

The membrane rejection describes the fraction of a component or molecular species that is rejected or retained by the membrane during filtration, and is usually expressed as a

percentage. Recovery of a component i, R_i (%), was defined and calculated by the following formula.

$$R_i = \frac{C_{r,i} - C_{p,i}}{C_{r,i}} \quad (5.3)$$

Where $C_{r,i}$ is the concentration of species i in the retentate (i.e. in the cell); and $C_{p,i}$ is the concentration of species i in the permeate.

5.2.4 Concentration product

Concentration product (CP) is a method that may be used for evaluating the tartrate stability of a wine (Boulton et al. 1996). It can be considered to represent an equivalent "solubility product" at which a salt will precipitate in a wine. CP was defined and calculated by the following formulae for potassium bitartrate (KHT) and calcium tartrate (CaT) salts.

$$CP_{KHT} = [K^+] \times [HT^-] \quad (5.4)$$

$$CP_{CaT} = [Ca^{2+}] \times [T^{2-}] \quad (5.5)$$

Where $[K^+]$, $[HT^-]$, $[Ca^{2+}]$ and $[T^{2-}]$ are molar concentrations (mol/L) of the ionic species contained within the square brackets.

Table 5.1 presents recommended CP values for potassium bitartrate and calcium tartrate in stable wines by DeSoto & Yamada (1963).

Table 5.1: Recommended values of CP.

Wine	**$CP_{KHT} \times 10^4$**	**$CP_{CaT} \times 10^6$**
White table wines	1.64	2.00
Red table wines	3.00	4.00

5.2.5 Supersaturation

Supersaturation, S, is a term that refers to how much the concentration of a salt exceeds its saturation or solubility limit. S was defined and calculated by the following formulae for potassium bitartrate and calcium tartrate salts.

$$S_{KHT} = \frac{[K^+][HT^-]}{CP_{KHT}} \quad (5.6)$$

$$S_{CaT} = \frac{[Ca^{2+}][T^{2-}]}{CP_{CaT}} \quad (5.7)$$

For many salts, the rate at which precipitation or crystallisation will occur depends on the level of S. Sometime the rate of crystallisation will be insignificant until S is much greater than a value of 1 or unless a nucleation source (e.g. seed crystals) is provided.

5.3 Materials & methods

5.3.1 Membrane cell & experimental arrangement

The laboratory-scale continuously-stirred batch-test membrane cell was purpose designed for the project and built by the Chemical Engineering Department Workshop at the University of Adelaide. The cell was designed to withstand pressures up to 20 bar and constructed so that all internal contact surfaces were food-grade materials including 316 stainless-steel, boro-silicate glass or rubber.

Figure 5.1 presents a photo and schematic of the experimental arrangement that was employed for the laboratory experiments. The cell was sized to hold a volume of 300 mL. During a laboratory experiment, wine was placed in the cell and the cell was pressurised by an external source of compressed nitrogen. This would force the wine through a circular (nanofiltration) membrane laid over a porous frit at the base of the cell. The wine passing through the membrane – the “permeate” – would be collected underneath the porous frit in a cavity, from which it flowed to external piping via a cylindrical outlet channel. As a consequence, the wine remaining in the cell – the retentate – was concentrated.

The cell was also fitted with a stirring element. This consisted of a freely rotating shaft attached to the top plate with a magnetic flea at the base of the shaft. The flea was positioned immediately above the membrane surface. During an experiment, the flea was actuated by placed the cell on a magnetic stirrer plate. This stirring was designed to prevent concentration polarisation and avoid build-up of fouling materials on the membrane surface.

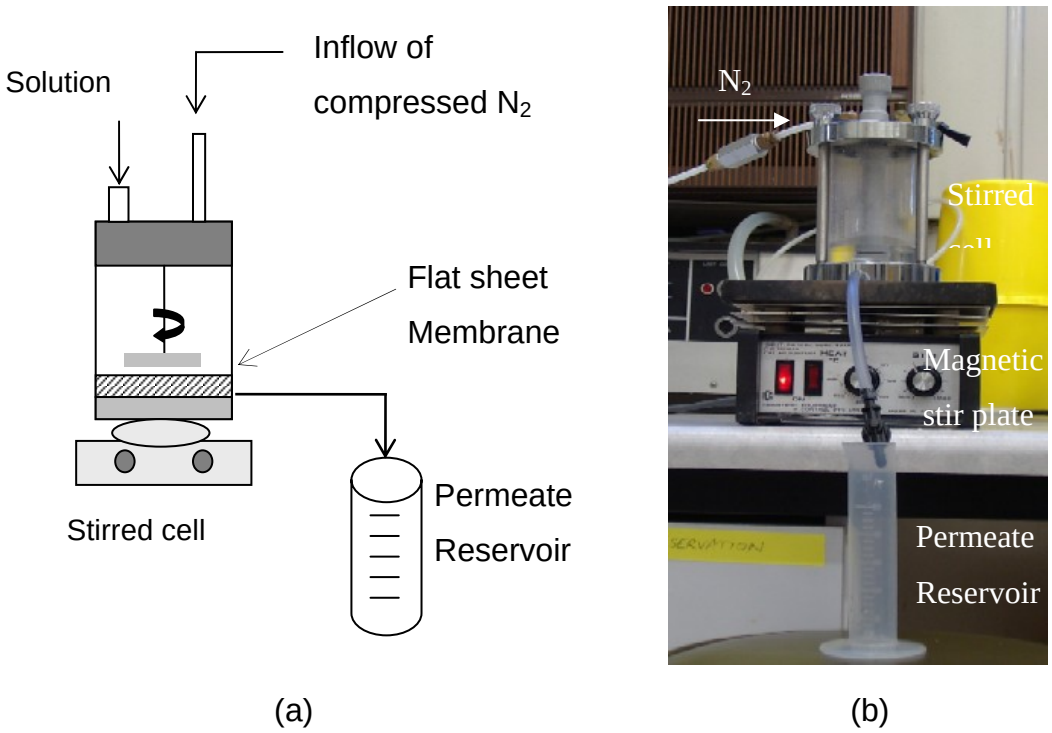


Figure 5.1: Experimental arrangement showing batch-stirred membrane cell: (a) schematic and (b) photograph.

5.3.2 Membranes

Four membranes were evaluated during the laboratory experiments. The type, manufacturer, material and performance characteristics (as provided by the manufacturer) of the membranes are summarised in Table 5.2. The table includes the molecular weight cut-off (MWCO) of each membrane and the measured rejection of $MgSO_4$.

Note that the MWCO of a membrane is not an absolute but a nominal value. Usually it represents the ability of the membrane to retain molecules larger than those of a given size determined by using a set of standards containing globular macro-solutes or mixed dextrans. In practice, some molecules less then the MWCO (particularly if charged) will be retained, and some compounds greater than MWCO may still pass through. Therefore, it can be seen that the combined rejection of Mg^{2+} and SO_4^{2-} ions is greater than 95 % in each case even though these ions have molecular weights much lower than the membrane's stated MWCO.

A membrane was prepared for experimentation by cutting out a circle 72 mm in diameter from rectangular sheets supplied by the manufacturer. The membrane was laid over the porous frit at the base on the cell and the other components of the cell assembled and fixed to seal the membrane.

Prior to initial use of a membrane, 250 mL of demineralised water was filtered through the membrane in the cell at a constant pressure of 10 bar. This was designed to condition the membrane and rinse away residual protective materials (Grandison et al., 2002). When not in use, membranes were removed from the cell and stored in 10 %v/v ethanol solution to prevent microbial contamination.

Table 5.1: Membranes and relevant properties.

Membrane (Manufacturer)	Material	MWCO (Da)	$MgSO_4$ Rejection
NF (Filmtec*)	Polypiperazine Amide Thin Film Composite	~ 200	< 98%
ATF (Domnick Hunter¥)	Thin Film Composite	~ 200	98%
NFA (Domnick Hunter¥)	Thin Film Composite	~ 400	98%
NF270 (Filmtec*)	Polyamide Thin Film Composite	~ 400 – 500	< 97%

* Dow Chemical Company, Michigan, USA

¥ Domnick Hunter Group plc, Durham, England

5.3.3 Wine samples

Tartrate unstable wines from Berri Estates Winery were obtained. This included *Semillon*, *Colombard* and *Shiraz* wines.

The wines were pre-clarified by centrifugation at 3000 rpm for 10 min, then filtered using PALL 0.45 μm, 47mm GN-6 Metricel Grid sterile membrane filters (Pall Co., Michigan, USA).

Each wine was analysed for pH, conductivity, potassium, calcium, tartaric acid, alcohol, and tartrate stability – refer Section 5.4 for description of analytical methods.

When not in use, wine was stored at 15 ºC.

5.3.4 Location

The laboratory experiments were performed in a constant temperature room of 15 ºC at the Hickinbotham Wine Science Laboratory on Waite Campus of the University of Adelaide. Analysis of samples was performed either on-site during experiments or subsequently at external laboratories located at the Australian Wine Research Institute or Hardy Wine Company: Reynella or Berri Estates Winery.

5.3.5 Experiment 1: Comparison of membrane performance

For each membrane, the permeate flux rate of reverse osmosis grade water through the membrane was measured at pressure intervals between 2 and 10 bar.

The water was replaced by Semillon wine and the permeate flux rate measured during concentration of the wine at a pressure of 10 bar. During concentration of the wine, samples of retentate and permeate were collected. These were analysed for pH, conductivity, potassium, calcium, tartaric acid and alcohol to evaluate rejection/performance characteristics – refer Section 5.4 for description of analytical methods.

5.3.6 Evaluation of tartrate stability and seeding requirement

The Colombard and Shiraz wines were used to consider the effect of nanofiltration on tartrate stability and seeding requirement.

The initial conductivities of the wines were measured prior filtering through the stirred cell.

After the desired recovery rate (i.e. 25, 50 and 75%) was attained, the retentate was transferred to a beaker with a magnetic flea and placed on a stirrer plate. Gentle stirring was commenced immediately and conductivity changes recorded. If crystallisation was occurring, there would be changes in salt concentrations in the wine, and thus, its conductivity. Therefore, conductivity could used to determine if crystallisation had/was occurring, and establish if/when crystallisation was complete – or “equilibrium” was achieved.

Once equilibrium occurred, a sample of retentate was filtered through PALL 0.45 μm, 25mm Acrodisc syringe filter (Part no. 4614, Pall Co., Michigan, USA) and blended with permeate in the appropriate proportions to reconstitute the original wine.

The remaining retentate in the beaker was then seeded with 500 mg/L of commercial KHT powder (Australian Tartaric Product). Conductivity changes were recorded. Once equilibrium occurred, another sample of retentate was filtered and blended with permeate to reconstitute the original wine.

5.4 Analytical techniques

5.4.1 Metal ions

The potassium (K^+) and calcium (Ca^{2+}) ion concentrations of wine samples were measured by flame photometry using a Varian SpectrAA-100 atomic absorption spectrophotometer (Varian, Inc., California, USA) operating in emission mode.

5.4.2 Tartaric acid

Tartaric acid (H_2T) concentration was determined by HPLC. The HPLC system was an Agilent 1100 series system with auto-sampler and diode-array detector. A Rezex ROA-Organic acid column (Phenomenex, California, USA), 300 x 7.8 mm was employed. The column was equilibrated in 0.005 M sulphuric acid and held at 60oC. 10 μL of sample was injected. The flow rate of the eluent was 0.6 mL/min. Peaks were detected at 210 nm. H_2T concentration was quantified by comparing measured peak areas with H_2T standards (i.e. 0.5, 2.0, 5.0 and 10.0 g H_2T/L).

5.4.3 Ethanol/Alcohol

Ethanol/alcohol concentration was inferred from measurements by two different instruments: 1) an ATAGO DR-A1 Digital Abbe Refractometer (ATAGO Co., Ltd., Tokyo, Japan); and 2) an Anton Paar's Alcolyzer Wine (Anton Paar Gmbh, Graz, Austria).

Refractive index, RI (nD) was measured at 20^{o}C; accuracy of measurement was approximately ± 0.0002 nD.

The Anton Paar Alcolyzer measures the amount of light absorbed by the sample across the NIR spectrum at 920 nm in a 30 mm cell. The ethanol concentration is inferred from the absorbance measurements by comparison with known standards. The accuracy of measurement is approximately ± 0.1% v/v ethanol.

5.4.4 pH and conductivity

pH and conductivity were measured by a TPS pH/conductivity meter WP-81 (T.P.S Pty Ltd, Brisbane, Australia). The pH/conductivity meter was calibrated with pH buffer of 4.0 and 6.88 (T.P.S. Pty Ltd, Brisbane, Australia) and conductivity standard of 2.76 mS/cm (T.P.S. Pty Ltd, Brisbane, Australia) prior to use.

5.4.5 Bitartrate stability test

Bitartrate stability was inferred from a laboratory test employed by Hardy Wine Company: samples are held at -3ºC for 72 hours and visually inspected for crystal deposit formation. This method required 100 mL of sample. The sample was filtered through a 0.45 μm membrane and placed in 200 mL medical flat glass bottle. The sample was incubated at -3ºC for 72 hours. The sample was then immediately checked for the presence of crystals. The sample was then allowed to warm up to 20ºC. The sample was considered unstable if crystals remained.

5.5 Results & discussion

5.5.1 Wine characteristics

Table 5.2 summarises analyses of wines employed in the laboratory study. (Measurements of free and total SO2 were provided by Hardy Wine Company.)

All of the wines produced crystal deposits during the tartrate stability test, and thus, were considered tartrate unstable. The CP values for the Semillon and Shiraz wines also exceeded the recommended values in Table 5.1 for potassium bitartate but not for calcium tartrate.

Table 5.2: Physical and chemical properties of tartrate unstable Semillon, Colombard and Shiraz used in this study.

Property	Unit	Semillon	Colombard	Shiraz
Ethanol	%v/v	13.1	12.57	13.98
pH		3.25	3.4	3.46
Free SO_2	mg/L	36	20	37
Total SO_2	mg/L	143	124	82
K^+	g/L	0.75	0.88	1.08
Ca^{2+}	g/L	0.070	0.039	0.073
Tartaric acid	g/L	2.56	2.60	2.55
CP_{KHT}	$(M)^2 \times 10^4$	1.85	2.46	3.07
CP_{CaT}	$(M)^2 \times 10^6$	0.79	0.72	1.57
Tartrate stability test*		SD^	HD#	SD^

^ Slight deposit

Heavy deposit

5.5.2 Experiment 1: Membrane performance

5.5.2.1 Permeate Flux rate

All membranes produced a linear relationship between the water flux and the applied pressure as shown in Figure 5.2. The order in the magnitude of fluxes was

NF270 > NFA > NF > ATF

This sequence correlates with the MWCO of the membranes given in Table 5.1. This is as expected because a higher MWCO usually implies a larger pore size in the membrane. This should produce less resistance and allow higher rates of permeate flux to be achieved (at equivalent pressures).

The permeate flux of the Semillon wine as a function of recovery rate (at 10 bar feed pressure) recorded during experiments with the different membranes is presented in Figure 5.3. The magnitude of the wine flux through the membranes was approximately one tenth of the water flux (at 10 bar).

Figure 5.3 also shows a decrease in permeate flux as the recovery rate increased. This is expected because the wine is becoming more concentrated, and thus, will be more difficult to filter. It usually occurs because osmotic pressure differences across the membrane increase as retentate is concentrated, thus reducing the driving force available for permeate flow through the membrane. Other factors also contributing to a decrease in flux rate would be an increase in wine viscosity and fouling of the membrane.

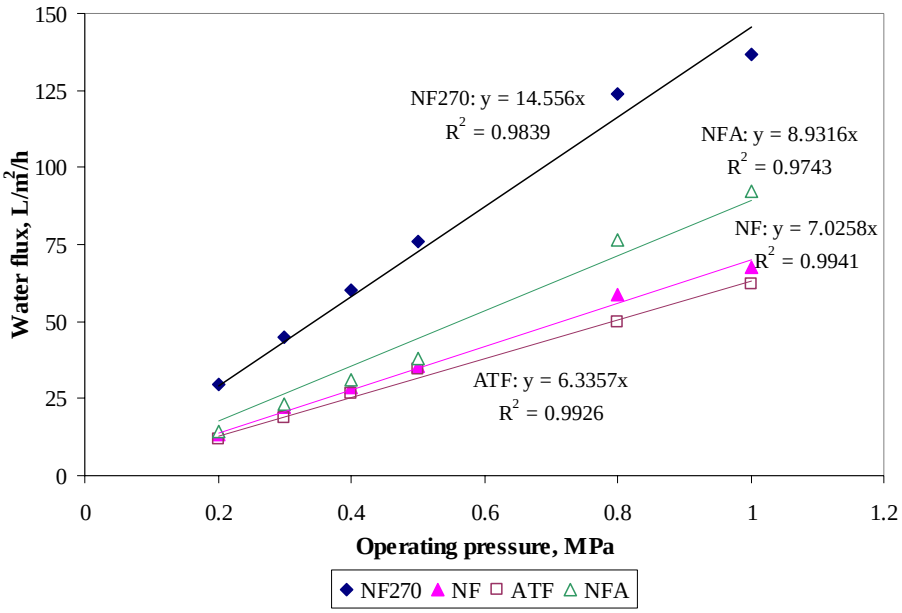


Figure 5.2: Water fluxes of four different membranes at various applied pressure.

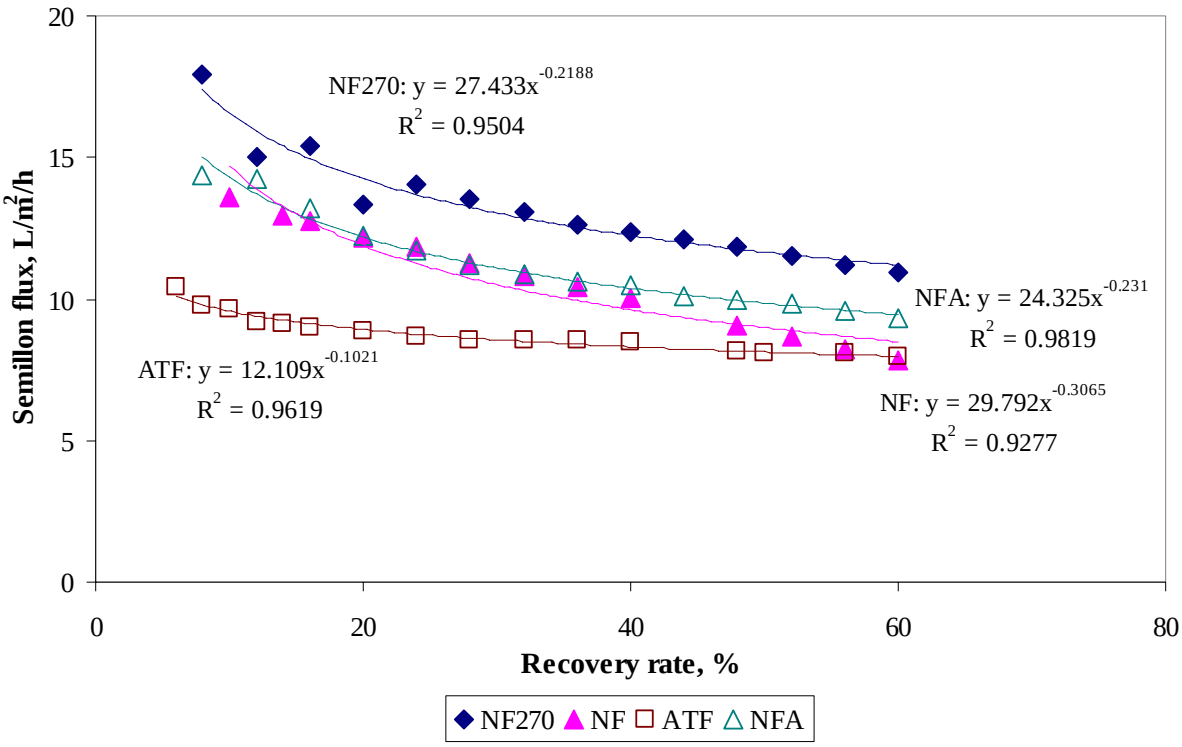


Figure 5.3: Fluxes of Semillon wine at different recovery rates.

5.5.2.2 Ethanol permeability

The ethanol permeability of each membrane was determined by comparing ethanol content in initial untreated wine and retentate (concentrated wine) obtained at different recovery rates. Data collected using the alcolyzer and refractometer is presented in Table 5.3.

There were slight increases in RI of the retentate during concentration of the wine. This might suggest that a slight increase in ethanol concentration had occurred and the membrane was rejecting ethanol during the experiment. However, RI does not solely measure ethanol content but also the presence of the other soluble solids in wine (e.g. sugar) (Zoecklein et al. 1995), which would have also been concentrated in the wine. Ethanol content determined by alcolyzer instead shows a slight decrease in ethanol concentration of retentate. These measurements appear more reliable. It is reasonable to conclude that all membranes tested possessed high levels of ethanol permeability.

Table 5.3: Ethanol content in retentate and initial Semillon feed: (a) values from alcolyzer (% v/v); and (b) refractive index (nD).

(a) Ethanol (% v/v) from alcolyzer (accuracy of ± 0.1 % v/v ethanol)

	Ethanol content, % v/v				
	Recovery rate %				
Membrane	0	20	40	50	60
NF270	13.1	13.0	13.0	13.1	12.9
NF	13.1	12.9	12.9	12.9	12.7
ATF	13.1	13.0	12.9	12.9	12.7
NFA	13.1	12.6	12.7	12.7	12.7

(b) Refractive index value (nD) (accuracy of ± 0.0002 nD)

	Refractive index, nD				
	Recovery rate %				
Membrane	0	20	40	50	60
NF270	1.3433	1.3436	1.3439	1.3446	1.3454
NF	1.3433	1.3435	1.3443	1.3450	1.3457
ATF	1.3433	1.3434	1.3436	1.3440	1.3450
NFA	1.3433	1.3440	1.3436	1.3440	1.3453

5.5.2.3 Ion rejection characteristics

The ion rejection characteristics of the membranes are summarised in Figure 5.4. Note: Between a pH of 3 and 4, 50 to 70 % of this tartaric acid will exist as bitartrate ion, and 2 to 7 % as tartrate ion (Boulton et al., 1996). Thus, the rejection of tartaric acid shown in the figure represents a combined value of the rejections experienced by the bitartate and tartrate ions and tartaric acid present in the wine.

All membranes showed higher rejection of calcium ions (98 to 99%), followed by tartaric acid (75 to 81 %), with potassium ion displaying the lowest rejection (62 to 70 %).

The *NF* membrane appears to provide the highest rejection for tartaric acid and calcium and potassium ions. However the rejection performance of all the membranes was quite similar despite the differences in MWCO stated by the manufacturers.

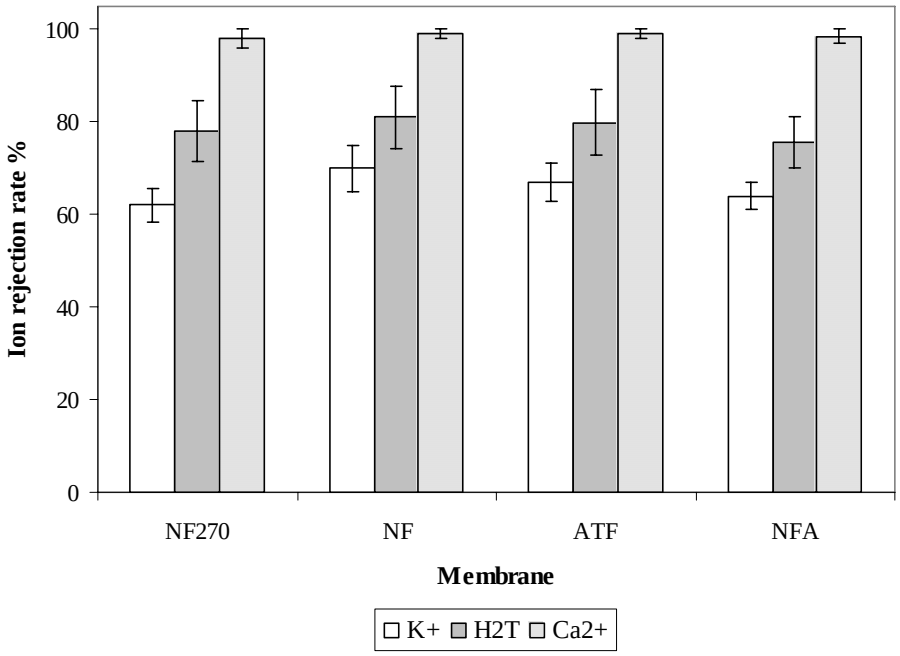


Figure 5.4: Ion rejection characteristics of four different membranes (standard deviation of each measurement is expressed as error bar).

5.5.3 Experiment 2: Tartrate stability and requirement for seeding

5.5.3.1 Tartrate stability

The results of tartrate stability in reconstituted wine at different recovery rates (25, 50 and 75%) for the Colombard and Shiraz are summarised in Table 5.4.

Both wines were initially tartrate unstable. Following treatment by nanofiltration, the wines were rendered stable in all cases except for the Colombard wine treated by NF270 and NFA membranes at a 25% recovery rate without seeding. Therefore, both wines were successfully tartrate stabilised by nanofiltration without seeding at a recovery rate of at least 50 %.

For the Colombard wine, the results also suggest that seeding was able to reduce the recovery rate required for nanofiltration to achieve stability when using the NFA and NF270 membranes.

Table 5.4: Tartrate stability of the reconstituted wine: (a) Colombard and (b) Shiraz.

(a) Colombard

Membrane	Initial	Tartrate stability					
		Without seeding			Seeding		
		Recovery rate %			Recovery rate %		
		25	50	75	25	50	75
NF270	×	×	✓	✓	✓	✓	✓
NF	×	✓	✓	✓	✓	✓	✓
ATF	×	✓	✓	✓	✓	✓	✓
NFA	×	×	✓	✓	✓	✓	✓

(b) Shiraz

Membrane	Initial	Tartrate stability					
		Without seeding			Seeding		
		Recovery rate %			Recovery rate %		
		25	50	75	25	50	75
NF270	×	✓	✓	✓	✓	✓	✓
NF	×	✓	✓	✓	✓	✓	✓
ATF	×	✓	✓	✓	✓	✓	✓
NFA	×	✓	✓	✓	✓	✓	✓

✓: Tartrate stable wine – No crystals visible during the -3^{o}C/3 day test.

×: Tartrate unstable wine – Crystals were formed during the -3^{o}C/3 day test.

5.5.3.2 Supersaturation calculations

Table 5.5 shows the estimated degree of supersaturation, S, for potassium bitartate in the nanofiltration retentate of Colombard and Shiraz at different recovery rates (25, 50 and 75 %) with and without seeding.

The order in the magnitude of *S* achieved by the various membranes for both *Colombard* and *Shiraz* was

NF > ATF > NFA > NF270

Table 5.5: Estimated degree of supersaturation of the retentate obtained at different recovery rate: (a) Colombard and (b) Shiraz.

(a) Colombard

Membrane	Degree of Supersaturation at 15°C, *S*						
		Without seeding			Seeding		
		Recovery rate %			Recovery rate %		
	0	25	50	75	25	50	75
NF270	2.39	2.00	4.50	18.02	2.64	5.43	19.83
NF	2.39	2.41	5.42	21.68	3.10	6.44	23.67
ATF	2.39	2.27	5.12	20.47	2.95	6.11	22.40
NFA	2.39	2.12	4.77	19.09	2.77	5.73	20.96

(b) Shiraz

Membrane	Degree of Supersaturation at 15°C, *S*						
		Without seeding			Seeding		
		Recovery rate %			Recovery rate %		
	0	25	50	75	25	50	75
NF270	3.37	2.82	6.35	25.40	3.64	7.55	27.74
NF	3.37	3.40	7.64	30.56	4.29	8.95	33.14
ATF	3.37	3.21	7.21	28.85	4.07	8.49	31.35
NFA	3.37	2.99	6.73	26.91	3.83	7.96	29.32

By adding 0.5 g/L of KHT crystal a seed, the degree of supersaturation of both Colombard and Shiraz wines was estimated to increase by approximately 9 to 30 % compared to without seeding. For instance, addition of 0.5 g/L of KHT provides addition of 0.1 g/L of potassium and 0.4 g/L of tartaric acid to the wine. This contributed to a rise in the *CP* value and an increased value of *S*.

According to Rhein and Neradt (1979) and Gerbaud et al. (1996a), spontaneous crystallisation only occurs in highly supersaturated wines when the relative KHT (or CaT) supersaturation level is greater than 3. Table 5.5 suggests that retentate obtained at recovery rates between 50 and 75 % for both wines exceeded this degree of supersaturation. Hence, spontaneous crystallisation should have occurred under these conditions.

As tartrate stability was also achieved at 25 % recovery in some cases, this suggests that these conditions also favoured sufficient nucleation for crystallisation to occur and stabilise the wines.

Furthermore, more rapid crystallisation would be expected at higher recovery rates with a greater degree of supersaturation.

5.5.3.3 Conductivity changes

The (percent) conductivity changes at equilibrium for the reconstituted wines (with and without seeding) relative to the initial untreated wine are summarised in Table 5.6. The time required to achieve equilibrium without seeding usually took 2 hours. This time was reduced by seeding to less than 1 hr.

The order of the magnitude of the conductivity changes for both *Colombard* and *Shiraz* wines was

NF > ATF > NFA > NF270

This sequence is consistent with that observed for membrane rejection characteristics and estimated degrees of supersaturation.

Conductivity changes in the reconstituted wine with seeding were noticeably less than the reconstituted wine without seeding. This can be attributed to the effect of KHT seeds, part of which will dissolve when added and alter the solubility equilibria in the wine.

Colombard wine experienced greater conductivity reductions during experiments compared with Shiraz wine. This difference could be a result of higher proportions of colloidal and organic compounds in red wines which can inhibit KHT nucleation and/or crystallisation (Vernhet et al. 1999b, Gerbaud et al.1996a, Tanahashi et al. 1992).

5.6 Concluding remarks

Commercial nanofiltration membranes with MCWOs between 200 and 500 Da were able to achieve tartrate stabilisation in wines without seeding at moderate pressures of < 20 bar and recoveries of at least 50 %. Seeding of wine following nanofiltration may reduce holding time for stability to be achieved and also could reduce the recovery rate necessary to values of less than 50 %. The flux rates achievable were between 10 and 20 $L/m^2/hr$.

Table 5.6: Conductivity changes between the reconstituted wine and initial untreated wine: (a) Colombard and (b) Shiraz.

(a) Colombard (initial conductivity = 2375 μS/cm)

	% ΔConductivity					
	Without seeding			Seeding		
	Recovery rate %			Recovery rate %		
Membrane	25	50	75	25	50	75
NF270	-3.3	-6.6	-21.0	-3.3	-7.7	-14.0
NF	-6.3	-12.9	-23.6	-5.5	-11.4	-18.5
ATF	-4.8	-10.3	-22.1	-4.4	-9.6	-15.9
NFA	-0.7	-4.8	-19.2	-0.7	-6.3	-12.2

(b) Shiraz (initial conductivity = 2710 μS/cm)

	% ΔConductivity					
	Without seeding			Seeding		
	Recovery rate %			Recovery rate %		
Membrane	25	50	75	25	50	75
NF270	-2.9	-4.2	-12.0	-2.4	-4.0	-9.5
NF	-5.7	-7.8	-14.9	-5.7	-8.2	-13.7
ATF	-4.4	-6.9	-14.1	-4.0	-6.5	-12.0
NFA	-0.6	-2.1	-9.1	-0.5	-1.7	-7.4

6 Field testing

6.1 Introduction

Field tests were undertaken at Berri Estates Winery to investigate use of nanofiltration (NF) for tartrate stabilisation.

The tests were conducted with tartrate unstable Colombard and Shiraz wines and performed under simulated production-scale conditions using an existing NF membrane system already operating at the Winery.

The field tests with the Colombard wine were performed in October 2006. The field testing of Shiraz wines took place in December 2006.

The NF-treated wines were evaluated for tartrate stability. The wines were also compared for sensory differences with wine that had been tartrate-stabilised by the existing cold stabilisation process.

6.2 Materials and Methods

6.2.1 Wine preparation

The Colombard and Shiraz wines were the same previously used for the laboratory experiments. The wines were pre-clarified by Westfalia SC150-06-777 centrifuge (Westfalia Separator AG, Oelde, Germany). The clarified wines were stored in insulated and jacketed tanks at 8 ^{o}C.

6.2.2 NF system & testing arrangement

The field testing arrangement is illustrated in Figure 6.1 and a photo of the membrane system taken at site is shown in Figure 6.2.

Wine was pumped from a feed tank through a 200 μm strainer to the high pressure pump, where it was pressurised and fed to the membrane system. The membrane system consisted of a "single train" of eight pressure vessels in series. Each pressure vessel contained three 8" diameter × 40" long spiral-wound nanofiltration membrane elements. The membrane elements were recommended and supplied by Osmoflo Pty Ltd. [Osmoflo is an Adelaide-based supplier of membrane systems and was responsible for fabricating and installing the Winery's NF membrane system.] The manufacturer and specifications of the membrane elements were confidential but the MWCO of the membranes was stated as 300 Da. Therefore it was assumed similar to NF and ATF membranes evaluated during the laboratory experiments.

The total membrane area of the membrane system was 344 m^2.

Permeate produced by the membrane system was collected in a separate tank. The retentate was recycled to the feed tank. The membrane system was operated continuously until the desired recovery was achieved.

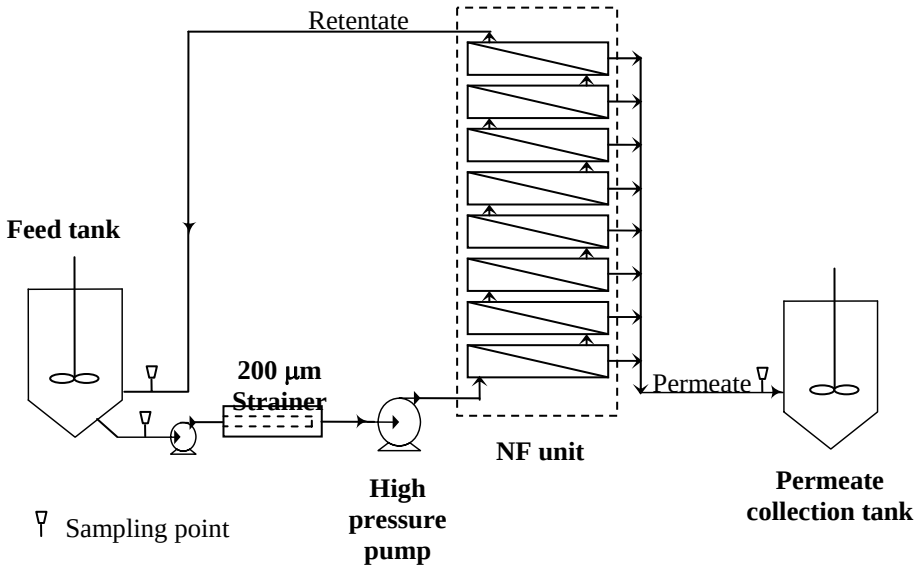


Figure 6.1: Process flowsheet illustrating the field testing arrangement.



Figure 6.2: Picture of the membrane filtration system at Berri Estates Winery.

6.2.3 Field testing

6.2.3.1 Introduction

The individual permutations for testing of each wine are summarised in the Figure 6.3. Further general information regarding test procedures are given below.

A key concern during the field testing was prevention of oxidative spoilage of the wines. There were often small volumes of wine being transferred and stored. The sizes of the tank used in the field tests were also variable and ranged from 15 to 45 kL and it was not always possible to avoid ullage. Therefore, care was taken to avoid oxidative spoilage of by judicious use of nitrogen sparging and dry ice addition to processing and sampling equipment and storage tanks and sampling receptacles to ensure inert gas environments/blankets, and thus, minimise potential O_2 pickup. These practices were discussed with and overseen by Hardy Wine Company technical personnel assisting with the field tests.

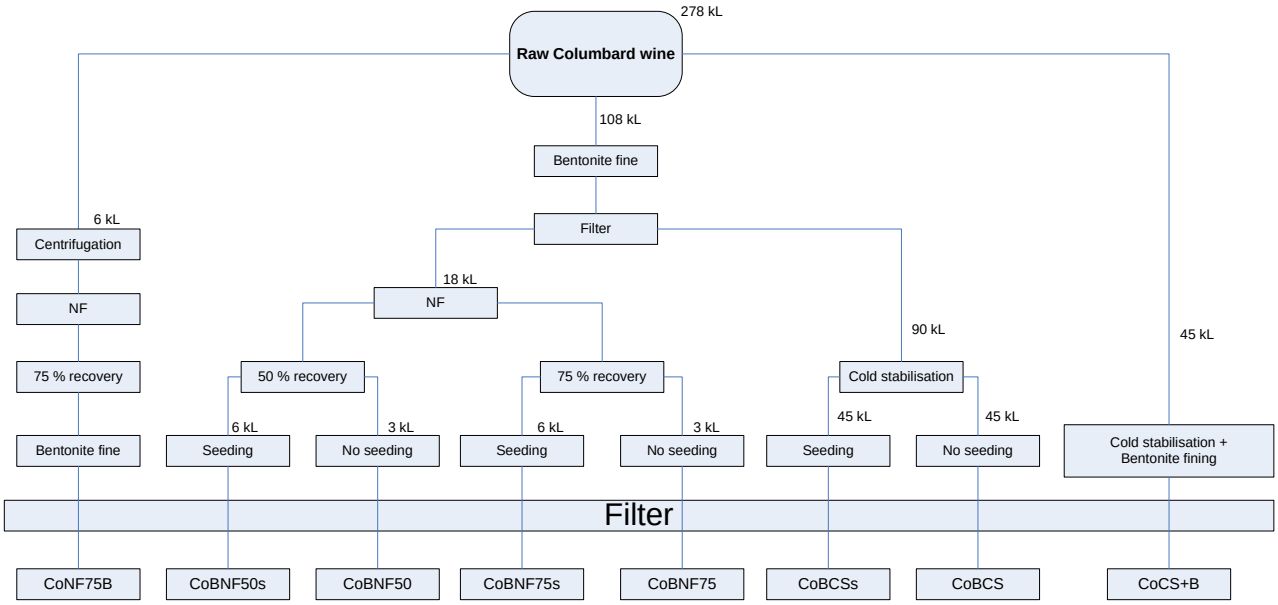
6.2.3.2 Bentonite fining

White wines at Berri Estates Winery are normally bentonite fined prior or during cold stabilisation. Therefore, the testing with the Colombard wine included scenarios where bentonite fining was applied both before and after nanofiltration and before or during cold stabilisation. The bentonite employed was a sodium bentonite, Vitiben (BPM Minerals, Denver, United States). The dose rates were determined by fining trials at the Winery's laboratory.

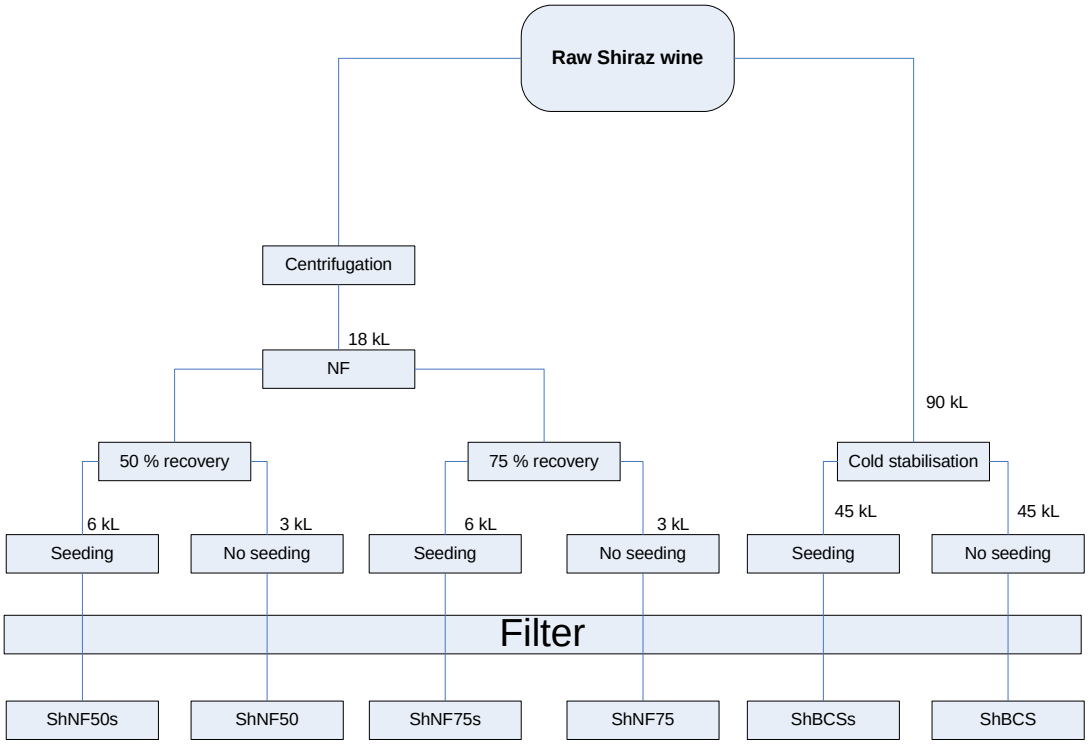
6.2.3.3 Nanofiltration

The NF membrane system was operated at ambient temperature and a feed pressure set point of approximately 18 bar. Wine was pumped from the feed tank to membrane system and retentate recycled until the desired recovery, 50 or 75 %, was achieved. During testing, a range of membrane system operating information was recorded including flow rates, volumes, pressures and temperatures. Samples of retentate and permeate were also collected for chemical analysis to determine the rejection characteristics of the membranes.

The concentrated wine in the feed tank was transferred to new tanks with or without seeding at 50 mg/L of powdered potassium bitartrate. The new tanks were held at ambient temperature for 4 hours (assuming this would be sufficient for crystallisation to occur and reach equilibrium) and conductivity changes were monitored. The retentate was racked and clarified by diatomaceous earth (DE) filtration, then blended with permeate to reconstitute the wine.



(a)



(b)

Figure 6.3: Summary of field testing performed for; (a) Colombard; and (b) Shiraz wines.

6.2.3.4 Cold stabilisation

Cold stabilisation testing of the wines was conducted at the same time as the nanofiltration field tests. The wines were chilled and maintained at -4 ^{o}C for a period of 7 days with or without seeding at 50 mg/L of powdered potassium bitartrate.

6.2.3.5 Sampling and analysis

Samples of raw, reconstituted and cold stabilised wines from the tests were collected for chemical analysis and sensory evaluation – refer Section 6.3 for details of analytical techniques. The samples for sensory evaluation were collected in 750 mL bottles with roll-on, tamper evident (ROTE) or Stelvin closures and stored under refrigerated conditions at 4 ºC until testing. Figure 6.3 shows the samples codes applied to each testing permutation.

6.3 Analytical Techniques

Analytical techniques for measurement of ethanol, pH, potassium, calcium, tartaric content and tartrate stability were the same as for the laboratory experiments – refer the Section 5.4 for relevant details. Additional analyses performed during the field tests included; spectral measurements of colour and phenolics; and sensory testing. The techniques employed for these analyses are briefly described in the following sections.

6.3.1 Phenolics and colour measurements

Spectrophotometric analysis was performed using a Varian Cary 50 Bio UV-Visible spectrophotometer (VARIAN Inc., Melbourne, Australia). Methods recommended by Iland et al. (2000) were followed.

6.3.1.1 Shiraz wine

Spectral measurements of the Shiraz wine included; wine colour density; wine colour hue; total phenolics; and total anthocyanins.

Wine colour density (a.u.) describing the colour intensity was the sum of absorbance measured at 420 nm and 520 nm ($A_{420} + A_{520}$).

Wine colour hue expressing colour tint or shade was obtained by dividing A_{420} with A_{520} (A_{420} / A_{520}).

Total phenolics (a.u.) were measured by diluting the wine with 1 M Hydrochloride (HCl) and measured the absorbance at 280 nm (A_{280}^{HCl}). In order to eliminate the absorbance of non-phenolic material, 4 was subtracted from the measured value. Hence, total phenolics was estimated as A_{280}^{HCl} - 4.

Total anthocyanins (in mg/L) were measured at 520 nm, after a portion of the wine was diluted with 1 M HCl.

6.3.1.2 Colombard wine

Total phenolics (a.u.) were measured using the same method as for *Shiraz*.

Total flavonoids (a.u.) were estimated by measuring the absorbance at 280 nm and 320 nm. The expression used to estimated total flavonoids was

$$[A_{280} - 4] - (0.66) \times [A_{320} - 1.4].$$

The factors included in the above expression are the correction factors to eliminate the absorbance of the non flavonoid component (i.e. hydroxycinnamates).

Relative brownness (a.u.), which estimates the concentration of brown pigment in wine, was measured by absorbance at 420 nm.

6.3.2 Sensory evaluation

Sensory evaluation was performed by duo-trio difference tests to identify differences between testing scenarios or treatments. The tests were performed by Provisor (Adelaide, South Australia). Tests were conducted in accordance with Australian Standard 2542.2.4 – 1988: Sensory analysis of foods – Specific methods – Duo-trio test. The duo-trio difference tests were performed for aroma and flavour with a panel consisting of twenty-five trained assessors. Samples were presented in coded ISO standard tasting glasses (30 mL) and assessed at room temperature. Under sodium lighting, each assessor was first presented a reference sample followed by two samples. The assessor was then asked to identify which sample matched the reference and was also asked to comment on the reasons for his/her choices. The results were analysed for significance by a binomial test.

6.4 Results and Discussion

6.4.1 Wine quality

The physical and chemical properties of the wines at the time of field testing are summarised in Table 6.1. The table includes the additional phenolics and colour measurements. The table shows no appreciable change in wine quality from when they were used for laboratory experiments.

Table 6.1: Physical and chemical properties of tartrate unstable Colombard and Shiraz wines.

Property		***Colombard***	***Shiraz***
Ethanol	%v/v	12.57	13.98
pH		3.40	3.46
Free SO_2	mg/L	20	37
Total SO_2	mg/L	124	82
K^+	g/L	0.88	1.08
Ca^{2+}	g/L	0.04	0.07
H_2T	g/L	2.60	2.55
CP_{KHT}	$(M)^2 \times 10^4$	2.46	3.07
CP_{CaT}	$(M)^2 \times 10^6$	0.73	1.50
Total phenolics	a.u.	4.52	39.00
Total anthocyanins	mg/L	-	280
Total flavonoids	a.u.	35.00	-
Colour density	a.u.	-	8.3
Hue		-	0.7
Relative brownness	a.u.	0.15	-
Tartrate stability test*		HD#	SD^

#: Heavy deposits observed

^: Slight deposits observed

6.4.2 Performance of NF system

Tables 6.2 and 6.3 presents operating conditions and performance parameters recorded during several of the field tests for Colombard and Shiraz wine, respectively. Flux rates achieved ranged between 5 and 12 L/m^2/hr for Colombard wine, and between 2 and 6 L/m^2/hr for the Shiraz wines. As a consequence of the lower flux rate, the Shiraz trials took longer to attain the same recovery as for testing of Colombard wine. For instance, the processing time of Shiraz to achieve 50 % recovery was 20 % longer than Colombard and approximately 70 % longer to achieve 75 % recovery.

In both tests, the flux decreased with time as the wine was concentrated. Again, as previously mentioned during the laboratory experiments this would be caused by increases in osmotic pressure and viscosity of the wines as they are concentrated, and incidence of membrane fouling.

6.4.3 Membrane rejection

Table 6.4 gives values from chemical analysis of retentate and permeate taken during at the commencement of a nanofiltration field test with Colombard wine. Similarly, values from chemical analyses of the retentate and permeate at the commencement of a nanofiltration field test with Shiraz wine is presented in Table 6.5. Included in both tables are calculations of the membrane's rejection characteristics for each component or species.

The membrane's rejection characteristics for potassium and calcium ions and tartaric acid were similar to membranes used during the laboratory experiments.

These tables also reveal some interesting membrane rejection characteristics for other wine components or species in the wine.

The membrane displayed complete rejection of phenolics in both wines. Additionally, there was nearly total rejection of flavonoid compounds in Colombard trials and anthocyanins in Shiraz trials.

There was also relatively high rejection of free and total SO_2 and titratable acidity. The rejection was more dramatic for the Shiraz than Colombard wine. As a consequence, the Colombard permeate from the membrane system had approximately half the free SO_2 and a quarter of the total SO_2 than in the raw wines. For the Shiraz wines, the remaining levels of free and total SO2 in permeate were 7 and 11 mg/L, respectively.

Table 6.2: NF operating conditions and performance during Colombard trials: (a) Raw Colombard at 75 % recovery; (b) bentonite fined Colombard at 50 %; and (c) bentonite fined Colombard at 75 %.

(a) Raw Colombard at 75% recovery

	Feed		Permeate			
Time, min	Flow, L/hr	T, ^{o}C	Flow, L/hr	Flux, L/m^2/hr	Throughput, L	Recovery, %
8	9400	12	2340	11.43	300	5
20	9235	13	1690	7.91	732	12.2
30	9088	13	1600	7.49	870	14.5
45	8960	13	1520	7.11	1260	21
60	8780	14	1475	6.60	1620	27
75	8723	14	1410	6.31	2010	33.5
90	8677	14	1385	6.20	2400	40
105	8620	14	1310	5.86	2940	49
120	8460	15	1290	5.51	3210	53.5
135	8293	15	1220	5.21	3612	60.2
150	8222	16	1178	4.76	3960	66
165	8094	17	1135	4.42	4251	70.85
170	8000	17	1115	4.34	4500	75

(b) Bentonite fined Colombard at 50% recovery

	Feed		Permeate			
Time, min	Flow, L/hr	T, ^{o}C	Flow, L/hr	Flux, L/m^2/hr	Throughput, L	Recovery, %
5	9460	12	2300	11.23	250	4.17
15	9080	12	1883	9.20	450	7.5
30	8790	13	1677	7.85	822	13.7
50	8626	13	1500	7.02	1371	22.85
60	8530	14	1430	6.40	1656	27.6
75	8440	14	1380	6.18	2016	33.6
90	8357	15	1298	5.55	2340	39
105	8145	16	1173	4.74	2682	44.7
120	8040	17	1089	4.24	3000	50

Table 6.3 continued.

(c) Bentonite fined Colombard at 75% recovery

	Feed		Permeate			
Time, min	Flow, L/hr	T, ^{o}C	Flow, L/hr	Flux, L/m^2/hr	Throughput, L	Recovery, %
5	9450	12	2400	11.72	210	3.5
15	9140	12	1995	9.74	738	12.3
30	8670	13	1800	8.42	1230	20.5
45	8517	13	1713	8.02	1584	26.4
60	8415	14	1600	7.16	2022	33.7
75	8351	14	1560	6.98	2418	40.3
90	8261	14	1505	6.74	2838	47.3
105	8197	14	1500	6.72	3216	53.6
120	8126	15	1450	6.20	3582	59.7
135	8035	15	1375	5.88	3930	65.5
150	7970	16	1300	5.25	4272	71.2
160	7930	16	1280	5.17	4500	75

6.4.4 Effect of differing treatments on composition & tartrate stability

The effects of differing treatment on physical, chemical and tartrate stability characteristics for the Colombard and Shiraz wines are presented in Figures 6.6 and 6.7, respectively. Also included in the tables are the same analyses of the raw wines and of the Colombard wine after bentonite fining.

6.4.4.1 Colombard wine

There appeared to be a slight change in wine composition and stability of the raw wine after bentonite fining. This included an improvement in tartrate stability, decrease in titratable acidity, and reduction in phenolics content and relative brownness.

Cold stabilisation was able to tartrate stabilise the wine regardless of whether bentonite fining was performed before or during the chilling of the wine. However, there appeared to be a marked difference in potassium concentration between the wine if bentonite fined before or during cold stabilisation. When the bentonite was added during the cold stabilisation step, the potassium concentration decreased significantly. The same effect was observed when the wine was seeded during cold stabilisation. In both of these cases, a decrease in tartaric acid concentration was also observed. This could suggest greater amounts of precipitation of potassium bitartate occurred under these treatment scenarios.

Table 6.3: NF operating conditions and performance during Shiraz trials: (a) Raw Shiraz at 50 % recovery; (b) Raw Shiraz at 75 %.

(a) Raw Shiraz at 50 % recovery

	Feed		Permeate			
Time, min	Flow, L/hr	T, ^{o}C	Flow, L/hr	Flux, L/m^2/hr	Throughput, L	Recovery, %
5	7170	17	1850	5.38	102	1.7
10	6260	17	1500	4.36	216	3.6
25	5550	17	1350	3.92	564	9.4
40	5380	19	1239	3.60	900	15
55	5079	19	1214	3.53	1176	19.6
85	4890	19	1181	3.43	1638	27.3
115	4826	21	1150	3.34	2310	38.5
145	4686	22	1120	3.26	2904	48.4
150	4674	22	1115	3.24	3000	50

(b) Raw Shiraz at 75 % recovery

	Feed		Permeate			
Time, min	Flow, L/hr	T, ^{o}C	Flow, L/hr	Flux, L/m^2/hr	Throughput, L	Recovery, %
5	7100	17	1770	5.15	72	1.2
10	6200	17	1600	4.65	147	2.45
25	5450	17	1400	4.07	372	6.2
40	5260	18	1280	3.72	624	10.4
55	5009	18	1245	3.62	864	14.4
85	4800	19	1200	3.49	1368	22.8
115	4796	21	1170	3.40	1878	31.3
145	4626	22	1158	3.37	2388	39.8
175	4380	26	1120	3.26	2904	48.4
220	4100	27	1050	3.05	3822	63.7
250	3850	28	1020	2.97	4110	68.5
270	3700	28	1000	2.91	4380	73
278	3690	29	995	2.89	4500	75

Table 6.4: Composition of permeate and retentate of Colombard wine and the estimated rejection characteristics of the membrane.

Property		Feed	Permeate	Retentate	% Rejection
Ethanol	% v/v	12.50	11.72	12.09	6.2
Titrable acidity	g/L as H_2T	7.16	3.49	10.00	51.3
Free SO_2	mg/L	25	15	27	40.0
Total SO_2	mg/L	141	33	213	76.6
K^+	g/L	1.09	0.54	1.22	50.5
Ca^{2+}	g/L	0.07	0.00	0.10	100.0
H_2T	g/L	2.72	0.75	4.49	72.4
Total flavonoids	a.u.	34.0	0.5	63.0	98.5
Total phenolics	a.u.	4.0	0.0	9.6	100.0
Relative brownness	a.u	0.11	0.06	0.18	-

Table 6.5: Composition of Shiraz permeate and retentate and the estimated rejection characteristics of the membrane.

Property		Feed	Permeate	Retentate	% Rejection
Ethanol	% v/v	13.98	13.39	14.03	4.2
Titrable acidity	g/L as H_2T	6.32	2.33	7.51	63.1
Free SO_2	mg/L	37	7	41	81.1
Total SO_2	mg/L	82	11	97	86.6
K^+	g/L	1.08	0.46	1.30	57.4
Ca^{2+}	g/L	0.07	0.00	0.11	100.0
H_2T	g/L	2.55	0.26	3.19	89.8
Colour density		8.3	0.0	10.0	-
Hue		0.70	0.71	1.65	-
Total phenolics	a.u.	39	0	53	100.0
Total anthocyanins	a.u	280	5	365	98.2

All nanofiltration treatments were able to stabilise the wine. Greater reductions in potassium and tartaric acid concentrations were observed at a 75 % recovery compared to reconstituted wines produced at 50 % recovery. Seeding appeared to have no effect on final wine composition or stability.

For all nanofiltration treatments, the ethanol content was lower when compared with the raw wine and cold stabilisation treatments. Relatively small parcels of the wines were processed by nanofiltration (see Figure 6.3). Sulphited water containing citric acid was used during the field tests to fill, and push wines through, pipes during testing. Whilst great care was taken when "cutting off" at water/wine interfaces, the slightly lower values of ethanol suggest that the wine may have experienced some dilution with sulphited water. This could have also produced the lower values recorded for other wine properties. Despite this, nanofiltration treatments did not appear to produce significant differences in free and total SO_2 or relative brownness when compared to cold stabilisation treatments. The relative brownness can be considered a useful indicator of whether wine oxidation might have occurred. That it did not change suggests that preventative measures implemented to avoid oxidative spoilage of the wine were successful.

However, nanofiltration seemed to produce lower values of total flavonoids and phenolics. [The values of total flavonoids and phenolics for BNF50s look aberrant and probably cannot be considered reliable.]

6.4.4.2 Shiraz wine

For the Shiraz wine, all cold stabilisation and nanofiltration treatments were able to tartrate stabilise the wine.

The same decreases in potassium, tartaric acid and titratable acidity with nanofiltration treatment can be seen. Likewise, these reductions were more marked at a 75 % recovery.

Slightly lower ethanol concentrations during nanofiltration were also recorded, again suggesting a dilution may have occurred.

Nevertheless, a noticeable decrease in the total anthocyanins, unlikely to be attributable to dilution was observed from nanofiltration treatment. However, this decrease was not accompanied by a reduction in coloured anthocyanins, colour density or hue.

Table 6.5: Physical, chemical and stability characteristics of Colombard wines for differing treatments.

Code		Raw wine	Raw wine/ Bentonite fined	CS+B	BCS	BCSs	NF75B	BNF50	BNF50s	BNF75	BNF75s
Ethanol	% v/v	12.57	12.50	12.51	12.48	12.49	11.37	10.94	10.94	11.45	11.16
Titrable acidity	g/L as H_2T	7.57	7.16	6.45	6.69	6.41	5.99	6.59	5.18	6.15	6.24
Free SO_2	mg/L	28	25	24	23	23	15	27	24	28	25
Total SO_2	mg/L	144	141	152	152	152	121	132	127	132	135
K^+	g/L	1.05	1.04	0.82	0.99	0.79	0.8	0.97	0.91	0.79	0.80
Ca^{2+}	g/L	0.07	0.07	0.08	0.07	0.07	0.07	0.08	0.05	0.07	0.08
H_2T	g/L	2.79	2.72	2.02	2.56	1.94	2.00	2.64	2.45	2.23	2.05
CP_{KHT}	$(M)^2 \times 10^4$	3.15	3.04	1.78	2.73	1.65	1.72	2.75	2.40	1.89	1.76
CP_{CaT}	$(M)^2 \times 10^6$	1.38	1.34	1.14	1.26	0.96	0.99	1.49	0.86	1.10	1.16
Total flavonoids	a.u.	35	34	33	34	33	27	31	18	27	30
Total phenolics	a.u.	4.52	4	3.88	3.96	3.95	2.97	3.8	1.43	2.8	3.38
Relative brownness	a.u	0.16	0.11	0.10	0.10	0.13	0.14	0.12	0.10	0.10	0.12
Tartrate stability		HD*	SD#	✓^	✓^	✓^	✓^	✓^	✓^	✓^	✓^

*: Heavy deposits observed

#: Slight deposits observed

^: No deposits observed and wine was considered stable

Table 6.6: Physical, chemical and stability characteristics of Shiraz wines for differing treatments.

Property		Raw wine	BCS	BCSs	NF50	NF50s	NF75	NF75s
Ethanol	% v/v	13.98	13.81	13.98	13.02	12.97	13.16	12.81
Titrable acidity	g/L as H_2T	6.32	6.22	6.33	5.52	6.08	5.94	5.85
Free SO_2	mg/L	37	30	29	27	29	28	29
Total SO_2	mg/L	82	70	68	63	68	65	70
K^+	g/L	1.08	1.06	1.05	1.06	1.03	0.98	0.96
Ca^{2+}	g/L	0.07	0.07	0.07	0.05	0.06	0.06	0.07
H_2T	g/L	2.55	2.54	2.52	2.54	2.51	2.08	2.09
CP_{KHT}	$(M)^2 \times 10^4$	3.07	3.00	2.95	3.00	2.88	2.27	2.24
CP_{CaT}	$(M)^2 \times 10^6$	1.50	1.50	1.48	1.07	1.27	1.05	1.23
Colour density		8.3	8.3	9.5	8.2	10.2	8.4	9.4
Hue		0.70	0.70	0.67	0.66	0.68	0.65	0.64
Total phenolics	a.u.	39	38	38	34	38	32	36
Total anthocyanins	mg/L	280	278	274	227	237	223	233
Coloured anthocyanins	mg/L	55.80	51.63	69.76	56.68	69.83	55.75	66.46
Tartrate stability		SD#	✓^	✓^	✓^	✓^	✓^	✓^

#: Slight deposits observed

^: No deposits observed and wine was considered stable

6.4.5 Conductivity measurements

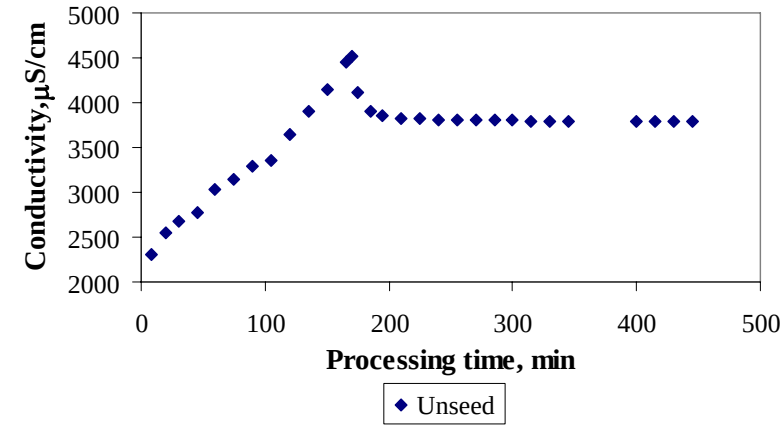
Figures 6.4 and 6.5 show conductivity changes recorded in the feed tank and retentate hold tank for Colombard and Shiraz wines during the concentration and holding periods of nanofiltration for different treatments. The conductivity of the wine during the concentration and holding period gives an insight into how long it takes for the wine to tartrate stabilise during nanofiltration treatment.

Consider Figure 6.4(a): raw wine concentrated to a 75 % recovery with no seeding. Between 0 and 170 min, the conductivity increases proportionally as the wine is concentrated. During this period, supersaturation of potassium bitartrate in the wine would have been increasing, eventually leading to nucleation and crystallisation of the potassium bitartate crystals. When nucleation occurred cannot be accurately discerned (without further sophisticated forms of analysis), but it is clear this has already happened because the conductivity is immediately decreasing following completion of the concentration phase. This decrease is initially rapid but then slows as the system comes to its new "solubility equilibrium" and the conductivity tends towards a constant value. From this figure, the crystallisation phase is virtually complete within 20 min from commencement of the holding phase.

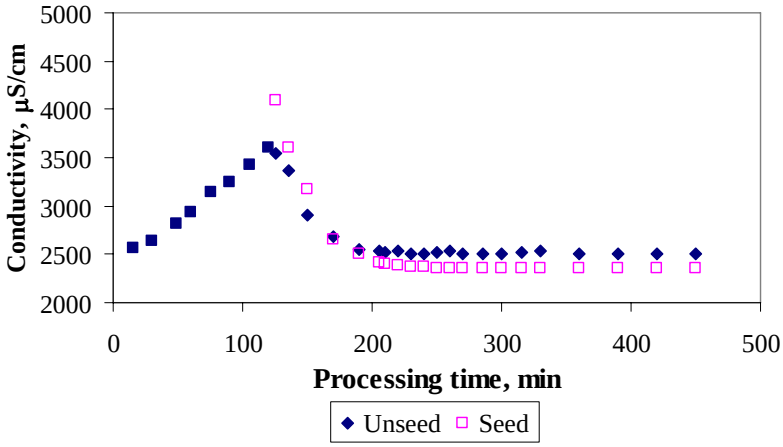
The behaviour of the un-fined Colombard wine in Figure 6.4(c) for the same recovery rate is almost identical. This figure also shows the effect of seeding on the holding period. Seeding appears to have increased the initial conductivity of the wine and produced slightly lower final steady state conductivity. However, it does not seem to decrease the holding time necessary for the stabilisation process to complete.

Figure 6.4(b) shows the conductivity changes of the un-fined Colombard wine at a recovery rate was 50 %, where the concentration phase was shorter (120 min). The same type of behaviour can also be observed. However, a longer time, approximately 80 min, is required for the wine to reach a new steady state during the holding phase. Again, seeding did not seem to reduce the required holding time.

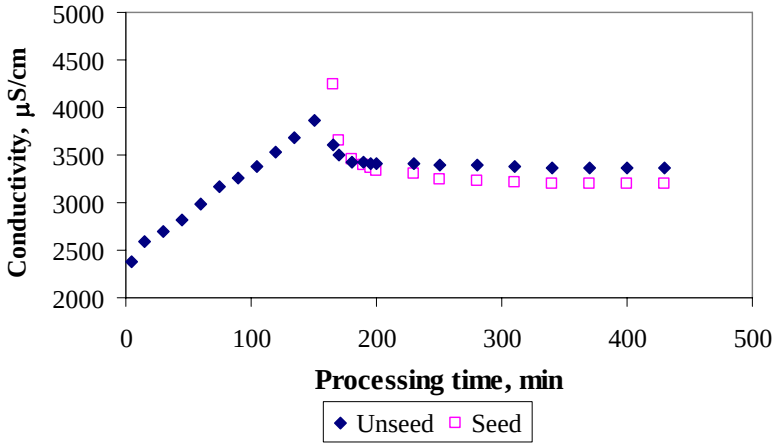
Almost exactly the same observations can be made for the Shiraz wine in Figure 6.5 except that even longer times, in the order of 100 to 150 min, are required for the wine to achieve a new steady state during the holding phase.



(a)

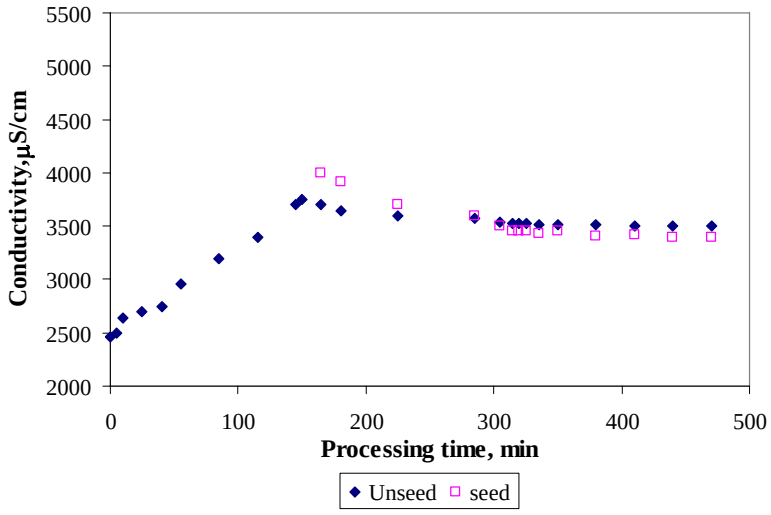


(b)

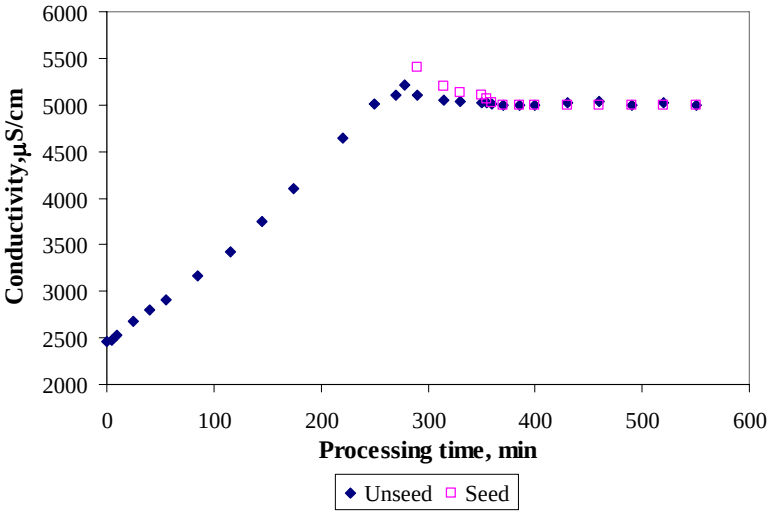


(c)

Figure 6.4: Conductivity changes of Colombard wine during concentration and holding periods: (a) Raw wine treated at 75 % recovery; (b) bentonite fined wine treated at 50 % recovery; and (c) bentonite fined wine treated at 75 % recovery,



(a)



(b)

Figure 6.5: Conductivity changes of Shiraz wine during concentration and holding periods: (a) treated at 50 % recovery; and (b) treated at 75 % recovery.

6.4.6 Sensory evaluation

The results of selected comparisons obtained by the duo-trio difference tests are presented in Table 6.7.

6.4.6.1 Colombard wine

Table 6.7(a) shows results for the Colombard wine. These results suggest that

- Bentonite fining of the wine did not have a significant sensory effect;
- Both cold stabilisation and nanofiltration had an effect on the raw wine;
- That there was a difference between the effect of cold stabilisation and nanofiltration; and

- Seeding of wine during cold stabilisation did not have an effect.

Review of informal tasting notes provided by the sensory panel suggested that

- The effect of cold stabilisation on the wine was not adverse;
- However, the effect of nanofiltration on the raw wine was considered negative;
- Furthermore, the effect of nanofiltration on the sensory quality of the wine was also negative when compared with cold stabilisation.

An obvious reason for the nature of the above negative effects observed with nanofiltration treatment on the wine could not be clearly determined. However, anonymous comments the sensory panel suggested that the nano-filtered wine appeared to taste musty and flat, whereas the raw and cold stabilised wines showed fresher tropical aromas with more lively acid.

6.4.6.2 Shiraz wine

Table 6.7(b) shows results of the sensory evaluation for the Shiraz wine. These suggest that

- Both cold stabilisation and nanofiltration had an effect on the raw wine;
- The effect of cold stabilisation was different to that of nanofiltration; and
- Seeding of wine during cold stabilisation did not have any effect.

Likewise, the informal notes from the sensory panel suggested

- The effect of cold stabilisation on the wine was not adverse;
- But the effect of nanofiltration on the raw wine was considered negative; and
- The effect of nanofiltration on the sensory quality of the wine was also negative when compared with cold stabilisation.

Again, these negative effects and the reasons for them could not be easily discerned. From anonymous comments by the sensory panel, assessors who correctly matched the wines indicated that the raw and cold stabilised wines had higher burnt rubber aroma and had more fruit flavour and acidity, whilst the nano-filtered wine appeared to possess off-notes of plastic, smoky and sweaty characters.

Table 6.7: Results of duo-trio difference tests for (a) *Colombard* wines; and (b) *Shiraz* wines.

(a) *Colombard* wine

Test	Wine 1		Wine 2	No. correct responses/ No. total responses	*P*-value
1	Raw	vs	Bentonite fined	10/25	0.097
2	Raw	vs	CS+B	17/25	0.032*
3	Raw	vs	BNF75	18/25	0.014*
4	CS+B	vs	BNF75	20/25	0.002*
5	CS+B	vs	BCSs	13/25	0.155

(b) *Shiraz* wine

Test	Wine 1		Wine 2	No. correct responses/ No. total responses	*P*-value
1	Raw	vs	CS+B	20/25	0.002**
4	Raw	vs	NF75	23/25	8.94×10^{-6}**
2	CS	vs	NF75	20/25	0.002**
3	CS	vs	CSs	14/25	0.133

* denotes significance at $P < 0.05$

** denotes significance at $P < 0.01$

6.5 Concluding remarks

Field testing at Berri Estates Winery demonstrated that nanofiltration could successfully tartrate stabilise Colombard and Shiraz wines at recoveries of greater than 50 %. The holding time required for completion of the crystallisation phase following concentration was between 30 and 150 min depending in the wine and recovery rate. The results suggest that red wines will required longer holding times than white wines. The holding time is reduced with increased recovery rate but a higher recovery rate may require a

longer concentration phase, so net savings in processing time might be neutral. Seeding did not reduce the holding time.

In these field tests, the NF system was operated in a batch mode. During operation of the nanofiltration system, flux rates of between 5 and 12 L/m^2/hr for Colombard wine, and between 2 and 6 L/m^2/hr for the Shiraz wines, were achieved at feed pressures of approximately 18 bar. With appropriate design, the NF system could be operated as a "single-pass" system. Furthermore, lower operating pressures and/or higher flux rates could be also achieved.

However, sensory evaluation suggested that nano-filtered wine produced by the field testing was different to the raw wine and the tartrate stabilised wine achieved by cold stabilisation. These differences were negative. The reasons for these negative changes in sensory quality have not yet been determined but may have been due to a number of factors:

- Possible oxidation or microbial contamination of nano-filtered wine;
- Dilution of the nano-filtered wine; and
- Membrane absorption of flavour and aroma compounds.

These are currently being investigated further by the PhD student and Chief Investigator.

7 Outcome/Conclusion

This project has demonstrated nanofiltration can successfully tartrate stabilise wine through laboratory experimentation and field testing approximately. This can be achieved at moderate feed pressures (<20 bar) and recoveries (50 %) without seeding and relatively short holding periods (< 3 hr). Under these conditions, flux rates of between 5 and 10 L/m^2/hr were obtained.

However, adverse sensory outcomes were observed in nano-filtered wine produced by field testing. The cause of these negative sensory outcomes has not yet been determined. This requires further investigation and it is essential to establish whether this problem is intrinsic to the process or arose from unrelated factors.

The above outcomes have achieved the project's objectives. Furthermore, if the problem with adverse sensory outcomes can be satisfactorily resolved, this project has confirmed that tartrate stabilisation is a technically viable process that can be used by the Australian grape and wine industry as an alternative to cold stabilisation.

The results of this project have been reported to the project's industrial collaborator and sponsor, Hardy Wine Company. This will likely decide the immediate prospects in the potential commercial application of nanofiltration by this company. If this occurs, it is envisaged this will involve

1. Reconsideration of estimated process cost estimates based on field testing data;
2. Further field testing and sensory evaluation of nano-filtered wines;
3. Assuming 1 and 2 are successful and favourable, optimisation of the process design for implementation of a production-scale nanofiltration system for tartrate stabilisation at targeted wineries.

Additional analysis of the laboratory and field testing data is presently being performed by the PhD student, Ms Lin Lin Low, and Chief Investigator, Dr Chris Colby. The outcomes of this work will soon be published in Ms Low's thesis and disseminated through conference presentations and/or journal publications.

Appendix 1: Communication

This project was undertaken is close association with the industry partner for the project, Hardy Wine Company. There was regular reporting and updates to the industry partner and they will receive a copy of this report. The AWRI also participated in the project and results are available to them to disseminate to industry through their industry outreach/extension activities. Various results of the project have also been presented at several conferences including the recent ASVO seminar - Maximizing the Value, in Adelaide on 12 October 2006. A journal publication is also already accepted for publication in the International Journal for Food Science and Technology. The citations for this journal publication and the conference presentations are given below. The laboratory experiments and field testing produced a large volume of data which is still being analyzed by the PhD student and Chief Investigator. When this process is complete, another two journal publications on the project are planned. It is intended to publish these in the Australian Journal of Grape & Wine Research or the American Journal of Enology & Viticulture. The Chief Investigator has been invited to speak on the project at the PROCESS IMPROVEMENTS FOR PROFITABILITY Workshop of the 13th Australian Wine Industry Technical Conference.

Conference presentations/papers

1. Colby CB, Low LL, Godden J, Gishen M, O'Neill BK (2006). Process engineering developments in wine production: Alternative technologies for tartrate stabilisation. Australian Society of Viticulture & Oenology seminar - Maximising the Value, Adelaide, South Australia, 12 October 2006.
2. Low L, Colby C, O'Neill B, Ford C, Godden J, Gishen M (2006). Use of nanofiltration for tartate stabilisation of wine. Chemeca 2006 - 34th Australasian Chemical Engineering Conference, Auckland, New Zealand, 17 - 20 September 2006.
3. Low LL, Colby CB, O'Neill BK, Ford C, Godden J, Gishen M (2005). Alternative Technologies for Tartrate Stabilisation of Wines: Which is Better. Chemeca 2005 - 33rd Australasian Chemical Engineering Conference, Brisbane, Australia, 25 - 28 September 2005.

Journal publications

1. Low L, O'Neill BK, Ford C, Godden J, Gishen M, Colby C (2007) Economic evaluation of alternative technologies for tartrate stabilisation of wines. Accepted for publication: International Journal for Food Science and Technology.

Appendix 2: Intellectual Property

The intellectual property associated with this project includes the experimental data obtained from the laboratory experiments and field testing. This data will be published in the PhD student's PhD thesis and conference presentation and journal publications. There is presently no intention to, nor any perceived merit, in restricting disclosure of this data unless at instigation of the Grape & Wine Research & Development Corporation, Australian Wine Research Institute or Hardy Wine Company.

Appendix 3: References

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Appendix 4: Staff

The principal staff involved in the project was as per original GWRDC Project Application – refer Table below. However, this list does not include the technical personnel and winemakers at Berri Estates Winery that contributed to the project during field testing.

Name	Title	Position	Qualification	Agency
1. Brian O'Neill	Assoc. Prof.	Assoc. Prof.	PhD	Adel. Uni.
2. Chris Colby	Dr	Senior Lecturer	PhD	Adel. Uni.
3. Mark Gishen	Mr	Quality Liaison Manager	MEngSc	AWRI
4. Jim Godden	Mr	Operations Manager		HWC
5. Tim Grosser	Mr	Market Specialist	BE	Osmoflo
6. Chris Ford	Dr	Lecturer	PhD	Adel. Uni.
6. Lin Lin Low	Ms	PhD Candidate	BE	Adel. Uni

Appendix 6: Budget reconciliation

Refer following page(s) for completed copy(ies) of Form B or equivalent.