EVALUATION OF TARTRATE STABILISATION TECHNOLOGIES FOR WINE INDUSTRY

by

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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 electrodialysis, 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 electrodialysis 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/m^2/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.

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LIST OF PUBLICATIONS

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CHAPTER 1 INTRODUCTION

Potassium hydrogen tartrate (KHT) and calcium tartrate (CaT) are tartrate salts naturally present in grape juice, usually at saturated levels. They become more insoluble in wine due to presence of ethanol and during subsequent storage of bottled product at low temperatures (Berg & Keefer, 1958). This precipitation can be a major source of “instability” in bottled wine. Tartrate crystals pose no risk to human health but they are unattractive to consumers. Consumers may incorrectly confuse the tartrate salt crystals with microbial spoilage, chemical additives, or even glass splinters. Therefore, treatment of wine prior bottling to prevent tartrate precipitation is an important step during commercial wine production.

Cold stabilisation is the most commonly used tartrate stabilisation treatment. It involves chilling the wine close to its freezing temperature (normally at -4^{o}C) for a period of up to a week to induce precipitation of tartrate salts. Although cold stabilisation has proven effective, it is perceived in the wine industry to incur some significant disadvantages. These include the combination of long processing time, high energy cost and large capital investment to provide tanks and extra refrigeration capacity. In addition, the wastes generated by cleaning tartrate-encrusted tanks may result in additional environmental costs.

Consequently, interest has grown in alternative tartrate stabilisation methods. Key processes include cold stabilisation with crystal seeding (Rhein & Neradt, 1979) or packed (Walter, 1970) and fluidized beds (Bolan, 1996); ion exchange; electrodialysis (Escudier, 2002; Gómez Benítez et al., 2003); nanofiltration (Mannaperuma, 2001); and the addition of metatartaric acid (Celotti, Bornia & Zoccolan, 1999; Goertges & Stock, 2000). A number of these methods are applied at an industrial scale whilst others are undergoing research and development or remain paper ideas.

Published literature includes studies on the relative costs of conventional cold stabilisation versus other treatment technologies (Rankine, 2004; Escudier, 2002; Mannapperuma, 2001). Unfortunately, these studies present limited information on relevant technical details and the underlying assumptions are seldom detailed. No studies have been undertaken for Australian conditions. As well, these studies only involved side-by-side comparisons of cold stabilisation against a single alternative technology. Consequently, these results cannot be applied with confidence to establish the best current technology available for either a particular or generic situation.

Hardy Wine Company (HWC) is a major wine producer in Australia. It owns and operates a string of wineries throughout Australia and internationally. These include Berri Estates Winery, the largest winery in the Southern Hemisphere, located in the Riverland Region of South Australia. Cold stabilisation is the primary treatment method at the company's Australian wineries. Company management is seeking to improve the efficiency and profitability of winery operations. Hence, this research was commissioned to investigate, demonstrate and evaluate alternatives to conventional cold stabilisation. This thesis describes this research and its findings.

Chapter 2 reviews the relevant literature, including technical details of current and proposed tartrate stabilisation processes. This information was used in addition to technical and economic data provided by Hardy Wine Company to perform concept engineering feasibility studies of selected alternative technologies. This is presented in Chapter 3. This study considered both greenfield and retrofit scenarios and different scales of operation. This work presents for the first time a comprehensive side-by-side comparison of alternative technologies for tartrate stabilisation in the wine industry.

In Chapter 4, the engineering feasibility studies were used as a basis for multi-criteria decision analysis (MCDA) of the selected alternative technologies. MCDA was applied to assist HWC to account for other important decision-making criteria, such as process complexity, process safety, environmental impact, in addition to economics or cost when deciding between cold stabilisation and the alternative technologies. MCDA methods have not previously been employed for decision making by the Australian wine industry.

The MCDA analysis from Chapter 4 identified a strong preference for decision making in HWC to evaluate nanofiltration combined with centrifugation as an alternative to cold stabilisation despite its higher capital and operating costs. As a consequence a series of experimental investigations were undertaken to obtain more accurate technical performance data to better evaluate the process for commercial application. These studies were divided into two phases. First, laboratory investigations were performed to examine suitability and performance of a series of commercially available nanofiltration membranes and to identify operating conditions that achieve the desired treatment outcomes (i.e. feed pressure and recovery to obtain acceptable throughputs and tartrate stabilisation). Next, this data was used as the foundation for phase two: field tests at a commercial winery to verify the process performance and effectiveness. The results from laboratory studies and field testing are presented in Chapters 5 and 6, respectively. The field testing performed in this work is the first published demonstration of production-scale application of nanofiltration combined with centrifugation for tartrate stabilisation.

Finally, the key conclusions and recommendations for future work are presented in Chapter 7.

CHAPTER 2 LITERATURE REVIEW

The goal of this project is to investigate alternative tartrate stabilisation processes suitable for commercial application at Hardy Wine Company's wineries. This chapter reviews the literature on currently available processes for tartrate stabilisation, multi-criteria decision analysis as a tool for to aid decision makers in complex decision making problems, the theory and knowledge regarding of tartrate salts in wine and the kinetics of tartrate crystallisation. The gaps in knowledge in the literature are highlighted.

2.1 Tartrate Stabilisation Processes

Various studies on tartrate stability have been performed on a variety of tartrate stabilisation methods. Wine can be stabilised physically or chemically. Physical stabilisation of wine eliminates tartrate salts through chilling/cold stabilisation, ion exchange (Rankine, 1955), filtration (Scott et al., 1981), electrodialysis (Uitslag et al., 1996b; Moutounet and Escudier, 1991), reverse osmosis, crystal flow (T.M.) or contact seeding (Rhein and Neradt, 1979). Alternatively, wine can be stabilised with the aid of chemicals.

Chilling is the traditional approach for achieving tartrate stability in wine, and is still universally employed. The temperature of the wine is reduced to render potassium bitartrate less soluble (Uitslag et al., 1996a). Precipitation of bitartrate crystals is induced. The normal procedure, commonly referred to as cold stabilisation, is to chill the wine using a heat exchanger to near its freezing point, in the range -4 to 2 °C, then store the contents in an insulated vessel for ten days to three weeks, and finally clarify the wine whilst still cold (Boulton et al., 1996; Uitslag et al., 1996a). Winemakers may elect to fine with bentonite for removal of protein haze during cold stabilisation (Zoecklein, 1988a). This allows the bitartrate crystals to assist with compaction of the bentonite lees, and hence, reduces the volume of wine occluded in the lees. This occluded wine either constitutes a loss of product and/or is substantially value downgraded if recovered by RVD.

However, the method is considered time consuming and costly (Dharmadhikari, 2002). Refrigeration is required to chill the wine and hold it at a low temperature. Low degrees of supersaturation may lead to poor (if any) spontaneous nucleation, and produce slow crystallisation rates (Boulton et al., 1996). Significant precipitation normally occurs as a thin crystalline layer on the tank walls. This layer is problematic to remove. Wines also contain natural colloids such as polysaccharides, peptide-tannin complexes, and proteins. These can simultaneously deposit on and foul the surfaces of the growing crystals, leading to cessation of crystal growth, and hence precipitation (Boulton et al., 1996).

Energy efficiency may be improved through a two-stage cooling sequence for the wine. The first stage performs energy recovery by contacting stabilised cold wines with warmer ones requiring stabilisation. Refrigerant is employed in the second stage to cool the wine to the required stabilisation temperature. Some winemakers employ a scraped-surface heat exchanger for the second stage. This allows a fraction of the wine, commonly 5 to 10 %, to freeze. This concentrates the wine and provides a higher supersaturation level which can improve nucleation and crystal growth.

Seeding may be used to improve the efficiency and performance of cold stabilisation (Dharmadhikari, 2002). A fine powder of potassium bitartrate crystals is added to the chilled wine. The seed crystals ensure a supersaturated solution is created and also provide nuclei for precipitation (Zoecklein et al., 1995). The optimal rate of crystal addition is 4 g/L with a particle size of 40 μm (Rhein and Neradt, 1979). Wine stability can be achieved within several hours. Constant agitation is recommended (Zoecklein et al., 1995) for optimal performance. Seed crystals may be reused between 5 to 8 times (Dharmadhikari, 2002), after which grinding is required to restore performance. During reuse, the seed crystals may require rinsing or washing to remove fouling contaminants from their surfaces (Dharmadhikari, 2002). This may produce a loss of 3 to 6 % of the seed crystal mass (Dharmadhikari, 2002). Dharmadhikari estimated that the added cost of seeding at 4 g/L during cold stabilisation ranged from 1.8 ¢US/L to 0.4 ¢US/L with reuse of the seed crystals, and it was concluded that the process could be very economical. However, it is unclear whether savings achieved from reduced energy consumption and shorter processing times outweighed the additional expense of the seed crystals and extra costs involved with washing and regrinding seed crystals for reuse.

A number of new processes have been developed to achieve faster and more complete stabilisation of wine by chilling, whilst reducing costs (Boulton et al., 1996). These include proprietary systems commercialised by Vinipal, Sietz (or the Spica process), Gasquet, Alfal-Laval (Crystal-flow system), Westfalia and Imeca (Boulton et al., 1996) as well as Polar System from Della Toffola. These processes normally employ dedicated crystallisation tank(s), diatomaceous filter or disc centrifuge for crystal removal and/or retention, and heat exchanger(s) for energy recovery between untreated and treated wine. Such systems are semi-continuous or continuous, designed to be energy efficient, and reuse bitartrate crystals for seeding to enhance crystallisation kinetics. They 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. Ferenczi et al. (1982) conducted a comparative review on technical performance of several systems but comparisons on operating costs have not been reported. Boulton et al. (1996) reports the higher costs have limited their adoption to fewer than two hundred installations worldwide. He also concluded that the choice depends on the trade-off between crystallisation efficiency, treatment capacity, energy minimization and installation, and operating costs. However, little or no contemporary data exists in the published literature that provides the information regarding installation and operating costs of these systems, or comparing them with other methods.

Chilling processes that involve packed or fluidized beds in a vertical column have also been considered (Bolan, 1996; Walter, 1970). These retain the seed crystals in a reactor physically, in the case of the packed bed, or by gravity with a fluidized bed. Packed or moving bed methods are reported to experience problems with blockage of flow channels as bitartrate crystals grow (Bolan, 1996). There are no reported commercial applications. Successful bench testing has been performed with fluidized bed crystallizers, but again there appears to be no industrial scale units. No published information can be found about the potential costs of these methods.

The concept of exploiting membrane filtration processes has also existed for some time. In 1978, Rhein - a Germany inventor 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 crystallisation process. However, industrial use has not been reported. Mannapperuma (2001) has published results of a recent pilot-scale study using membranes to stabilise tartrate in wine. Nanofiltration was employed to concentrate the wine, thereby inducing precipitation of the bitartrate salt crystals. The crystals were removed from the nanofiltration retentate by microfiltration. Permeates from the nanofiltration and microfiltration were combined to reconstitute the wine. Mannapperuma (2001) commented on likely cost savings following treatment by nanofiltration, using microfiltration to separate tartrate crystals. He concluded that such a system could achieve lower treatment costs compared with cold stabilisation. This study appears to be the sole technical analysis and experimental investigation of the application of nanofiltration to tartrate stabilisation. It involved pilot testing of the process. No technical analysis of the operating principles or theory associated with the process concept was presented. A clear understanding of these issues is essential if further developments of this process for tartrate stabilisation are to be achieved. A significant gap in the knowledge base exists.

The technical feasibility of electrodialysis was demonstrated more than thirty years ago. However, industrial use is only recent. 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). Proposed advantages 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/m^3 of wine treated (Wucherpfennig, 1974) and 0.2 to 0.5 kWh/m^3 (Moutounet and Escudier, 1991)); and equipment involves 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 greater than the unit operating costs of an electrodialysis unit. These researchers also concluded that electrodialysis was economically competitive with chilling methods based on the estimated fixed costs such as investment and operating costs. There are commercial installations of electrodialysis operating successfully at wineries in Europe, America and Australia.

Ion exchange involves replacement of potassium in wine with sodium using a cation exchange resin; tartrate is not removed. Usually, a fraction of the wine is ion exchanged, and then recombined with the untreated wine fraction to achieve a stable product. Ion exchange may increase wine pH slightly as some hydrogen ions in the wine are replaced with sodium (Rankine, 2004). The process is employed industrially; it appears particularly favoured by winemakers in America. However, ion exchange may not be considered suitable for some wines where high sodium content is a concern. Furthermore, some countries do 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 No. 6, 1994)). This constraint may 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 whilst mixing it with other winery waste effluent may increase treatment costs and limit disposal options. These issues appear to have limited wider industrial application of ion exchange.

Another option is addition of Meta-tartaric. Meta-tartaric (the hemipolylactide of tartaric acid) is an additive principally used in younger wines to inhibit the crystallisation process for extended periods (Uitslag et al., 1996a). Unfortunately, it slowly hydrolyses to tartaric acid rendering the wine unstable after a certain period. Hence, it is only suitable for use with wines that are consumed within 12 months. This option is seldom used in Australia.

In conclusion, this section has summarised numerous potential treatment options available to wine producers to achieve tartrate stabilisation. However, whilst the literature provides broad descriptions of process sequence and the operating principles of these options, with some technical and performance data, there is limited or no information on their relative economics or costs when compared with cold stabilisation or with each other. For Hardy Wine Company (HWC) and the wine industry, accurate and reliable economic cost information is crucial for decision making as to the merits of alternative tartrate stabilisation options. As such comparisons are not presently available, such a study is the first step to select appropriate alternative technologies that might replace cold stabilisation. In addition to economics, other important factors for the wine industry must be accounted for before deciding to adopt new technologies or processes. Such considerations include impact on environment, occupational health and safety issues, convenience of operation and operator acceptance, and consumer or winemaker perceptions (whether right or wrong) as to the potential adverse effects on wine quality.

Clearly, more accurate economic and cost data is required for the alternate tartrate stabilisation options. This will be addressed in Chapter 3 of the thesis, where the results of conceptual feasibility studies for selected alternative technologies will be presented.

The decision maker in the winery must combine this economic or cost data with other important criteria to decide which option is most suitable. A new approach to decision making which is broader than traditional economic or cost evaluation paradigms conventionally employed by the wine industry will be used. Such an approach exists and is well known in other process industries as multi-criteria decision analysis (MCDA). This subject will be considered in the next section. MCDA will be used as the basis for analysing alternative technologies for tartrate stabilisation at a HWC winery in Chapter 4.

2.2 Multi-criteria Decision Analysis (MCDA)

Multi-criteria decision analysis (MCDA) was developed to provide a consistent approach to compare alternative options for the decision maker in the presence of multiple objectives and criteria. MCDA is particularly effective when problem attributes are not able to be quantified as a dollar value, and thus, the decision cannot be made solely on a single economic criterion, e.g. net present value (NPV). The simple classic example is the use of MCDA to assist a new graduate to select a job. In this example, salary is not the sole criterion to be considered e.g. potential for personal and career development, travel opportunities and relocation assistance etc. MCDA has been widely employed in a wide range of areas including water and environmental management (Ozelkan and Duckstein, 1996; Roy et al., 1992; Salminen et al., 1998), energy planning (Afgan and Carvalho, 2000; Barda et al., 1990; Borges and Antunes, 2003; Schulz and Stehfest, 1984), and transportation project planning (Roy and Hugonnard, 1982). However, its application in wine industry for technologies selection has not been reported.

The MCDA is normally performed as a sequence of eight basic steps which are briefly described below (Keeney and Raiffa, 1976). The sequence is presented as a flow chart in Figure 2-1.

Steps:

1) Establish decision context - define the purpose of the MCDA and choose decision makers and other key players not solely based on their potential investment but also on their knowledge and expertise that may significantly contribute to the analysis.

2) Identify alternatives for appraisal - identify possible alternatives for assessment and allow modification of these alternatives as the analysis proceeds.

3) Identify objective and criteria - identify criteria for assessing the consequences of each alternative. Normally, a simple performance matrix for each alternative which accounts for each criterion is presented to the panel of decision makers.

4) Score - score the alternatives on the criterion which represents decision maker's preference.

5) Weight - assign weights to each criterion again reflecting its relative importance to the decision making process.

6) Calculate overall value - determine the overall preference score for each alternative using either one or several different MCDA methods.

7) Examine results.

8) Sensitivity analysis - perform a sensitivity analysis which involves:

    - examining the extent to which changes in preferences or weights alter the final results;
    - considering the advantages and disadvantages of the selected alternatives and comparing the alternatives in pairs. The principal differences between pairs of alternatives may aid in the development of new and better alternatives;
    - generating new alternatives (if any); and finally
    - repeating the previous steps until a viable model is obtained.

To calculate the preference score (steps (vi) above), three different methods are normally applied (Brans and Vincke, 1985):

1) aggregation methods using utility functions;

2) outranking methods; and

3) interactive methods.

Each of these MCDA methods is briefly reviewed in the following sections. In the description of each method, the theory is presented followed by an example to illustrate application of theory to a real-world decision making problem.

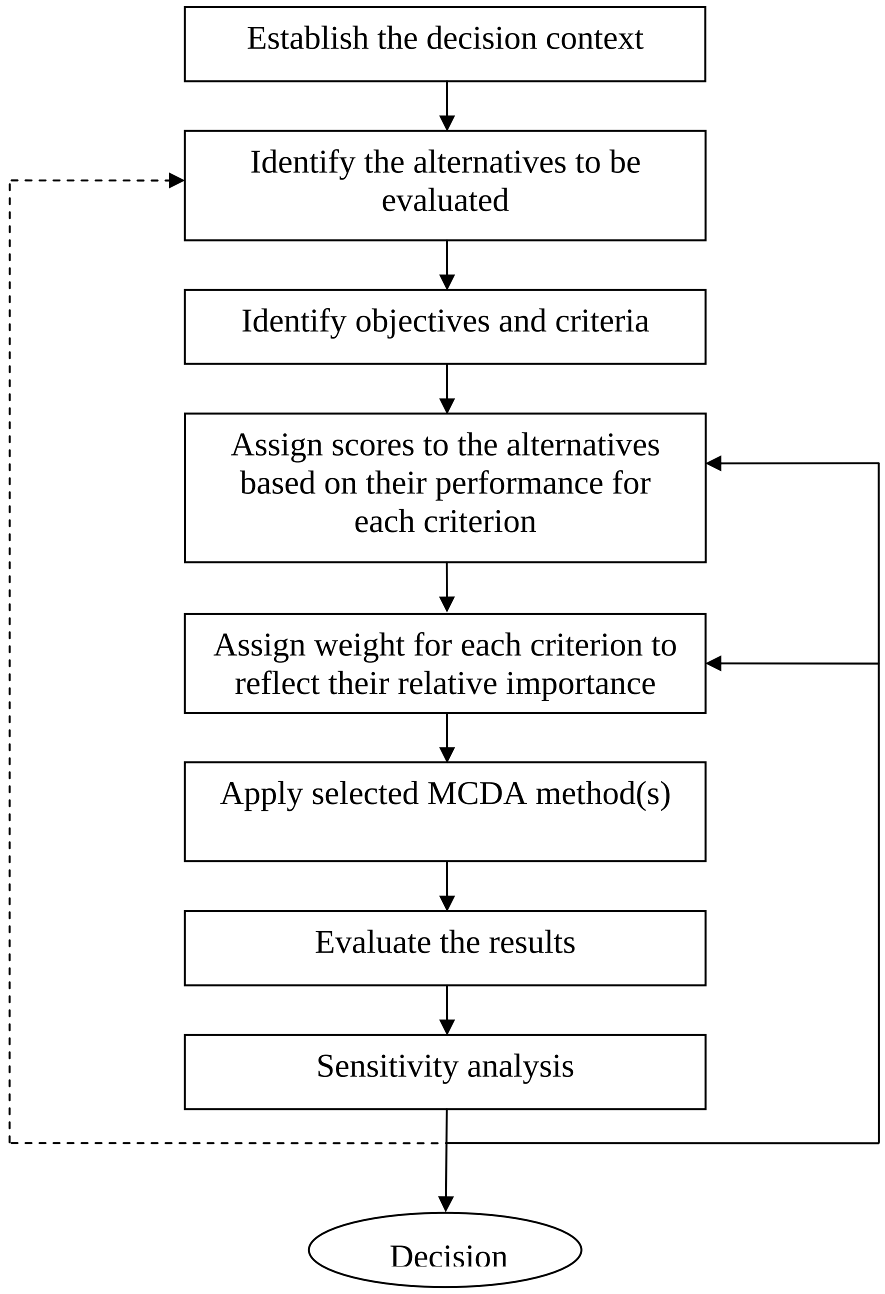


Figure 2-1. A flowchart summarising the logic of the MCDA process.

2.2.1 Simple aggregation function - weighted average method (WAM)

The weighted average method (WAM) is the most common comparative evaluation procedure. Basically, this method involves collection of a score for each alternative on each criterion e.g. r_{ij} (i = 1, 2, …, m and j = 1, 2, …, n) represents the score for ith alternative on the jth criterion, and assignment of weights to each criterion, w_j. The weight reflects the relative importance of the criterion. The total value for the ith alternative, V_i, is weighted average score as shown below (Pohekar and Ramachandran, 2004; Goicoechea et al., 1982).

$$V_i = \sum_{j=1}^{n} w_j r_{ij} \quad \textbf{(2-1)}$$

The optimal alternative satisfies the following criterion:

$$V_{optimal} = \max_{all\ i} V_i \quad \textbf{(2-2)}$$

This method is normally robust and straightforward; however, difficulties may be experienced when applying the method to multi-dimensional decision making problems.

An example developed for the purpose of discussion is provided below to illustrate the method.

Example 2-1 An Illustrative Numerical Application of WAM in Wastewater Management

A company planned to construct a new wastewater system for its new plant. Four alternatives wastewater systems are available. The director of the company (decision maker) will rank the systems (a_1, …, a_4) against six criteria. Let g_j (j = 1, …, 6) represent the criterion as follows.

g_1: construction cost (thousand AUD)

g_2: maintenance cost (thousand AUD)

g_3: area requirement (m^2)

g_4: treatment capacity (kL/hr)

g_5: detention time (hr)

g_6: Biochemical Oxygen Demand (BOD) reduction (%).

The director assigns the criteria weights in the range - 1 to 10. The score of 10 denotes the most important. Next, the decision maker (DM) rates the relative capacity of each alternative to meet each criterion, on the scale of 1 to 10. The performance value of the six criteria against the four alternatives are summarised in Table 2-I and the DM's evaluation of the alternatives is presented in Table 2-II .

Table 2-I. Properties of the wastewater systems.

Criteria	**Target**	**Alternative**			
		a_1	a_2	a_3	a_4
g_1	Min	50	60	80	95
g_2	Min	10	10	12	15
g_3	Min	1000	1000	500	250
g_4	Max	2.5	6	10	5
g_5	Min	36	24	10	0
g_6	Max	30	20	40	50

For a given alternative, its total value (Eq. (2-1)) is determined by multiplying each criterion's weight, w_i by the rating of the alternative's ability to meet the criterion, and summing over all criteria. For example, for Alternative a_1, the weight assigned to the construction cost is 3 while the rating of this criterion is 10. Accordingly, this criterion contributes 30 points to the total value of the alternative. The total value of a_1 is the sum across all criteria, that is, 185. By referring to Table 2-II, a_3 attains the highest combined value, that is

$$V_{optimal} = \max_{all\ i} V_i = 316$$

Hence, Alternative a_3 is the recommended option.

Table 2-II. Evaluation of alternative wastewater treatment systems.

		Alternative							
		a_1		a_2		a_3		a_4	
Criteria	**Relative weight, w_j**	r_{ij}	$V_{ij}= w_jr_{ij}$	r_{ij}	$V_{ij}= w_jr_{ij}$	r_{ij}	$V_{ij}= w_jr_{ij}$	r_{ij}	$V_{ij}= w_jr_{ij}$
g_1	3	10	30	8	24	4	12	1	3
g_2	7	8	56	8	56	6	42	2	14
g_3	2	1	2	1	2	5	10	10	20
g_4	9	2	18	5	45	10	90	4	36
g_5	9	1	9	3	27	8	72	10	90
g_6	10	7	70	5	50	9	90	10	100
Total rating, V_i			**185**		**204**		**316**		**263**

2.2.2 Outranking methods

The fundamental principles for the outranking methods were developed by Bernard Roy (1968) resulting in the development of the ELECTRE (Elimination and Choice Translating Algorithm).

This approach focuses on the establishment of preference ordering amongst alternatives. The key is to discover a consensus ranking of the alternatives. Outranking performs pair wise comparisons of alternatives. The goal is determination of the preferability of each alternative over the others (for each criterion). Next, a concordance (agreement or harmony of opinions) relationship is determined by aggregation of relative preference. As well, a discordance relation is also established to determine veto values against dominance of one alternative over others. Finally, the final dominance relation may be deduced by aggregating the concordance relation.

The key to such methods is depending on the outranking relation, **S** which is binary. $a_i\mathbf{S}a_k$ holds if in the DM's preference model the following is true:

> "a_i is at least as good as a_k"

To validate this assertion, two conditions must hold:

1. majority of criteria support $a_i\mathbf{S}a_k$ (majority principle); and

2. none of the non-concordant criteria strong refute the assertion (respect of minority principle)

The differences between aggregation methods and outranking methods are summarised in

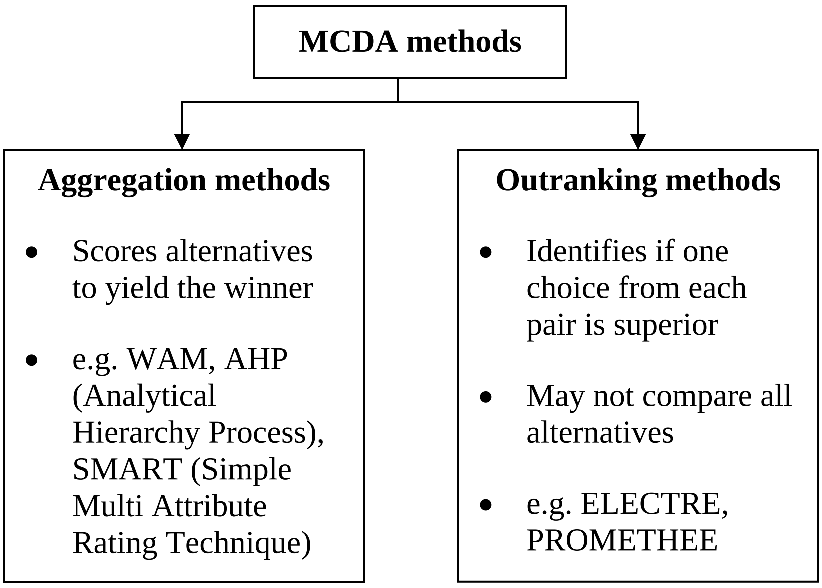


Figure 2-2. Summary of the differences between aggregation and outranking methods.

ELECTRE and PROMETHEE (Preference Ranking Organisation Method for Enrichment Evaluation) which are two best known outranking methods and these are discussed briefly below.

2.2.2.1 Description of ELECTRE methods

ELECTRE has evolved through a sequence of versions (I to IV, IS and TRI). These methods address different types of problems, which include choice (ELECTRE I, IS), ranking (ELECTRE II, III and IV) and classification (ELECTRE TRI) (Spronk et al., 2003).

Any ELECTRE method may be employed given a set of alternative $A = \{a_1, a_2, \ldots., a_m\}$ depending on the objective of the analysis. All ELECTRE methods are based on the identification of the strength of affirmation of the relationship between the alternatives for a given criterion.

To synthesize the outranking relationship, determination of concordance and discordance indices are required. The concordance index measures the degree of dominance of one alternative over another whereas the discordance index measures the degree to which an alternative performed worse than another.

The concordance index, $C(a_i, a_k)$, can be calculated for every pair of alternatives (a_i, a_k) by summing all the weights for those criteria where alternative a_i performs at least as good as alternative a_k. The following equation is used to determine the concordance index (Huang and Chen, 2005; Goicoechea et al., 1982).

$$C(a_i, a_k) = \frac{W^+ + \frac{1}{2}W^=}{W^+ + W^= + W^-} \tag{2-3}$$

where $W^+ = \sum_{j\in I^+} w_j$, $W^= = \sum_{j\in I^=} w_j$ and $W^- = \sum_{j\in I^-} w_j$. w_j is the weight of the criterion g_j ($j = 1, \ldots, n$) and I^+, I^- and $I^=$ are the subsets of a set of criteria, $I = (g_j : j = 1, \ldots, n)$. These subsets are express in a function of the difference between performance of a_i and a_k on criterion g_j (Huang and Chen, 2005):

$$I^+ = I^+\left(g_j(a_i), g_j(a_k)\right) = \left\{j \in I : g_j(a_i)\ \textit{better than}\ g_j(a_k)\right\} \tag{2-4}$$

$$I^= = I^=\left(g_j(a_i), g_j(a_k)\right) = \left\{j \in I : g_j(a_i)\ \textit{same as}\ g_j(a_k)\right\} \tag{2-5}$$

$$I^- = I^-\left(g_j(a_i), g_j(a_k)\right) = \left\{j \in I : g_j(a_i)\ \textit{worse than}\ g_j(a_k)\right\} \tag{2-6}$$

I^+ represents the set of criteria where the performance value, $g_j(a_i)$ of alternative a_i is better than alternative a_k, with its weight W^+.

$I^=$ represents the set of criteria where the performance value of alternative a_i is the same as alternative a_k, with its weight $W^=$.

I^- represents the set of criteria where the performance value of alternative a_i is less than alternative a_k, with its weight W^-.

To calculate the discordance index, $D(a_i, a_k)$, a performance level for all criteria is defined. $D(a_i, a_k)$ is zero when alternative a_i performs better than or same as alternative a_k on all criteria. However, if alternative a_k outranks alternative a_i on any of the criteria, then for each of those particular criteria, a ratio is calculated between the difference in performance level between a_k and a_i. The maximum ratio (ranging from zero to one) is the discordance index as shown in the following equation (Goicoechea *et al.*, 1982).

$$D(a_i, a_k) = \frac{maximum\ ratio\ where\ a_i\ outranks\ by\ a_k}{total\ range} \tag{2-7}$$

Once the concordance and discordance indices are determined, their results are combined to construct the final outranking relation. Alternative a_i is preferred to a_k if and only if $C(a_i,a_k) \geq y$ and $D(a_i, a_k) \leq z$, where the concordance (y) and discordance (z) threshold values are normally defined by the decision maker and range between 0 and 1.

Based on the defined outranking relation, a graph illustrating strong and weak relationships is constructed. Finally, the kernel of the graph consists of a set of non-dominated alternatives is determined (Goicoechea et al, 1982). Only alternatives in the kernel are chosen for further consideration. An example of outranking graph used to obtain the kernel is shown in Figure 2-3.

In Figure 2-3, alternatives a_2 and a_3 are not dominated by any other alternatives. Alternative a_3 dominates alternatives a_1 and a_4. Therefore, the kernel consists of alternatives a_2 and a_3. Hence, the choice is now between two alternatives rather than the initial four.

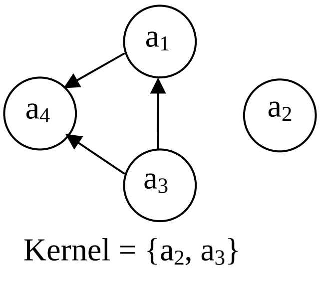


Figure 2-3. An example of determination of kernel from an outranking graph.

Overall, ELECTRE is very useful for a decision making problem that involves a few criteria with a large number of alternatives as it provides a clearer view of alternatives by eliminating less attractive ones (Pohekar and Ramachandran, 2004).

An example of this method is given below to illustrate the method.

Example 2-2 An Illustrative Application of ELECTRE I in Wastewater Management

This example is identical to Example 2-1.

The weights of criteria have been assigned by the decision maker as follow:

Construction cost: $w_1 = 3$

Maintenance cost: $w_2 = 7$

Area requirement: $w_3 = 2$

Treatment capacity: $w_4 = 9$

Detention time: $w_5 = 9$

BOD reduction: $w_6 = 10$

Total weight, $\sum w_j = 40$

The concordance index calculation (Eq. (2-3)) is illustrated for alternatives a_1 and a_2 and alternatives a_4 and a_3. Note that if both alternatives score equally for certain criterion then the weight for the criterion is one-half:

Comparing performance of alternative a_1 against alternative a_2, a_1 outranks a_2 on criteria g_1, g_2 and g_6, and both alternatives have equal score for g_3.

$$C(a_1,a_2)=\frac{W^{+}+\frac{1}{2}W^{=}}{\sum W_j}$$

where $W^{+}=w_1+w_2+w_6$ and $W^{=}=w_3$.

$$\therefore\quad C(a_1,a_2)=\frac{(3+7+10)+\frac{1}{2}(2)}{40}=0.4375$$

Similarly, alternative a$_4$ outranks alternative a$_3$ on criteria g$_3$, g$_5$ and g$_6$. There is no equal performance on any criterion. Hence, $W^{+}=w_3+w_5+w_6$ and $W^{=}=0$. The concordance index for alternatives a$_4$ and a$_3$ is

$$\therefore\quad C(a_4,a_3)=\frac{(2+9+10)+\frac{1}{2}(0)}{40}=0.525$$

The complete set of concordance indices is shown in Table 2-III:

Table 2-III. Concordance matrix.

$C(a_i,a_k)$	a$_1$	a$_2$	a$_3$	a$_4$
a$_1$	-	0.438	0.25	0.25
a$_2$	0.563	-	0.25	0.475
a$_3$	0.75	0.75	-	0.475
a$_4$	0.75	0.525	0.525	-

The discordance index is now calculated. First, the maximum scale intervals of 100 are allocated to each criterion by the decision maker. The value of each level for each criterion can then be calculated. For example, Table 2-IV summarises the scale intervals allocated for Example 2-1. In the case of construction cost, g$_1$, each level is worth $\frac{100}{4}=25$ points. This value applies for others criterion except treatment capacity, g$_4$, which possess five levels which are each worth 20 points.

The discordance coefficient for each criterion where a_k is preferred over a_i is calculated before selecting the maximum coefficient as the discordance index (Eq. (2-7)).

The calculation of the discordance index for alternative a$_4$ and alternative a$_2$ is illustrated below. In this case, alternative a$_2$ outranks alternative a$_4$ on criteria g$_1$, g$_2$ and g$_4$. Hence,

$$D(a_4, a_2)_{g_1} = \frac{100 - 50}{100} = 0.5$$

$$D(a_4, a_2)_{g_2} = \frac{100 - 25}{100} = 0.75$$

$$D(a_4, a_2)_{g_4} = \frac{80 - 60}{100} = 0.2$$

$$\begin{aligned} \therefore \quad D(a_4, a_2) &= \frac{\text{maximum ratio where } a_4 < a_2}{100} \\ &= D(a_4, a_2)_{g_2} \\ &= 0.75 \end{aligned}$$

Table 2-IV. Specification of criteria.

Criteria	Performance Levels	Scale value
g_1	< 50	100
	> 50 to 70	75
	> 70 to 90	50
	> 90 to 100	25
g_2	< 10	100
	> 10 to 12	75
	> 12 to 14	50
	> 14 to 16	25
g_3	< 400	100
	> 400 to 600	75
	> 600 to 800	50
	> 800 to 1000	25
g_4	> 10	100
	> 10 to 8	80
	> 8 to 6	60
	> 6 to 4	40
	> 4 to 2	20
g_5	< 10	100
	> 10 to 20	75
	> 20 to 30	50
	> 30 to 40	25
g_6	> 40 to 50	100
	> 30 to 40	75
	> 20 to 30	50
	< 20	25

The complete set of discordance indices is shown in Table 2-V:

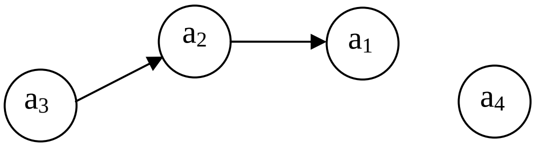
Table 2-V. Discordance matrix.

$D(a_i,a_k)$	a_1	a_2	a_3	a_4
a_1	-	0.4	0.8	0.75
a_2	0.25	-	0.5	0.75
a_3	0.5	0.25	-	0.25
a_4	0.75	0.75	0.6	-

Suppose that the decision maker specifies a minimum acceptable concordance condition of 0.5 and a maximum acceptable discordance condition of 0.4. This implies that $C(a_i, a_k) \geq 0.5$ and $D(a_i, a_k) \leq 0.4$. The outranking relationships, **S** between the alternatives that satisfy these specifications are presented in Table 2-VI and illustrated in Figure 2-4.

Table 2-VI. Outranking relationships between the alternatives.

S(0.5, 0.4)	a_1	a_2	a_3	a_4
a_1	-	No	No	No
a_2	Yes	-	No	No
a_3	No	Yes	-	No
a_4	No	No	No	-



Kernel = $\{a_3, a_4\}$

Figure 2-4. The composite graph of ELECTRE I.

Alternative a_2 is preferred over alternative a_1 and alternative a_3 is preferred over a_2. Consequently, the new situation is that two alternatives – a_3 and a_4 outrank the remaining alternatives. Hence, these alternatives are selected for further consideration.

2.2.2.2 Description of PROMETHEE methods

PROMETHEE methods (Preference Ranking Organization METHod for Enrichment Evaluations) can be used to determine the best alternatives (PROMETHEE I) or to rank alternatives (best to worst) (PROMETHEE II) (Spronk et al., 2003).

In PROMETHEE, the relationship between the alternatives (a_i, a_k) is evaluated using a preference index, $\prod(a_i, a_k)$. The preference index, which is similar to the concordance index of the ELECTRE methods, measures the degree of preference of a_i over a_k and is defined as follows (Hokkanen and Salminen, 1997a and b):

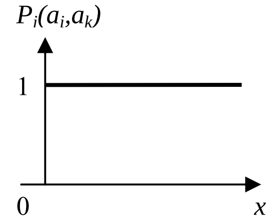
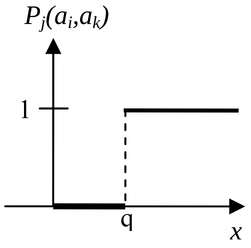
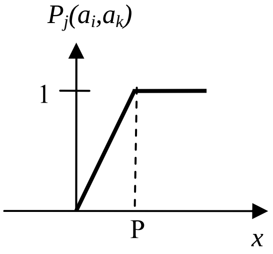
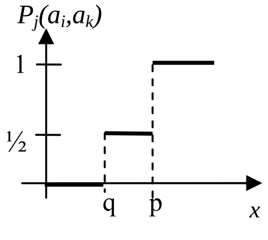
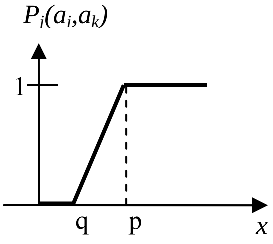
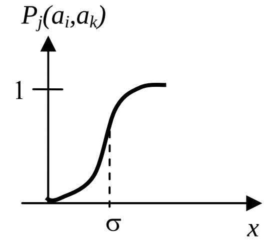
$$\prod(a_i, a_k) = \frac{1}{W}\sum_{j=1}^{m} w_j P_j(a_i, a_k) \quad \in [0, 1], \tag{2-8}$$

where $W = \sum_{j=1}^{m} w_j$ and an associated preference function, $P_j(a_i, a_k)$ is defined for each pair of alternatives for criterion g_j.

There are many forms of preference functions. These depend on the judgment of the decision makers. Six types of generalized criteria for estimating $P_j(a_i, a_k)$ have been proposed by Brans and Vincke (1985) and these are shown in Table 2-VII.

Table 2-VII. The six types of generalised criteria for applications

(reproduced from Brans et al. 1986).

Types of criteria			**Parameters**
I. Usual criterion		$P_j(a_i,a_k)=\begin{cases}0 & x=0\\1 & x>0\end{cases}$	-
II. Quasi-criterion		$P_j(a_i,a_k)=\begin{cases}0 & x\le q\\1 & x>q\end{cases}$	q
III. Criterion with linear preference		$P_j(a_i,a_k)=\begin{cases}\dfrac{x}{p} & x\le p\\1 & x>p\end{cases}$	p
IV. Level criterion		$P_j(a_i,a_k)=\begin{cases}0 & x\le q\\ 1/2 & q<x\le q+p\\1 & x>p\end{cases}$	p, q
V. Criterion with linear preference and indifference area		$P_j(a_i,a_k)=\begin{cases}0 & x\le q\\ \dfrac{x-q}{p-q} & q<x\le q+p\\1 & x>p\end{cases}$	p, q
VI. Gaussian criterion		$P_j(a_i,a_k)=1-exp\left(-x^2/2\sigma^2\right)$	σ

In Table 2-VII, x represents $g_j(a_i) - g_j(a_k)$ where alternative a_i is preferred over alternative a_k for criterion g_j. The indifference (q) and preference (p) thresholds are specified by the decision maker. The value of σ required for Gaussian type criterion is the distance between the origin and the point of inflexion in the cumulative Gaussian distribution and again σ may be set by the decision maker.

Next, the values of $\prod(a_i, a_k)$ for all pairs of alternatives are summarised in a "value outranking graph". The arcs connecting the nodes in this graph represent flow of preference. The flows can be defined for each alternative as follows (Hokkanen and Salminen, 1997a and b):

- outgoing flow $\Phi^+(a_i)=\sum \prod(a_i, a_k)$ **(2-9)**;
- incoming flow $\Phi^-(a_i)=\sum \prod(a_k, a_i)$ **(2-10)**;
- net flow $\Phi(a_i)= \Phi^+(a_i) - \Phi^-(a_i)$ **(2-11)**.

A PROMETHEE I partial relation refers to the ranking given by the first two flows, $\Phi^+(a_i)$ and $\Phi^-(a_i)$. The larger the value of $\Phi^+(a_i)$, the more a_i dominates the remaining alternatives, conversely the smaller the value of $\Phi^-(a_i)$ less a_i is dominant. In PROMETHEE I, some alternatives may be incomparable. By contrast, in PROMETHEE II comparison between all alternatives is possible.

Using the previous example, this method will be illustrated.

Example 2-3 An Illustrative Application of PROMETHEE in Wastewater Management

This example is the same as presented in Example 2-1. The original data are tabulated in the left-hand part of Table 2-VIII. Type of generalised criterion and the corresponding parameters specified by the decision maker are presented in the right-hand side of Table 2-VIII.

Table 2-VIII. Evaluation of alternative in the waste treatment model.

Criteria	Target	Weight, w_j	Alternative a_1	 a_2	 a_3	 a_4	Type of criteria	Parameters
g_1	min	3	50	60	80	95	V	$q = 10$; $p = 50$
g_2	min	7	10	10	12	15	IV	$q = 2$; $p = 10$
g_3	min	2	1000	1000	500	250	I	-
g_4	max	9	2.5	6	10	5	III	$p = 2$
g_5	min	9	36	24	10	0	VI	$\sigma = 20$
g_6	max	10	30	20	40	50	II	$q= 5$

The preference function, $P_j(a_i, a_k)$ for each specified criterion may be summarised as:

$$P_1(a_i, a_k) = \begin{cases} 0 & x \le 10 \\ \dfrac{(x-10)}{50} & 10 \le x \le 60 \\ 1 & x \ge 60 \end{cases}$$

$$P_2(a_i, a_k) = \begin{cases} 0 & x \le 2 \\ 1/2 & 2 < x \le 12 \\ 1 & x > 12 \end{cases}$$

$$P_3(a_i, a_k) = \begin{cases} 0 & x \le 0 \\ 1 & x > 0 \end{cases}$$

$$P_4(a_i, a_k) = \begin{cases} x/2 & x \le 2 \\ 1 & x \ge 2 \end{cases}$$

$$P_5(a_i, a_k) = 1 - e^{-x^2/800} \qquad x \ge 0$$

$$P_6(a_i, a_k) = \begin{cases} 0 & x \le 5 \\ 1 & x > 5 \end{cases}$$

Note: These choices are made by the decision maker.

The weights for each criterion, w_j are as specified in Table 2-VIII where $\sum w_j = 40$ and $x = g_j(a_i) - g_j(a_k)$ where alternative a_i outranks alternative a_k for criterion g_j.

Calculation of the preference index (Eq. (2-8)) for alternative a_4 and alternative a_2, $\prod(a_4, a_2)$ is illustrated below. In this instance, a_4 outranks a_2 for criteria g_3, g_5 and g_6. Hence,

$$\prod(a_4,a_2) = \frac{1}{W}\left(w_3 P_3(a_4,a_2) + w_5 P_5(a_4,a_2) + w_6 P_6(a_4,a_2)\right)$$

where $P_3(a_4, a_2) = 1$,

$P_5(a_4, a_2) = 1 - e^{-(24)^2/800} = 0.513$, and

$P_6(a_4,a_2) = 1$.

$$\therefore \quad \prod(a_4,a_2) = \frac{1}{40}(2 \times 1 + 9 \times 0.513 + 10 \times 1) = 0.415$$

The resulting preference indices are summarised in Table 2-IX.

Table 2-IX. Values of ∏ (a_i, a_k).

∏	a_1	a_2	a_3	a_4
a_1	-	0.25	0.03	0.14
a_2	0.262	-	0.015	0.238
a_3	0.653	0.574	-	0.32
a_4	0.705	0.415	0.326	-

To construct the outranking graph, the values of $\Phi^+(a_i)$ and $\Phi^-(a_i)$ must be determined. Values of $\Phi^+(a_i)$ are the sum of each row of Table 2-IX while values of $\Phi^-(a_i)$ are the sum of each column. The resulting values are presented in Table 2-X.

Table 2-X. Summary of preference flows.

	a_1	a_2	a_3	a_4
$\Phi^+(a_i)$	0.420	0.515	1.547	1.446
$\Phi^-(a_i)$	1.985	1.352	0.371	0.698
$\Phi(a_i)$	-1.565	-0.837	1.175	0.748

It is now possible to use either PROMETHEE I and II to select the best alternatives for the wastewater treatment problem.

PROMETHEE I

Figure 2-5 illustrates the partial PROMETHEE I relation. This figure illustrates the incomparability between a_3 and a_4.

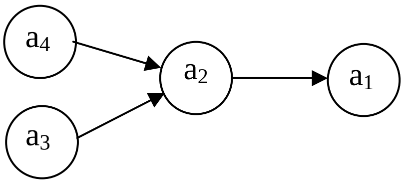


Figure 2-5. Partial PROMETHEE I relation.

PROMETHEE II

The complete preference generated from Table 2-X is shown in Figure 2-6.

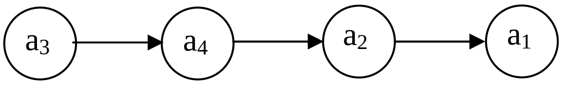


Figure 2-6. Complete PROMETHEE II relation.

Clearly, PROMETHEE II provides a complete ranking but lacks information on incomparability.

2.3 Principles and Theory of Tartrate Stabilisation by Crystallisation

As mentioned in the Introduction, an outcome of the MCDA analysis performed constitutes part of this study. Nanofiltration was identified as a preferred alternative technology. Unfortunately, there is currently limited technical understanding and performance data relating to this process. This section summarises the relevant knowledge on tartrate stabilisation by nucleation and crystallisation of bitartrate crystals. This is the modus operandi for treatment by nanofiltration. As well, it provides a valuable background for understanding the operation and performance of cold stabilisation and other alternative options that exploit the same treatment paradigm. A key feature of this section is discussion of tartrate stability testing methods. This is essential knowledge for the interpretation of experimental data derived from laboratory and experimental studies presented in this thesis.

2.3.1 Tartaric acid in juice or wine

Tartaric acid is a nonvolatile and non-odorous grape acid naturally present in grapes and wines. The various ionized forms of tartaric acid in grapes and wines are illustrated in Figure 2-7. These ionized forms are associated with various cations. The most common cations occurring in grape juice or wine are potassium and calcium. The concentrations of tartaric acid and associated cations (ionized forms) depend on the grape variety, the region, the climate and viticultural practices. Table 2-XI presents the typical values of tartaric acid, calcium and potassium for different wines.

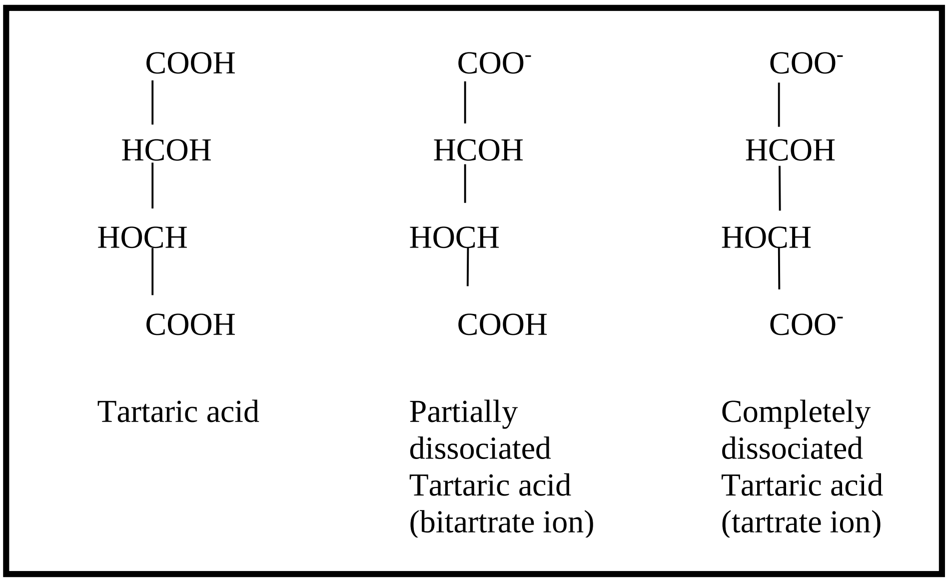


Figure 2-1. The structures of tartaric acid, bitartrate ion and tartrate ion. (Reproduced from Zoecklein, 1988a).

Table 2-I. The concentrations of tartaric acid and the cations present in wines after pH adjustment (reproduced from Pilone and Berg, 1965).

			mM/L	
Variety	**pH**	**H_2T**	**Ca^{2+}**	**K^+**
Red Wines				
Pinot noir	3.49	14.0	2.6	28.9
Cabernet Sauvignon	3.51	13.7	2.0	27.7
Cabernet franc	3.50	10.7	1.7	33.2
Petite Shiraz	3.50	12.0	2.8	35.3
White wines				
Chardonnay	3.50	16.7	2.9	12.8
Sauvignon blanc	3.49	15.7	2.0	4.1
Palomino	3.51	13.0	2.1	10.1
Sémillon	3.51	9.0	2.4	2.8

2.3.2 Solubility of bitartrate

A common problem for winemakers is the effect of tartrate salts on wine stability. The concentrations of bitartrate ion, potassium and calcium may exceed the total solubility for potassium bitartrate (KHT) and calcium tartrate (CaT). In grape juice, KHT is normally soluble. However, the production of alcohol during fermentation and pH changes in other winemaking processes may decrease the solubility product (Zoecklein et al., 1995). This can lead to precipitation of these salts as crystals, which may be visually discernable.

In wines, the solubility product for potassium bitartrate varies with alcohol content, pH, wine temperature, the concentration of other cations and anions (Zoecklein et al., 1995). For example, Table 2-XII presents the solubility for KHT in ethanol-water solutions at different alcohol percentage and temperatures.

Table 2-I: Solubility of potassium bitartrate (g/L) in ethanol-water solutions (Reproduced from Boulton et al., 1996).

	Ethanol content (%v/v)				
Temperature (°C)	**0**	**10**	**12**	**14**	**20**
0	2.25	1.26	1.11	0.98	0.68
5	2.66	1.58	1.49	1.24	0.86
10	3.42	2.02	1.81	1.63	1.10
15	4.17	2.45	2.25	2.03	1.51
20	4.92	3.08	2.77	2.51	1.82

In addition, “complexing factors” including metals (such as magnesium and calcium), sulfates, proteins, gums, polyphenols and others affect KHT formation and precipitation (Figure 2-8) (Zoecklein, 1988a). These constituents can form complexes with free tartaric acid and potassium ions (Betrand et al., 1978; Pilone and Berg, 1965). This behaviour explain why wines exhibit higher KHT holding capacity than ethanol-water solutions with the identical ionic strength and ethanol content (Berg and Keefer, 1958). As well, bitartrate (and perhaps tartrate) ions bind to the proteins in white wine and to the pigment-tannin of red wines. Such binding with free tartaric acid inhibits the formation of KHT. However, the extent to which these tartrate complexes inhibit precipitation remains unknown.

Crystallisation of KHT is strongly dependent on its solubility in wine. In the following section, KHT crystallisation phenomenon and some factors controlling the crystallisation rate are addressed.

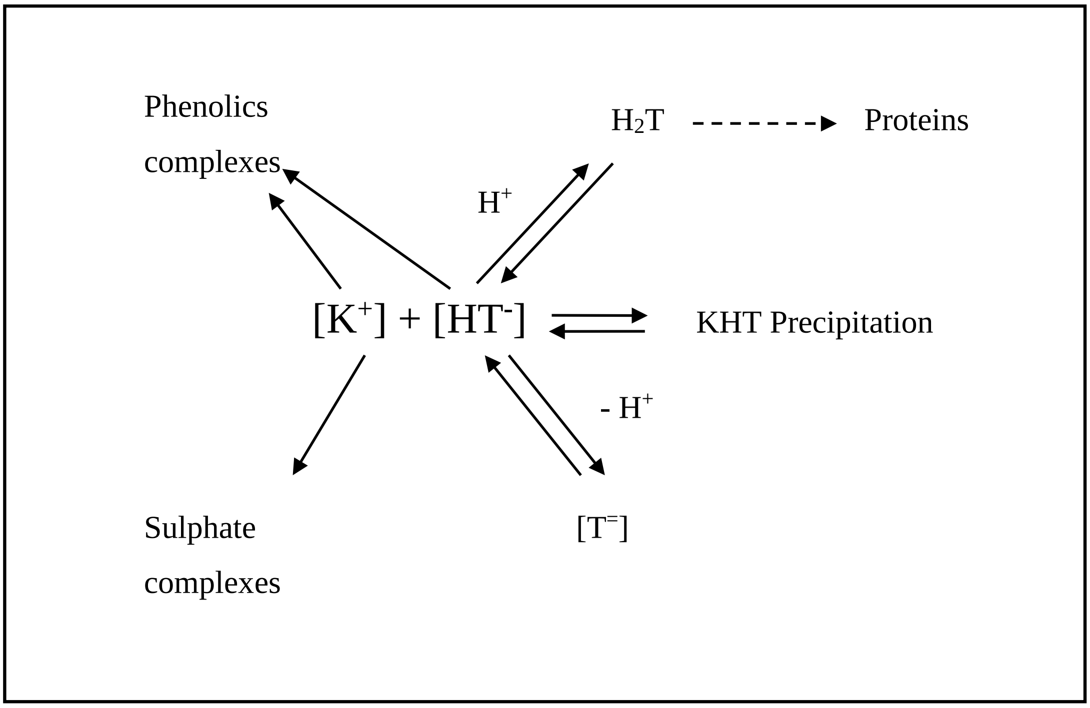


Figure 2-1. KHT equilibria and the interaction of the complexing factors (Reproduced from Zoecklein et al., 1995).

2.4 Crystallisation of Potassium Bitartrate

Normally, the crystallisation process proceeds in three discrete steps:

1. Attainment of supersaturation;
2. Formation of nuclei for solute growth; and
3. Growth of crystals by diffusion then surface integration.

2.4.1 Degree of supersaturation

The deposition of KHT crystalline from wine only occurs if some degree of supersaturation is achieved either by cooling and/or addition of a precipitant. The degree of supersaturation, Δc can be estimated as follows:

$$\Delta c = c - c^* \tag{2-12}$$

where c represents the concentration of active KHT; and c^* is the equilibrium KHT saturation or the solubility according to Berg and Keefer (1958) at a given temperature.

Alternatively, Gómez Benítez et al. (2004) determined the relative KHT saturation level by measuring the ratio, S between concentration product (CP) and the solubility product (K_{SP}) of the KHT. Basically,

$$S = \frac{CP}{K_{SP}} \tag{2-13}$$

where CP is the product of the concentration of potassium ion and the concentration of bitartrate ion in the wine (further described in Section 2.5.2). K_{SP} refers to solubility of KHT in a KHT saturated water-alcohol mixture with identical alcohol content to the wine obtained directly from Berg and Keefer (1958). If S is positive, the wine is supersaturated with KHT.

According to the studies of Rhein and Neradt (1979) and Gerbaud et al. (1996a), highly supersaturated wine with S greater than 3 results in spontaneous crystallisation. In cold stabilisation and other chilling processes, the wine is chilled to near sub-zero temperature for a period of time to achieve this high saturation level. In nanofiltration, the same effect is achieved by concentrating the potassium and tartrate ions in the wine.

2.4.2 Nucleation and crystal growth

Crystallisation from solution occurs when the solute concentration in a solvent exceeds its solubility. However, for a system to commence crystallisation, nucleation must occur first (Mullin, 1972). Nucleation can occur by either primary or secondary mechanisms (Figure

2-9). Primary nucleation occurs at high supersaturation solution and involves long induction times. Conversely, secondary nucleation occurs when additional homogeneous-solute, fine crystals are introduced which increases the degree of supersaturation of the solute in the solution considerably (Ribéreau-Gayon et al., 2000). The addition of the crystals means that the induction time required for primary nucleation is eliminated.

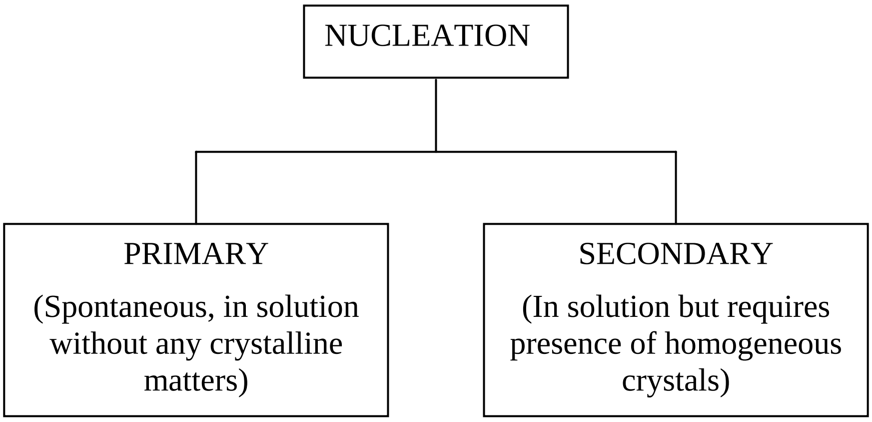


Figure 2-9. Nucleation Mechanisms.

According to Van der Leeden et al. (1992), the nucleation rate, J can be calculated using the following expression:

$$J = K_J S \exp\left(\frac{-B}{T^3 (\ln S)^2}\right) \qquad \textbf{(2-14)}$$

with

$$B = \frac{\beta \Omega^2 \sigma_s{}^3}{\delta^2 k_B{}^3} \qquad \textbf{(2-15)}$$

where S is the supersaturation ratio; K_J is an S-independent factor; β is a shape factor; Ω is the molecular volume; δ is the number of ions per molecule of electrolyte; T is the absolute temperature; k_B is the Boltzmann constant; and σ_s is the specific surface energy.

Gerbaud et al. (1996a) used Gibbs adsorption isotherm as the basis to estimate the specific surface energy, σ_s as:

$$\sigma_s = 0.414 k_B T \left(\frac{\rho_s N_A}{M_S} \right)^{2/3} ln \left(\frac{\rho_s}{M_S c^*} \right) \qquad \textbf{(2-16)}$$

where molecular weight, M_s equals 188.177 kg mol^{-1} and the density, ρ_s is 1984 kg m^{-3} for KHT.

Once stable nuclei have formed in the supersaturated solution, the nuclei commence growing into visible crystals. The mechanism for crystal growth involves two steps, a diffusion step followed by a surface-integration step.

The diffusion step occurs when the solute species are transported by diffusion and/or convection from the bulk solution to the crystal surface. In 1904, Nernst discovered that the crystal growth was limited by the rate of diffusion across a thin stagnant film of liquid adjacent to the crystal surface (Mullin, 1972). The growth rate may be expressed as:

$$-\frac{ds}{dt} = \frac{k_D A}{\delta}\left(c - c^*\right) \qquad \textbf{(2-17)}$$

where $-\frac{ds}{dt} =$ rate of solute disappearance.

Referring to Eq. (2-17), the growth rate is linearly dependent on

- the diffusion coefficient, k_D;
- the surface area of crystal, A; and
- the degree of supersaturation, $(c\text{-}c^*)$.

Clearly, the growth rate is inversely proportional to the film thickness, δ, which depends on the relative solid-liquid velocity.

From the experimental data obtained by Mullin (1972), film thickness varies between almost zero in vigorously stirred solutions to as large as 150 μm in stagnant conditions. The effect of agitation on the KHT crystallisation rate has been studied by Dunsford and Boulton (1981a) and this work will be discussed in Section 2.4.3.5.

The second stage in crystal growth is known as surface integration. In this stage, the solute ions migrate to the crystal surface and are only integrated into the crystal lattice in the positions where the attractive forces are greatest. In this case, the crystal face grows in layer (Dunsford, 1979). The rate of solute removal from solution can be expressed as:

$$-\frac{ds}{dt} = k_S A\left(c - c^*\right)^n \tag{2-18}$$

where k_s is the surface integration coefficient; and n is the order of the surface reaction, which has been reported to be in the range between 2 and 5 (Nyvlt, 1971).

2.4.3 Factors affecting growth and nucleation

An understanding of the factors controlling the growth and nucleation of KHT in wines is essential for improving wine stabilisation. This section will focus on the key influences namely particle size and surface area, agitation level, temperature, and impurities and additives on crystallisation processes.

2.4.3.1 Effect of crystal size and surface area

In general, crystal growth can be categorized as size-dependent (proportional) or size-independent (constant) growth. The mechanism for proportional growth involves supply of reactants to the crystals surface by advection, whereas in constant growth, the supply of reactants occurs by diffusion (Kile and Eberl, 2003). The “delta L law” (postulated by McCabe, 1929), describes the constant growth, where all geometrically similar crystals (regardless of their size) grow at an identical rate. The growth rate is defined as

$$G \equiv \lim_{\Delta L \to 0} \frac{\Delta L}{\Delta t} = \frac{dL}{dt} \tag{2-19}$$

where G is the growth rate over time internal t; and L a characteristic dimension of a crystal of selected material and shape.

Hence, the growth rate is independent of crystal size and all crystals in the suspension are treated alike (Perry and Green, 1997). Unfortunately, the “delta L law” fails when the crystals are very large or when the movement of the crystals in solution is so rapid so that diffusion-limited growth of the faces changes extensively. The use of “delta L law” fails to model growth of KHT crystals when the wine is well agitated during cold stabilisation.

Dunsford and Boulton (1981a) studied the kinetics of KHT crystallisation from table wine. They found that the growth rate of KHT was limited by nucleation, mass transport or surface reaction at various times. The length of time interval for which each process was controlling was dictated by crystal size, crystal loading and to a lesser extent, the level of agitation. For a given wine temperature and agitation level, the secondary nucleation rate could be scaled by multiplying crystal loading with the crystal size while the crystal growth could be scaled by dividing the loading with crystal size. The ratio of rate of growth to rate of nucleation was inversely proportional to the square of the crystal size whereas the absolute rates vary with the crystal loading. Thus, fastest crystallisation rate was achieved by the highest loading of fine particles. Furthermore, under these conditions the crystallisation rate was controlled by the nucleation rate.

2.4.3.2 Effect of agitation

Agitation is routinely used to induce crystallisation. Nucleation occurs spontaneously in most agitated solutions at low degrees of supersaturation compared to the un-agitated case.

This result was confirmed by Rodriguez-Clemente and Correa-Gorospe (1988) for KHT precipitation from wines and model solutions. The study confirmed that once the desired temperature and supersaturation are attained, then the induction period for nucleation commences. The duration of this period is determined by mode of agitation. If propellers are used, the induction period is significantly shorter compared with magnetic stirring.

The effect of agitation on crystallisation rate of blended white wine was also investigated by Dunsford and Boulton (1981a). Higher values of the first-order constant, $\frac{k_D A}{\delta}$ occurred at higher agitation levels. This could be caused by either higher surface area produced by small particles from a higher nucleation rate, or a smaller film thickness formed. A more pronounced effect on the agitation on film thickness might be expected with the powdery seed crystals.

2.4.3.3 Effect of temperature

The Arrhenius equation is normally used to relate the reaction constant, *k*, and the absolute temperature, *T*:

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \tag{2-20}$$

where *E* is the energy of activation of a particular reaction (constant). Integrating Eq. (2-20) yields

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{2-21}$$

or taking logarithms,

$$\ln k = \ln A - \frac{E}{RT} \tag{2-22}$$

This model is routinely applied to diffusion, dissolution or crystallisation processes where *k* represents the relevant rate constant.

The crystal growth processes are seldom solely controlled by either surface integration or diffusion. The surface integration step often dominates (rate limiting) at low temperature whilst diffusion is paramount at high temperature. However, a significant intermediate range occurs where both processes proceed at comparable rate. Hence, the Arrhenius plots for crystal growth data usually produce curves rather than straight lines, indicating that the apparent activation energy of the overall growth process is temperature dependent.

Several studies have been performed on the effect of temperature on crystallisation. Botsaris and Sutwala (1976) used 1200μm crystals in saturated sodium chlorate solutions and confirmed that the number of secondary nuclei formed increased with the degree of subcooling up to 4 K whilst heterogeneous nucleation commenced for sub-cooling exceeding 7 K. The effect of temperature on crystallisation from table wines has been investigated (Dunsford and Boulton, 1981b) and two first-order rate-controlling processes were observed especially at lower temperatures. This result suggested that complexation occurred. The first region persisted when crystallisation is limited by the rate of transport of free ions to the crystal surface. Whilst, the second region is controlled by either the dissociation rate or by the rate of transport of a bulkier complex species to the crystal surface. Interestingly, temperature had little effect on the first-order rate constants but produced a significant effect on the second-order rate constants.

2.4.3.4 Effect of impurities and additives

The presence of impurities and additives may produce a pronounced effect on the crystallisation kinetics even for trace concentrations of the contaminants. The impurities produce different effects on the different crystallographic faces of crystal and significantly influence crystal habit. The effect of impurities or additives on growth rates also reflects an effect on solubility.

Several studies have addressed the effect of impurities or additives on the crystallisation of potassium hydrogen tartrate in ethanol solutions and wines. For instance, the solubility of KHT increases in wines when compared to model ethanol solutions primarily due to the presence polysaccharides and polyphenols (Rodriguez-Clemente and Correa-Gorospe, 1988; Balakian and Berg, 1968; Pilone and Berg, 1965). The solute species, K^+ and HT^- are probably complexed to some extent, and are no longer available for crystallisation (Balakian and Berg, 1968; Pilone and Berg, 1965). Several studies confirmed that wine constituents also affect the crystal growth rate. Crystallisation kinetics are significantly slower in wines compared to model ethanol solutions with a similar level of supersaturation (Gerbaud et al., 1996a; Tanahashi et al., 1992). Their influence on crystal growth results from their adsorption on to growth sites of crystal faces, thereby preventing the uncorporation of new units into the crystal lattice. As observed by Rodriguez-Clemente and Correa-Gorospe (1988), Tanahashi et al. (1992) and Vernhet et al. (1999a and b), the morphology of the KHT crystals formed in the model solutions differs from those formed in wines. The crystal morphologies of precipitates obtained from model solution and from white and red wines are illustrated in Figure 2-10. Again, these differences are a consequence of adsorption of wine organic components.

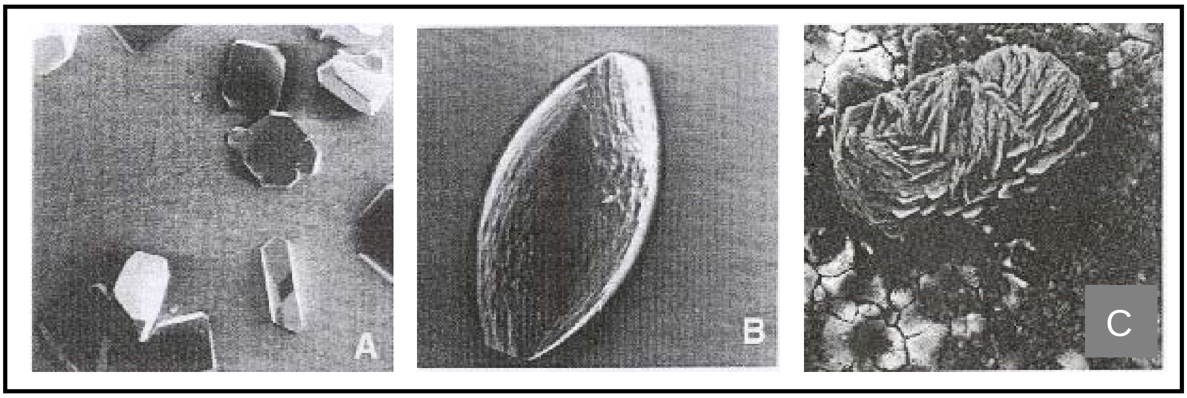


Figure 2-1. Scanning electron microscopy views of the tartrate crystals obtained from: A: model solutions; B: white wine; and C: red wine (Vernhet et al., 1999a and 1999b).

To understand the process involved in this phenomenon, a recent theory of crystallisation phenomena in the presence of an additive can be used. It accounts for the growth of nuclei to a detectable size, postulates that nucleation occurs heterogeneously and that additive molecules act as secondary nucleation sites. Studies of the inhibiting effect of additives on KHT nucleation identified carboxymethylcelluloses (CMC) are very efficient inhibitor. CMC is classified according to its substitution and degree of polymerization. The degree of polymerization is related to viscosity. The most pronounced inhibition effect is observed at low viscosity and high concentration of substituted CMC (Gerbaud et al., 1996b). Besides CMC, addition of rhamnogalacturonan (RG) II accelerates nucleation of KHT in ethanol solutions but RG-I produces no effect. Both RG I and II decrease the growth rate as their concentration increases (Gerbaud et al., 1996b). The effect of adding sodium salts and magnesium salts to the model potassium bitartrate solution was studied. The induction time (lag time before significant crystallisation) was prolonged with adding these salts. Berg and Keefer (1958) noted that the solubility of potassium bitartrate is increase by adding 45 to 165 ppm of magnesium salts to wine. However, Dunsford and Boulton (1981b) interpreted this finding as the inhibition of nucleation, which is coherent with the observation made by Botsaris and Sutwala (1976). The KHT levels would be expected to be the same if sufficient nuclei are provided.

2.5 Determination of Crystallisation Rate by Measuring Conductivity

According to Dunsford (1979), measuring crystallisation rate by the conductometric method is only applicable if the conductivity is mainly dependent on the supersaturation domain's concentration. In wine, the average concentration of potassium ion is within the range of 0.02 - 0.05 mol/L. Therefore, potassium is recognised as the dominant ionic species. According to Handbook of Chemistry and Physics (1998), the potassium ion has high electrical mobility – 74 Ω^{-1} m^2 mol^{-1} at 25°C. During crystallisation, potassium bitartrate is transformed from ionized state to a crystalline state (Ribéreau-Gayon et al., 2000). Hence, changes in concentration of potassium can be measured by conductivity changes, which may be used to monitor KHT crystallisation rate.

2.6 Potassium Bitartrate Stability Tests

A variety of stability tests have been developed to predict the likelihood of tartrate precipitation in bottled wine. Methods include:

- the cold or freeze test,
- the *CP* (concentration product) test,
- the conductivity test, and
- others – e.g. mini-contact test and determination of the temperature of saturation.

The following sections outline these methods in more detail.

2.6.1 Hold-cold or freeze-thaw test

A common practice within Australian wine industry is to perform tests based on the formation of crystals by holding filtered wine samples at low temperatures for specific time interval. Various combinations of time and temperatures are used for such analysis. In a freeze test, the filtered sample is frozen for 8 to 24 hour whereas the hold-cold test maintains a sample at a temperature close to freezing point for several days or weeks

(Boulton et al., 1996). The sample is then defrosted to determine if the induced crystals re-solubilize in wine. The wine is considered stable if crystal formation is absent.

The freeze test is considered to be crystal-rate of formation test rather than an actual stability test (Boulton et al., 1996; Zoecklein et al., 1995). Increasing ice formation increases the relative concentration of all species in the sample, including alcohol, thereby enhancing nucleation and crystallisation. Unfortunately, crystal formation in this concentrated wine sample is difficult to correlate conclusively with potassium bitartrate instabilities. A more accurate measure of potassium bitartrate stability requires that wine is seeded with potassium bitartrate (Zoecklein, 1988a). A reduction in tartaric acid and potassium concentration, titratability acidity, and electrical conductivity occurs as the excess tartaric acid and potassium are deposited onto the added crystals.

The freeze-thaw test is often considered too severe. If the wine passes the freeze-thaw test then stability is guaranteed however failure does not necessary imply instability. Hence, most wineries will employ a cold-hold test with results verified using a freeze-thaw test. According to Leske et al. (1996), storage of the wine at -4^{o}C for three days is the preferred test rather than the freeze, conductivity or *CP* test. No wine that passed the -4^{o}C/3 days test has subsequently produced a crystalline deposit after long term storage (23 to 99 months).

2.6.2 *CP test*

The Concentration Product (*CP*) quantifies the relationship between tartaric acid and potassium ions (Berg and Keefer, 1958). The pH, ethanol content, temperature, and potassium and tartaric acid concentrations are measured. The *CP* value of KHT in wines may then be calculated as follows:

$$CP = \left[K^{+}\right](mol/L) \times \left[H_2T\right](mol/L) \times \left(\%HT^{-}\right) \tag{2-23}$$

where value for % HT^{-} is given by Berg and Keefer (1958) at measured pH and alcohol levels.

Recommended *CP* values (DeSoto and Yamada (1963)) are summarised in Table 2-XIII. These are commonly used as a reference for KHT stability in wines. These values were obtained by averaging the *CP* values for each type of wine following storage at ambient temperature for a period of 16 to 27 months. If the calculated *CP* values exceed the recommended safe levels, KHT in wine may deposit. Unfortunately, the recommended *CP* values from different studies varied substantially. For instance, Berg and Akiyoshi (1971) suggested a limit for of 4.1×10^{-5} (powdered KHT addition) and 9.4×10^{-5} (without seeding) whereas 16.5×10^{-5} was suggested by DeSoto and Yamada (1963). Ewart (1984) suggested a significantly lower limit of 3.1×10^{-5}. Leske et al. (1996) found that the limits proposed by DeSoto and Yamada (1963) were excessive and suggested a *CP* for white and red wines of 8.0×10^{-5} and 18.0×10^{-5}, respectively. Leske et al. (1996) concluded that the *CP* test is reliable, however it requires relatively expensive instrumentation and is time consuming.

Table 2-I: Suggested safe Concentration Product Levels of KHT in various types of wines (Reproduced from DeSoto and Yamada, 1963).

Wines type	**Suggested safe level *CP* value x 10^{-5}**
Sherry	17.1
Pale dry sherry	10.0
Cream sherry	10.0
Dry vermouth	6.0
Muscatel	17.5
White port	10.5
Port	20.0
White table wine	16.5
Red table wine	30.0

2.6.3 Conductivity test

The conductivity test utilizes a measured change in the conductivity of a seeded juice or wine sample at a designated temperature to reveal instability. The electrical conductivity (EC) of a cold seeded sample may be changed when free potassium ions (K^+) deposits on the added seed (Boulton et al., 1996; Zoecklein, 1988a). In this test, powdered KHT is added to obtain a supersaturated wine, and hence initiate crystal growth.

The magnitude of reduction in conductivity indicates the wine's stability. The stability of wine is confirmed if the difference between the initial conductivity (prior seeding) and the final value differ by less than 5% (Zoecklein, 1988a). Leske et al. (1996) set the limit at 3% and yet some wines that satisfied this criterion failed during long-term storage. Hardy Wine Company considers a conductivity change below 3% to be unstable for Róse and white wines. For red wines, the stability limit is set at 1.5% to account for interferences from color and tannins. However, the reliability of this test remains unknown.

2.6.4 Other tests

Another analytical method to evaluate tartrate stability was developed by Müller-Späth (1979). It is known as mini-contact test. The wine is cooled to temperatures $\leq 0^oC$ and powdered KHT is added to induce KHT precipitation during a fixed time period. To determine tartrate stability, the mass of KHT precipitated is measured by either weighing the crystals or by measuring the resulting conductivity changes.

Gómez Benítez et al. (2004) studied the predictability of mini-contact test for sherry wines. They observed that the wines experiencing a 10 μS/cm conductivity changes remain stable at -4^oC for more than a week.

Another method is based on determination of the saturation temperature (T_{sat}). The apparent saturation temperature can be related to a wine's stability. At high temperatures, KHT is soluble in certain wines. As the temperature reduces, KHT concentration in wine attains equilibrium when T_{sat} is reached. The lower the T_{sat}, the more stable the wine as it can tolerate lower temperatures without risk of KHT precipitation.

To determine T_{sat}, the conductivity of two samples of a wine (one with and one without seeding) is measured over a range of temperature, where temperature is raised at constant rate (Maujean et al., 1986; Würdig et al., 1982). The temperature at which the two conductivity curves intersect is the saturation point. According to Maujean et al. (1986), the stability temperature of most wines should be 15^{o}C lower than T_{sat}. However, Vallee et al. (1990) suggested that stability temperature should be 5^{o}C below T_{sat} for white wine and 10 ^{o}C below T_{sat} for red wine.

Interestingly, recent work by Gómez Benítez et al. (2004) confirms no direct relationship between stability and T_{sat} for sherry wines. Thus, lack of agreement over the key parameters for estimating stability of different wines renders it unattractive.

2.7 Review of Nanofiltration Technology

2.7.1 Introduction

Nanofiltration (NF) is a pressure-driven separation process where the driving force is the pressure difference between the feed or retentate and the filtrate side at the separation layer of the semipermeable membrane. NF separation characteristics fall between reverse osmosis (RO) and ultrafiltration (UF) as shown in Figure 2-11. According to Peeters et al. (1999), Raman et al. (1994), Tsuru et al. (1994) and Rautenbach and Gröschl (1990) , NF separation is dominated by size exclusion and electrostatic interactions. Size exclusion provides the mechanism for separation of uncharged molecules (e.g. sugars) (Chilress and Elimelech, 2000; Raman et al., 1994). The pore size of NF membrane provides a molecular weight cut off (MWCO) at approximately 200-1000 daltons (Da). Hence, water and other substances with molecular weights below 200 Da are able to pass through the membrane.

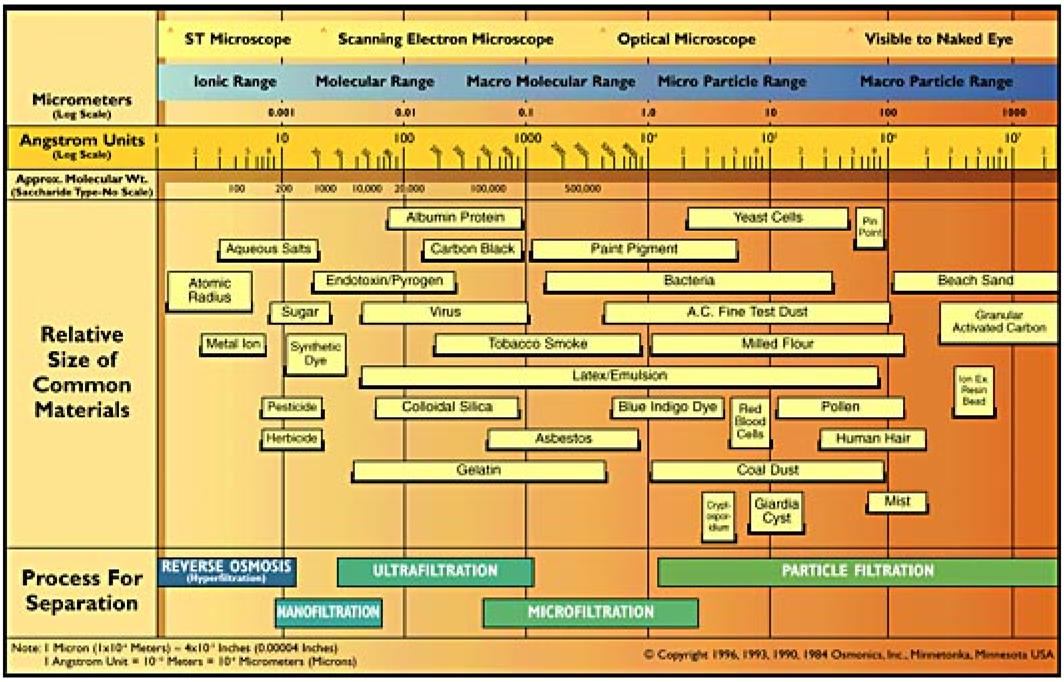


Figure 2-1. Filtration spectrum (extracted from GE Osmonics, 2007).

Moreover, NF membranes surface are slightly charged. The resulting electrostatic interaction permits separation of ions with different valences. For instance, NF membrane will retain divalent and multivalent ions while allowing monovalent ions to pass through.

Given these properties, NF has been applied to diverse industrial applications in food and dairy, textile, pulp and paper, chemical, electronic and water production industries. A brief overview of NF applications in various industries is presented in Table 2-XIV.

Table 2-XIV. Summary of some NF applications in different industries.

Industry	Application
Food and Dairy	Concentration fruit juice and sugar (Snow et al., 1996)
	Separation whey protein and lactose (Snow et al., 1996)
	Demineralisation of whey (Kelly et al., 1991)
	Treatment of plant wastes (Alkhatim et al., 1998; Srivastava and Pathak, 1998)
	Purification of organic acids (Timmer et al., 1993 and 1994)
Textile	Removal of dyes (Achwal, 1998; Chakraborty et al., 2005; Rozzi, 1997; van’t Hul et al., 1997)
Pulp and paper	Removal of colour (Koyuncu et al., 1999)
	Recovery of water (Ahn et al., 1998; Geraldes and Noberta de Pinho, 1995)
Chemical	Separation of bromide (Lin, 1998)
	Removal of sulphate (Barr, 2001; Galiana-Aleixandre, 2005; Hagg, 1998; Maycock et al., 1998)
Electronic	Production of ultra pure water (Snow et al., 1996)
Water production	Removal of heavy metals (Brandhuber and Amy, 1998; Khalik and Praptowidodo, 2000)
	Removal of natural organic matter (Alborzfar et al., 1998; Schafer et al., 1998; Orecki et al., 2004)
	Reduction of water hardness (Schaep et al., 1998; Orecki et al., 2004)

2.7.2 NF membrane and membrane modules

There are two types of NF membranes currently available: homogeneous asymmetric membranes and thin film composite (TFC) membranes. Asymmetric NF membranes possess a very thin permselective layer above a more porous layer of the same polymer (e.g. cellulose acetate and sulfonated polysulfone). TFC membranes consist of multiple layers made from different polymers but commonly possess an active thin-film layer of polyamide polymer supported by a porous layer. The porous support layer is generally formed using a crosslinked polymer (e.g. polysulfone, polyethersulfone and polyvinyledene fluoride). The active layer of TFC membrane is normally much thinner than the thin permselective layer in an asymmetric membrane. TFC membranes normally exhibits higher selectivities and water fluxes.

NF membrane modules include spiral-wound, tubular, hollow-fiber, and plate-and-frame elements. The spiral-wound element (as shown in Figure 2-12) is most commonly used due to its high packing density, moderate fouling and cost effectiveness.

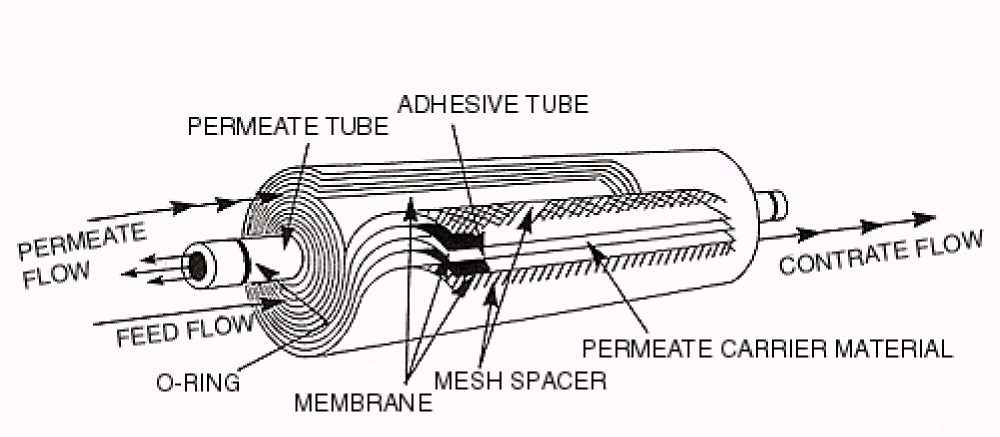


Figure 2-1. The schematic diagram of a NF spiral-wound element (extracted from Reef Online, 2003).

2.7.3 NF process description

As shown in Figure 2-13, industrial applications of NF are usually operated as a crossflow filtration process. The feed is pumped through the membrane system at a pressure range of 10 – 34 bar (approximately half the pressure required for reverse osmosis of seawater). Within the system, the feed is split into purified product, known as permeate, and a concentrated product, known as concentrate or retentate.

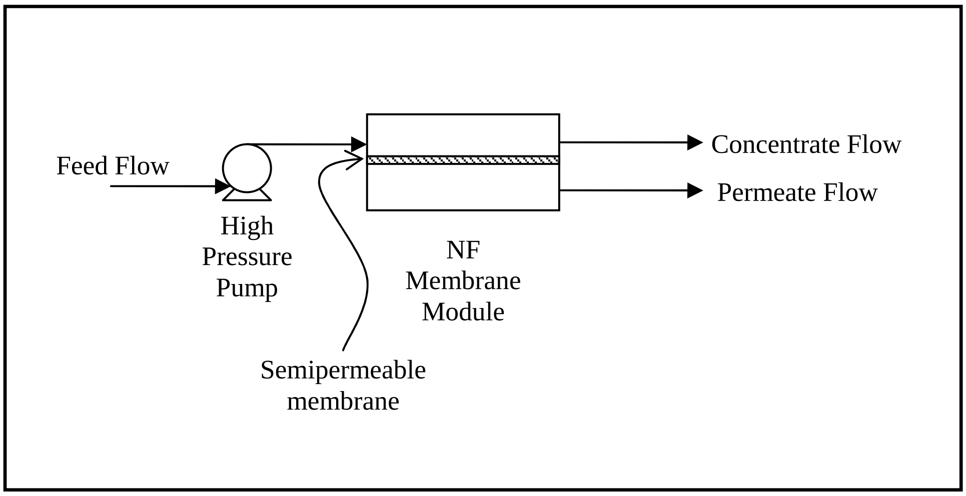


Figure 2-13. A schematic diagram of a simplified NF process.

The performance of the NF system is measured by permeate flux, J_v and rejection of solute, R_i.

The volumetric flux of permeate, J_V (L/m^2/h) may be calculated using Eq. (2-24).

$$J_V = \frac{V_p}{A \times t} \qquad \textbf{(2-24)}$$

where V_p is volume of permeate collected (L), A is membrane effective area (m^2), and t is time required for the collection of V_p (hours).

Membrane rejection rate for each species may be calculated using the following equation.

$$R_i = \frac{C_{r,i} - C_{p,i}}{C_{r,i}} \times 100\% \qquad \textbf{(2-25)}$$

where R_i is the rejection of certain solute i, $C_{r,i}$ is concentration of solute in retentate, and $CP_{,i}$ is concentration of solute in permeate.

The permeate flux and solute rejection are generally influenced by:

- Pressure (Yacubowicz and Yacubowicz, 2005): At net pressures (difference between hydraulic and osmotic pressures) of 10 bar or higher, separation of solute and permeate flux are improved.

- Temperature (Yacubowicz and Yacubowicz, 2005): At higher operating temperature, viscosity of the solvent reduces and hence increases the permeate flux.

- Recovery (DOW Chemical Company, 2003): Recovery, r is defined as

  $$r = \frac{V_p}{V_f} \times 100\% \qquad \textbf{(2-26)}$$

  where V_f and V_p are the volume of feed and permeate (L), respectively.

  As the recovery increases, the permeate flux reduces and solute concentration increases. When solute concentration reaches a point where the osmotic pressure of the concentrate is equals the hydraulic pressure, the flow ceases.

- pH (Yacubowicz and Yacubowicz, 2005): As noted earlier, NF membranes surface are slightly charged. At different pH regimes, the charged sites on the NF membranes surface are charged differently depending on their pKa. For example, the membranes surface are charged negatively at neutral or alkaline pH and lose their charge at acidic pH. Generally, at low acidic pH, NF membranes provide lower solute rejection.

2.7.4 Application to wine industry

In the past decade, application of NF in wine industry has increased in particular for (Grosser, 2003):

- concentrating wine flavour and colour,
- adjusting alcohol levels,
- removing volatile acidity, and
- reducing wine taints.

As noted previously, Rhein (1978) patented the use of membranes to reduce KHT concentration in wine. Several membrane companies claimed to have developed membrane systems for the tartrate crystallisation process. However, there are no reports of industrial use to date with the exception of a report from Mannapperuma (2001) of a recent pilot-scale NF study. Unfortunately, Mannapperuma’s study fails to provide any technical analysis of the operating principles or theory associated with the process concept.

The use of membranes for inducing crystallisation occurs in other industries. For instance, Donovan and Hlavacek (2002) patented a process for purification of low grade sugar syrups using NF. NF increases concentration of sucrose and reduces the inverse sugars content in the syrup in retentate which then promotes crystallisation. Hoffmann et al. (1997) studied the use of NF to remove calcium sulfate ($CaSO_4$) from waste water. Their study successfully demonstrated that NF able to generate highly saturated $CaSO_4$ solutions which then promoted crystallisation to occur. Hoffmann et al. (1997) also showed that increased the amount of crystal seeds added, the subsequent reduction of the degree of super saturation increased. Such information outlined some technical details on ways to induce crystallisation using NF. However, no such studies have been conducted using wine.

2.8 Summary and Research Gaps

Cold stabilisation is a widely applied industrial process to prevent tartrate instability in bottled wines. Current knowledge of the performance and cost of cold stabilisation, and alternative technologies for tartrate stabilisation have been reviewed. Whilst occasional cost comparison between cold stabilisation and individual alternative technologies are available, there remains inadequate contemporary data that could be confidently used for accurate comparison of relative economics of different processing options. Clearly, a comprehensive review of both technical and economic performance of alternative technologies to cold stabilisation, including the Westfalia process, nanofiltration and electrodialysis based on operating conditions in Australian wine industry is desirable. To incorporate a wide range of criteria other than economic performance (e.g. environment, ease of operation, etc.) before choosing the alternative technologies for further study, multi-criteria decision analysis (MCDA) which has not been applied to decision problems in the Australian wine industry should be explored. As well, comparisons of sensory analysis of wine treated by various alternative technologies to wines conventional processed by cold stabilisation are limited. In this study, wine treated by nanofiltration (identified by application of later MCDA in this work) will be collected from field trial for sensory analysis to provide a comparison with identical wine treated by conventional cold stabilisation.

2.9 Aims

The goal of this project is to research and develop improved or alternative technologies for removal of KHT from wine with a constraint that wine quality must be maintained while overall costs are reduced. A review of current available tartrate stabilisation methods, fundamental knowledge regarding the kinetics of KHT crystallisation and the controlling factors is clearly required.

Thus, the specific aims of this study are to:

- develop a detailed technical and conceptual design of various process sequences as a framework for a comprehensive technical and economic analysis of the selected technologies. This will be the first comprehensive analysis where six different tartrate stabilisation routes are compared side-by-side.

- introduce the key concepts of MCDA and demonstrate the application of three MCDA variants: the weighted average method and two outranking methods (PROMETHEE and ELECTRE) to allow broad evaluation of tartrate stabilisation technologies. This work represents the first published application of MCDA to a decision problem in Australian wine industry.

- demonstrate the suitability of selected tartrate stabilisation technologies for commercial implementation with bench-scale and field trials. Key technical, environment and operating knowledge will be discovered. From such study, nanofiltration (NF) coupled with centrifugation is identified as a possible alternative to cold stabilisation.

- establish relevant KHT supersaturation levels required in order to induce spontaneous crystallisation for wine treated with the NF during bench-scale and field trials.

- optimize and provide scale-up of NF if required.

CHAPTER 3 TECHNICAL AND ECONOMIC ANALYSIS OF SELECTED TARTRATE STABILISATION PROCESSES

This chapter presents details of conceptual designs and production cost estimates for commercial implementation of a number of tartrate stabilisation options. These are based on a case study, namely a retrofit scenario at Berri Estates winery in Australia. This winery is the largest in the Southern Hemisphere. It is owned and operated by Hardy Wine Company (HWC). Chilling without seeding (conventional cold stabilisation), 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 based on previous operating experience where adverse effects on wine quality were observed. As well, wine products are exported to Europe, where there are difficulties with commercial acceptance of the use of ion exchange. The company wishes to identify if a more cost effective process strategy (other than cold stabilisation) is available. The company personnel have expressed strong interest in emerging technologies such as fluidized beds, electrodialysis and nanofiltration. These processes were considered together with the use of seeding and application of the Westfalia process as an example an available proprietary system.

As well, the effect of winery scale on production cost estimates, and the alternative situation of constructing a new winery – the greenfield scenario – will be considered.

These analyses will provide invaluable knowledge for wine producers contemplating a change from cold stabilisation to an alternative treatment method, or for synthesizing an optimal process strategy when designing and constructing a new winery.

3.1 Selection of Technologies for Evaluation

It is not practical to consider all possible process sequences and it was decided to limit the processing strategies in the study. This decision was undertaken in consultation with the wine producer. Berri Estates winemakers were provided with process descriptions and a summary of the potential advantages and disadvantages of the various options for discussion and comment.

The use of seed in the crystallisation process was perceived to be the option involving least incremental change at the winery.

The Westfalia process is an example of an established treatment option with strong similarities in process configuration and operation to cold stabilisation, which is the normal unit crystallisation operation at the company. It was also considered one of the more successful proprietary chilling systems on the market, and the company utilized Westfalia process equipment at the winery and had an excellent relationship with this equipment supplier.

Whilst there appeared to be no commercial examples of fluidization, the process concept appealed to the winemakers. Hence, it was included.

Nanofiltration generated significant interest as this process had been successfully implemented at the winery for other processing applications. The company believed that existing equipment could be readily adapted for tartrate stabilisation. However, wine losses for nanofiltration if combined with microfiltration were considered excessive. Hence, this process sequence was omitted. It is proposed that wine losses could be reduced to more acceptable levels by using centrifugation rather than microfiltration. Consequently, nanofiltration combined with centrifugation was retained as an option.

Electrodialysis was recently implemented by another wine producer in the same region. Anecdotal reports suggested that processing costs were higher than anticipated. This work also provided an excellent opportunity to examine the merits of this new processing technology.

The treatment options to be evaluated are;

Option 1 –Cold stabilisation;

Option 2 – Cold stabilisation with seeding;

Option 3 – Cold stabilisation by Westfalia process;

Option 4 – Cold stabilisation by fluidization;

Option 5 – Nanofiltration (combined with centrifugation); and

Option 6 – Electrodialysis.

3.2 Technical and Conceptual Design

3.2.1 The current cold stabilisation process

Approximately 60 % of wine cold stabilized at Berri Estates winery is red wine. These wines are stored at 8 ºC. The cold stabilisation process involves chilling in a heat exchanger to –4 ºC and holding the batch in an insulated tank for at least 7 days. Normally, the chilling process will include energy recovery from a wine that has finished cold stabilisation. A refrigerant is employed as the final step to reduce the temperature to the target.

At the conclusion of the holding period, for red wines, the tank is agitated to re-suspend all loosely settled crystals. The wine is then centrifuged to recover the tartrate crystals. These are sold as a by-product.

At Berri Estates Winery, normal practice is to clarify white wines prior to storage and further treatment. This ensures that high quality wine is produced by minimizing contact with solids. For white wine, bentonite fining is performed during cold stabilisation. The stabilized wine is racked from the bentonite and tartrate lees and then clarified using diatomaceous earth (DE) filtration. Occluded wine in the bentonite or tartrate lees is then recovered by rotary vacuum drum (RDV) filtration using perlite as a filter aid.

For red wines, tank cleaning after cold stabilisation is a two-step process. Any loose crystals remaining at the bottom of the tank are manually collected and sold as by-product. Tanks are then cleaned to remove crystal deposits from the exposed surfaces. These deposits are estimated to be approximately 50 % of the tartrate removed from the wine. Concentrated caustic is used as a cleaning agent. Caustic solution is re-circulated through the tank under pressure using a spray-ball. The caustic dissolves all remaining tartrate salts.

Following cleaning with caustic, the tanks are sanitized with a citric acid solution containing potassium metabisulfite.

For white wines, the tanks are simply cleaned with caustic and there is no tartrate recovery.

The current cold stabilisation process results in losses and value downgrading of the product. Losses occur each time a wine is transferred through pipe work, into and out of a tank, in the discharge from the centrifuge, and at the RDV. Value downgrading occurs for white wine recovered from bentonite/tartrate lees due to oxidation during processing by RDV. For example, observations at Berri Estates Winery suggest that only 60 % of the lees volume is recovered as wine by RDV, and that this recovered wine is only half its original value.

3.2.2 Analysis strategy

The primary scenario considered for technical and economic evaluation is the retrofit of a new technology to replace cold stabilisation at the winery based on a production capacity of 106.5×10^6 litres per annum. This analysis was later extended to consider a greenfield scenario where a new winery (identical capacity) is built. Next, the effect of scale on the retrofit and greenfield scenarios was considered and the analysis was performed for a winery with a production capacity equivalent to 10×10^6 litres of wine per annum.

3.2.3 Tartrate content and removal during treatment

A key step to ensure a fair comparison between cold stabilisation and the new technologies was the decision on the treatment scenario reflecting the typical operating situation at the winery. This decision posed considerable challenge as individual wines possess dissimilar concentrations of potassium and tartrate which, in each case, may react distinctly depending on the treatment method.

For simplicity, it was decided to work with a common initial value of KHT salt in all wines regardless of treatment strategy. Typical values are published in literature and were summarised by Boulton et al. (1996) and Zoecklein et al. (1995). The concentration of KHT in wine was defined as follows: 1000 mg/L of K^+ and 1500 mg/L of tartaric acid at a pH of 3.5. At this pH approximately 67 % of the tartaric acid is present as bitartrate ion (Boulton et al., 1996).

Normally, stabilisation of a wine following treatment would be evaluated using a stability test/criterion. A number of different tests/criteria are used by the industry for this purpose. These include, inter alia, freeze tests (Baldwin, 1992; Rankine and Pocock, 1976), conductivity test (Zoecklein, 1988a), calculation of concentration product (Ewart, 1984; Berg and Akiyoshi, 1971; DeSoto and Yamada, 1963; Berg and Keefer, 1958), determination of tartrate saturation temperature (Narciso et al., 2005; Cameira dos Santos et al., 2002; Würdig et al., 1982) and the mini-contact test (Müller-Späth, 1995).

In this study, experimental data was not available to evaluate the reduction in K^+, HT^- and tartaric acid that would define stability when the wine was subject to treatment by different processes. Therefore, an estimate had to be made. For cold stabilisation, seeding, contact processes and nanofiltration, this was achieved by analysing concentration product (*CP*) values for potassium bitartrate that have been observed in stable wines. The *CP* value is defined by the equation suggested by Berg and Keefer (1958) (refer Eq. (2-4)).

The *CP* values were used to predict the final potassium, bitartrate and tartaric acid concentrations in the stabilised wines from molar balances and the equilibria relationship between bitartrate ion and tartaric acid. In performing these calculations a simplifying assumption was that pH remained relatively stable, and thus, the ratio of bitartrate ion and tartaric acid remained constant (i.e. approximately 67 % of tartaric acid as bitartrate ion).

Additional information about *CP* values that were assumed for the different processes and method of calculation is summarised below.

DeSoto and Yamada (1963) suggest typical *CP* values for red and white table wines stabilised at 0°C are 16.5×10^{-5} and 30×10^{-5}, respectively. These values were assumed in stable white and red wines following treatment by cold stabilisation.

Seeding during cold stabilisation treatment decreases the *CP* value required for wine stability (Zoecklein et al. 1995). In this study, a seeding rate of 4 g KHT/L was assumed. At this rate, Blouin et al. (1979) found that the *CP* value of young red and white wines decreased from 15.1 x 10^{-5} to 7.6 x 10^{-5}. This lower *CP* value was applied to both stable red and white wines following treatment by cold stabilisation with seeding. In the absence of any other information, this *CP* value was also assumed for stable wine following treatment by other contact processes (i.e. Westfalia process and fluidisation).

Nanofiltration is performed at near ambient or wine storage temperatures. For the purpose of this study the nanofiltration treatment temperature was assumed constant at 8 ºC, which is the tank wine storage temperature currently employed at Berri Estates winery. No reliable information could be found indicating *CP* values at this temperature or the actual effect of temperature on the *CP* value. However, Boulton et al. (1996) reports that KHT solubility in model wine solutions at 10 ºC is approximately 1.62 times that at 0 ºC. Assuming that *CP* values in wine vary with temperature in a similar fashion, this suggests *CP* values at 15 ºC of approximately 30 x 10^{-5} and 56 x 10^{-5} for red and white table wines, respectively. These *CP* values would dictate the solubility limits of KHT in the retentate produced during nanofiltration. Therefore the analysis involved calculation of *CP* in retentate following concentration by nanofiltration using assumed values (given later) of membrane rejection for potassium and bitartrate ions. This allowed determination of the (retentate) concentration or (feed) recovery rate necessary to exceed these *CP* values and produce sufficient KHT precipitation so that when clarified retentate was blended with permeate, the *CP* values of the reconstituted wine were below that normally achieved during cold stabilisation treatment (as indicated above).

In the case of electrodialysis, there is no precipitation. Values for potassium and tartrate ion removal published in the literature for stabilisation of wine using this process were utilised.

3.2.4 Sensory attributes

The published literature does not contain any explicit information regarding the effect of different treatments on the sensory quality of wines except for electrodialysis.

While some laboratory studies of electrodialysis membranes suggested they may change the pH and colour intensity of treated wines (Cottereau, 1993; Moutounet and Escudier, 1991), other workers reported no significant difference in sensory quality of wines treated by electrodialysis when compared to cold stabilised wines (Cameira dos Santos et al., 2000; Moutounet et al., 1997).

Even though the use of reverse osmosis membranes for tartrate stabilisation has been patented by Rhein (1978) and a pilot-scale study has been conducted by Mannapperuma (2001), none of these works involved sensory evaluation of the resulting wine quality. However, the uses of cross-flow ultra and microfiltration in wine filtration have been studied extensively. Studies conducted by Delfini et al. (1994), Dietrich and Weinand (1990), Junge and Spadinger (1988), and Escudier et al. (1987) reported that wine filtered by membrane did not suffer any adverse sensory effects.

No studies are available where the effect of either seeding, Westfalia process or fluidisation on sensory quality of wine is compared with cold stabilised wines.

However, the focus of this study is the relative economics of the different treatment processes. The results will be used to identify those technologies, which based on their cost effectiveness, merit further technical investigation. During these subsequent technical investigations the potential sensory or quality effects on wine can be properly evaluated.

Therefore for the purpose of this study it was assumed that all treatments would produce a similar effect on wine quality and the economic impact of any potential changes in sensory attributes was neglected.

3.2.5 Process configurations and operational performance

The following section provides broad descriptions of the process configurations that were developed and key assumptions that formed the basis for technical analysis and engineering design to permit preliminary cost estimation for each option. These descriptions are not intended to be comprehensive but they provide an insight into how sizing of process equipment was performed and how operating performance was established.

3.2.5.1 Option 1 – Cold stabilisation

Estimates of wine losses had been prepared previously by HWC personnel and were used in this study.

Whilst energy recovery is not always practised and low approach temperatures impact on efficiency, an average energy recovery of 40% was assumed across the site for this operation.

Additional cooling is required to maintain tanks at treatment temperature during the holding period. Typical values for heat losses from insulated tanks published by Rankine (2004) were assumed.

The effective coefficient performance (COP) of the refrigerant plant at the Winery, taking into account heat losses arising from brine cooling and reticulation was assumed equal to 2.5.

Energy calculations included pumping requirements, not only to and from the tank after chilling and holding, but also for clarification of wine.

The above assumptions were also applied to energy calculations for Options 2, 3 and 4.

Direct labour demands for cold stabilisation primarily involve chilling, centrifugation and cleaning activities. Requirements are already well established at Berri Estates winery and data was taken directly from existing records.

3.2.5.2 Option 2 – Cold stabilisation with seeding

This was essentially the same process strategy for cold stabilisation under the greenfield scenario, but with addition of KHT crystal seeds to reduce holding time.

The KHT crystals would be added to the tank after chilling to a treatment temperature of -4 °C. The seeding would be applied manually to chilled wine followed by a period of agitation to disperse and suspend the nuclei. After the contact period, all wine would be centrifuged for clarification.

The rate of seed addition was 4 g KHT/L and a 4 hour contact time was assumed. The mean particle size of the KHT powder is assumed to be approximately 40 μm, which is consistent with the size of commercially available products (Zoecklein et al., 1995).

The bulk of tartrate salts in the wine should precipitate on seed crystal surfaces. Therefore, there would be less surface deposits and more of the tartrate present as part of seed crystals at the bottom of a tank. However, no reuse of seed crystals would occur. The seed crystals and other loose deposits would be separated during centrifugation and sold as by-product. Caustic cleaning would be employed to remove surface deposits from the tank walls.

3.2.5.3 Option 3 – Cold stabilisation by Westfalia process.

This option would operate identically to Westfalia's proprietary process, as depicted in Figure 3-1. Design information and operating characteristics for the process was inferred from previous work by Bott (1988) and data provided by Westfalia. Dose and contact time following crystal addition would be the equivalent to Option 2.

Almost all tartrate salt removed from the wine would be recovered on the seed crystals. The final crystals are recovered by the hydro-cyclone. Apart from the initial charge, recovery and reuse of seed crystals would be self-sustaining. Periodic wasting of crystals from the process would prevent accumulation. Seed crystals would be reused ten times before replacement.

At the end of a treatment cycle, wine in contact tanks would be drawn down to near empty, to minimize product loss. For the same purpose, crystals in the collection tank would be allowed to settle and the free wine racked off.

The Westfalia process would require caustic cleaning and sanitization with every batch of wine processed, but virtually no tartrate contamination would be discharged to waste effluent system.

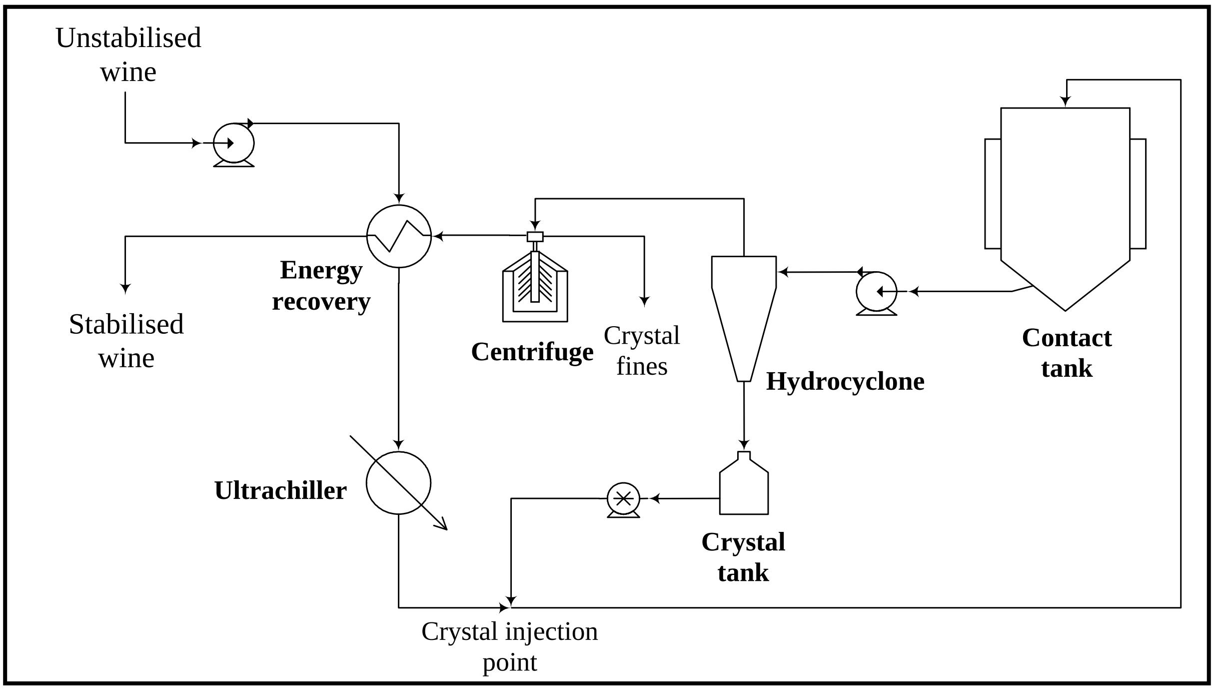


Figure 3-1. Schematic of Westfalia continuous contact process for tartrate stabilisation of wine.

3.2.5.4 Option 4 – Cold stabilisation by fluidization

Scrutinization of work from previous bench-scale studies by Bolan (1996) combined with elementary engineering calculations was employed to size process equipment and to decide on suitable operating conditions for industrial-scale implementation. The proposed process arrangement is illustrated in Figure 3-2.

Crystal size in the bed would be much larger than that used in a seeding process. A mean crystal size of 200 μm was assumed.

The operating flowrate would be fixed at just above minimum fluidization velocity to avoid crystal carry-over. This would obviate the need for a clarification step. The fluidized bed would have a residence time of 5 minutes. Periodic discharge from fluidized bed would maintain a steady crystal population. Discharged crystals would be sold as by-product.

At the end of every cycle, the bed would be purged with nitrogen gas to recover occluded wine, flushed with water for cleaning, sanitized, then gas purged again. This would minimize product loss. Crystals in the fluidized bed would be replaced after ten cycles at which time for a rigorous cleaning of process equipment with caustic would also be conducted.

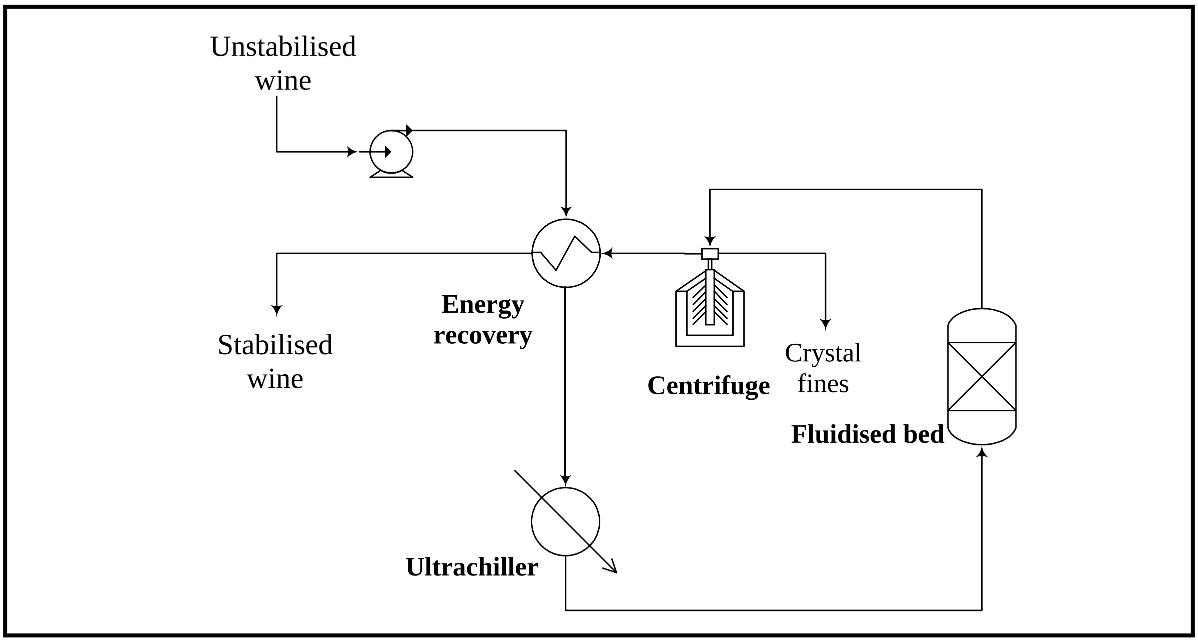


Figure 3-2. Conceptual process arrangement for continuous contact process using fluidised bed to tartrate stabilise wine.

3.2.5.5 Option 5 – Nanofiltration (combined with centrifugation)

The process arrangement is depicted in Figure 3-3. Membrane configuration is spiral wound. Feasible operating conditions were deduced from results of previous pilot plant studies (Mannapperuma, 2001) and discussions with Osmoflo Pty Ltd (Adelaide, South Australia), an Australian manufacturer of membrane systems for wine industry applications.

Red wine would be pre-clarified by centrifugation. The clarified wine would be processed by nanofiltration, producing retentate and permeate components. The retentate would be centrifuged to separate tartrate crystals and blended with permeate to reconstitute the wine.

The feed pressure would be at approximately 15 bar (gauge). An average flux rate of 5 L/m^2/h was used, which was assumed to approximate the long-term performance of the membranes during their life of operation. A permeate recovery of 50 % was applied to achieve sufficient crystallisation for wine stabilisation. No energy recovery from retentate would be attempted.

At the commencement of the treatment cycle, process operation would be initiated with water before introducing wine. At the end of the cycle, membranes would be gas purged to minimize wine losses, then cleaned with caustic to sanitize and remove fouling deposits. Flushing with citric acid and water and another gas purge would follow, prior to processing the next batch of wine. Cleaning and flushing solutions would be discharged to waste effluent.

During separation of crystals from nanofiltration retentate, negligible carry-over of crystals was assumed; no further clarification would be necessary. Crystal slurry discharged from the centrifuge would be spadeable. This would be recovered as by-product.

Product wastage would include wine occluded in the centrifuge discharge. There would also be wine losses occurring at the commencement and conclusion of treatment cycles during flushing of equipment and pipework.

Automation of the nanofiltration system would be utilized to minimize labour requirements. Annual replacement of membranes was assumed.

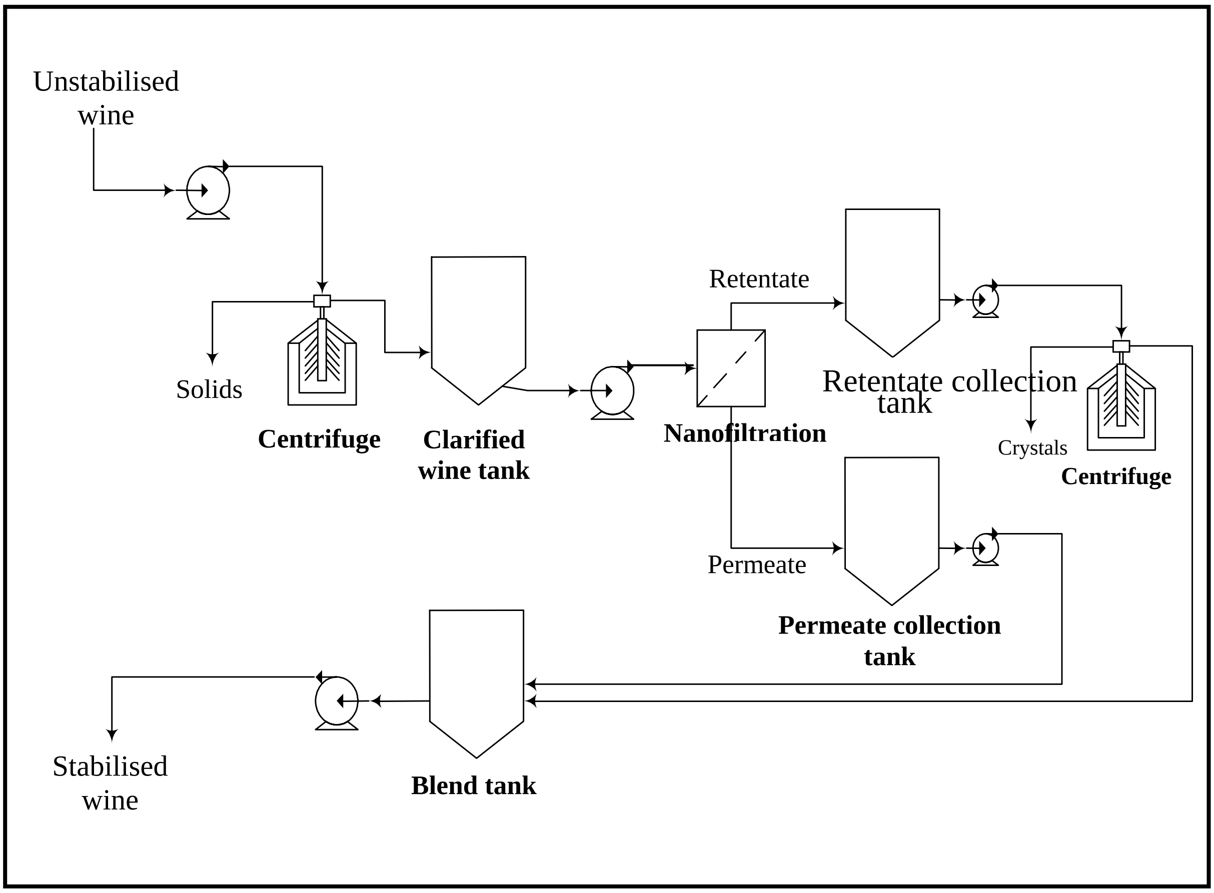


Figure 3-3. Concept process arrangement for tartrate stabilisation of wine by nanofiltration (with crystal separation by centrifugation).

3.2.5.6 Option 6 – Electrodialysis

The process arrangement would be similar to that depicted in Figure 3-4. Specific design and operating information for electrodialysis units are proprietary and were not available from suppliers, who were only willing to provide basic operating and cost data for a complete system based on the intended application. However, the following describes a probable system configuration and its performance based on information that can be gleaned from the published literature and what suppliers – Boccard (Le Couteau, France) and Winesecrets (California) – would reveal.

Pre-clarification of red wine would be performed by centrifugation, to minimize membrane fouling. The electrodialysis step would use self-contained units of several hundred membranes stacked together between electrodes. The membrane stacks provide alternating channels in which wine treatment and collection of removed tartrate and potassium ions would occur. Satisfactory treatment of wine would be achieved in a single pass. Residence time of wine in electrodialysis units would be approximately 20 minutes. Continuous re-circulation of a dilute salt solution through each electrodialysis unit would be used to collect and accumulate tartrate and potassium ions in a separate tank. These would be discharged as waste effluent.

Centrifuge and electrodialysis units would be cleaned separately after each cycle. Cleaning would be with caustic solution, followed by flushing with citric acid and water.

It was assumed that automation of the unit would significantly reduce labour demands. Total energy consumption value would be approximately 0.5 – 1.0 kWh/m^3 for electrodialysis treatment with pumping included (Escudier, 2002). Periodic replacement of membranes in electrodialysis units would be required. Current commercial practices by equipment suppliers appear to be that they supply and install replacement membranes (as well as maintain equipment) and charge the customer a fixed rate per litre of wine processed to cover this cost.

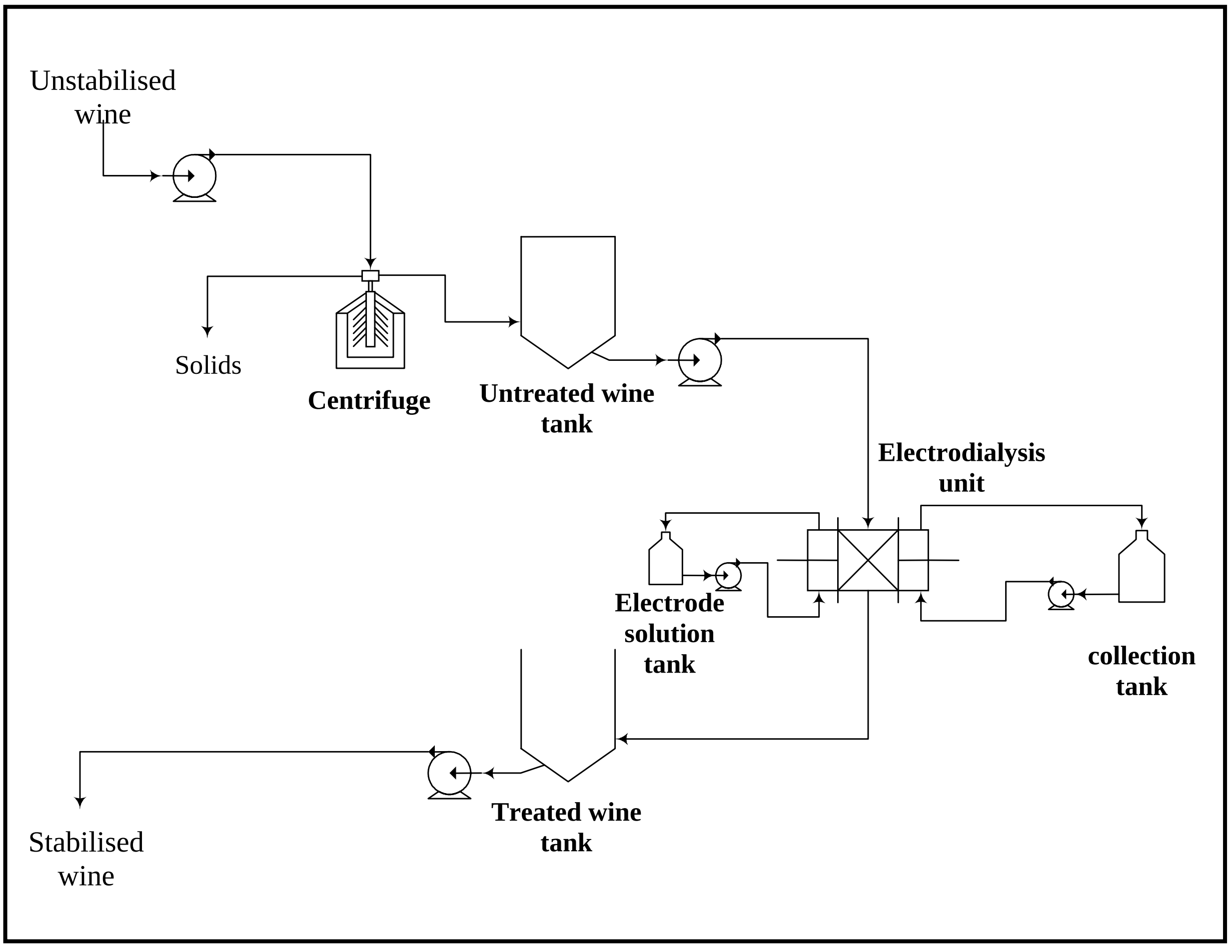


Figure 3-4. Schematic of process concept for tartrate stabilisation of wine by electrodialysis.

3.3 Cost Estimation and Economic Analysis

From preliminary engineering designs, estimates were produced for capital and operating costs for each option under retrofit and greenfield scenarios. For retrofit investigations, equipment already in place at Berri Estates Winery was taken into account when considering new capital investment required.

Capital cost estimation was made by standard engineering practices, i.e. refer Peters and Timmerhaus (1991), using a combination of methods. This involved scaling and updating equipment costs from historical data and applying Lang factors, as well as direct quotation from suppliers for equipment or entire plant. Sources of historical data, scaling factors and indices included HWC records and industry handbooks, e.g. Perry’s Chemical Engineers' Handbook (1998), or published literature, e.g. Chemical Engineering journal (1990, 2002 and 2004). Direct quotations included nanofiltration and electrodialysis units, which were obtained from Osmoflo and Boccard, respectively. On-site nitrogen gas generation was not included in capital cost estimates as the existing generator on site is not specifically used for tartrate stabilisation and would have adequate capacity to meet additional demands. Detailed calculation is presented in Appendix A.

Operating costs for maintenance, labour, consumables (i.e. membranes, filters, etc.), chemicals, electricity and water were based on material and energy balances and market or internal HWC data and discussions with equipment suppliers and HWC operating personnel. Illustration on the calculations is presented in Appendix A.

On several occasions, it was impossible to obtain verifiable operating or performance data. This inevitably involved having to make an informed and reasonable estimates based on experience and available information; in particular for establishing labour demands, wine losses, recovery of tartrate and water consumption.

Where specific information was not available, standard heuristics were assumed for estimation of annual maintenance costs: 5% value for mechanical and electrical equipment; and 2% for civil, structural and process equipment. Summaries or samples of the calculations performed are presented in Appendix A.

The effect of each option on waste effluent treatment at the Winery was not included in the analysis as these were difficult to isolate and estimate. It was assumed that such effects would be cost neutral.

Furthermore, increased revenue that might accrue from improvements in wine quality was neglected, as this was virtually impossible to accurately quantify (except to say that without treatment the wine may not be marketable, and hence, valueless).

Depreciation costs were calculated using a straight line model, with salvage at 10 % of initial value and service lives of; 60 years for civil and structural; 25 years for non-mechanical equipment (e.g. tank); and 10 years for the mechanical and electrical equipment except pumps where 5 years was assumed.

Economic analyses included net present value (NPV), unit operating cost (UOC) and unit production cost (UPC).

For this study, the NPV analysis provides an indication of accumulated expenditure: capital investment and operating costs (as listed in Table 3-II), and revenue: tartrate recovery, over a period of time. The analysis was performed for a time period of 10 years. A discount factor of 8 % was assumed.

The UOC is the operating cost per unit product. The UPC adds an amortized capital cost component to UOC, hence suggesting how much it costs to manufacture an individual unit. A litre of wine was used as the reference unit for UOC and UPC.

Standard approaches, i.e. refer Peters and Timmerhaus (1991), for calculation of these economic indicators were followed.

3.4 Results and Discussion

3.4.1 Technical performance

Results of engineering analyses and estimates for technical performance indicators of each option are summarized in Table 3-I. These include energy consumption; processing time; labour requirements; chemical utilization; wine losses; water usage; tartrate by-product recovery; volume and effluent quality. For ease of presentation, some data is presented as the requirement per 275 kL batch of wine processed. This volume is the standard size of large tank typically found at Berri Estates Winery. The best performing technology for each indicator is highlighted in the Tables by shading of the relevant cell.

Table 3-I. Summary of technical and environmental performance of each option

		Option					
	Units	**1**	**2**	**3**	**4**	**5**	**6**
Energy consumption	kWh/kL	10.19	10.26	10.16	10.01	6.84	8.03
Operating time	h/batch	188	52	56	41	48	44
Labour	h/batch	24	30	34	36	40	34
Net chemicals cost	$AUD/kL	1.15	12.13	0.97	2.26	0.64	2.11
Wine loss	%	0.40	0.76	0.56	0.75	0.72	0.70
Wine downgrades	%	1.90	1.90	1.90	1.90	1.90	1.90
Tartrate resale	kg/batch	15	547	164	207	61	0
Tartrate recovered	kg/batch	15	121	121	121	61	0
Water Usage	ML/yr	4	7	7	9	8	22
Liquid waste							
Wine loss	L/kL wine	4.0	7.6	5.6	7.5	7.2	7.0
Water	L/kL wine	42.0	67.5	67.5	83.5	78.4	208.8
Chemical solution	L/kL wine	0.20	0.15	0.15	0.15	0.22	0.20
Total volume	L/kL wine	46.2	75.3	73.2	91.1	85.8	215.9
Tartrate content	g/kL wine	216	60	60	60	30	570
COD Load	kg/kL	1.08	1.82	1.35	1.78	1.70	2.01
Caustic	g/L	3.0	1.4	1.4	1.1	1.9	0.7
Citric acid	g/L	0.81	0.36	0.37	0.29	0.39	0.33
Solid waste$^+$	kg/kL	2.42	2.42	2.42	2.42	2.42	2.42

+: Non-tartrate

All alternative methods to conventional cold stabilisation could reduce processing time. Options 2 to 6 were able to substantially reduce processing time for a single, 275 kL tank, from 188 hrs to less than 60 hours.

Despite this reduction in processing time, there was no substantial saving in energy consumption between the alternative chilling methods and conventional cold stabilisation. The majority of the energy required for these methods was expended for the initial chilling of the wine. Tanks at Berri Estates Winery are well insulated; hence, subsequent heat losses during the holding period were predicted to be relatively minor.

Nanofiltration, on the other hand, offered the prospect of sizeable energy saving. An approximately 40 % reduction in energy consumption was predicted for nanofiltration compared to conventional cold stabilisation.

The estimated energy consumption for electrodialysis, however, was only 25 % less than Option 1. This contradicts comparisons reported by electrodialysis equipment suppliers, who claim this technology requires significantly lower energy – a fifth of energy required for Option 1 (Escudier, 2002). This discrepancy may be attributable to; (i) their omission of energy requirements for pre-clarification by centrifugation as well as clarification after bentonite fining, which must be performed separately; and (ii) over estimation of energy demands for cold stabilisation by falling to properly account for the coefficient of performance associated with refrigeration plant.

Labour demands for each option are proportional to the number of steps involved in the process. More steps increased time requirements for setting up, performing transfers or treatment(s), and cleaning and sanitising tanks, pipe work and equipment. In particular, options that pre-clarified wines before treatment and required separate bentonite fining had higher labour requirements. Nanofiltration required the highest labour demand, approximately 40 hours.

Different numbers and quantities of chemicals are utilised for each option. Options 2, 3 and 4 require KHT crystal seeds in varying quantities. Electrodialysis requires chemicals for salt collection and electrode compartment electrolyte solutions. All options involve cleaning and/or sanitization chemicals to varying degrees. Consequently, total chemicals cost was utilised in Table 3-I as an indicator of gross chemical usage.

For most options, caustic and citric acid for cleaning activities were the major contributors to chemicals usage, and hence, cost. Even though Option 1 had lowest requirements for these cleaning chemicals, Option 5 – Nanofiltration - provided nearly three times more in tartrate recovery than Option 1, hence lowest cost. Despite similar cleaning chemical usage, the chemicals cost of Option 4 – Fluidised bed – was higher because of added expense involved with more frequent replacement of tartrate crystal seeds. Electrodialysis had comparable cleaning chemical demands, but incurred a slightly higher chemical cost arising from added expense of electrode compartment electrolyte solutions and tartrate that was not recovered. Option 2 – cold stabilisation with seeding – had substantially larger chemicals cost than all other options due to the single use (per treatment) of tartrate crystal seeds. Although most seed material is recovered, it can only be re-sold at a reduced value.

Product losses were principally associated with wastage in lees and residual product in hold-up volumes of process equipment and piping lost during flushing at the commencement and/or conclusion of a treatment cycle. For all options, there were no substantial advantages in separating bentonite fining from the tartrate stabilisation process. This increased the number of treatment steps and wine transfers involved, which increased wine loss. Product losses for Options 1 (all scenarios) consisted solely of losses incurred during flushing of pipe work and centrifugation equipment and wastage in tank lees, which were almost identical in each case. Option 2 incurred the largest wine loss as the volume of wine occluded in crystal seeds was high but this fraction cannot be recovered completely by centrifugation. Fluidisation had the next largest wine loss due to the large hold-up volume in the crystalliser. The occluded wine could not be efficiently recovered by gas purging. Nanofiltration and electrodialysis had similar product losses. Cold stabilisation had the lowest product loss.

Water consumption was proportional to flushing, cleaning and sanitisation requirements. As a consequence, electrodialysis was predicted to have greatest water demands, nearly five times more than cold stabilisation technologies. This arose because of additional water that was required for make up electrode compartment electrolyte solutions and the requirement for cleaning the system every 100 kL of wine processed. This consumption of additional water could be reduced by membrane treatment (e.g. nanofiltration and reverse osmosis (RO)) of the electrolyte solutions to allow reuse and/or separation and recovery of bitartrate salts removed from treated wine. Such additional requirement is not considered in this study.

Currently, tartrate by-product collected during conventional cold stabilisation at HWC wineries is sold to *Australian Tartaric Product*. This produces additional revenue and reduces waste disposal costs. Table 3-I suggests how much tartrate could be recovered batch wise for re-sale (without additional on-site processing, which was considered nonviable) to *Australian Tartaric Product* with each option. Options 2 to 4 present the opportunity to recover nearly all tartrate removed from the wine during stabilisation. Nanofiltration has the next highest tartrate recovery, as virtually all tartrate precipitating in the wine may be re-gained in crystal form. Electrodialysis was assumed to provide no opportunity for tartrate recovery, because tartrate salts were removed in the electrode compartment electrolyte solutions, which would have necessitated further on-site processing (e.g. using a RO unit).

For each option, Table 3-I includes the estimated volume of liquid waste effluent produced; theoretical contribution to effluent COD load of wine losses (ethanol component only), cleaning chemicals (citric acid only) and unrecovered tartrate; and amount of caustic and citric acid in cleaning solutions, which would contribute to pH variations in liquid waste. This information provides a useful indication of the relative effect that each option might have on overall waste effluent quality. Electrodialysis is projected to produce much larger volumes (nearly five times) of liquid waste effluent than other options. It was estimated that this could increase volume of total liquid waste effluent produced at Berri Estates Winery by up to 10 %.

Option 1 – current scenario –generated the lowest COD load of all options. Westfalia process, with the least product loss, is forecast to produce the next lowest COD load. Under retrofit and greenfield scenarios for Option 1, the additional processing and wine losses caused by separating bentonite fining and tartrate stabilisation was projected to significantly increase the COD load. Electrodialysis had the highest COD load when compared with other options because no tartrate was recovered, and thus, all tartrate removed was discharged to the waste stream.

Winery effluent is frequently characterised by substantial pH variations, as wine and alkaline and acidic solutions from cleaning activities are discharged into the effluent collection and treatment system. The potential effect of each option on winery effluent pH spikes may be elucidated from the average concentration of caustic and citric in the liquid effluent produced by each option. Even though using more cleaning chemicals, electrodialysis produces lower average concentrations of these chemicals, as a result of dilution in a larger liquid waste volume.

Outside tartrate recovery, all options will also produce a solid waste stream (DE and perlite from white wine clarification, and bentonite lees), requiring disposal.

Overall, current cold stabilisation method appears to perform best in most of the technical performance indicators, and Option 5 – Nanofiltration process – can probably be considered as the next superior option.

3.4.2 Economic performance

Economic performance of each option for retrofit and greenfield scenarios are summarised in Tables 3-II and 3-III.

Table 3-II gives the capital and operating cost estimates for both retrofit and greenfield scenarios. The accuracy of cost estimates can be considered at ± 20 to 30 %, which would be typical for this type of conceptual process costing exercise.

Table 3-III presents NPV_{10} , UOC and UPC - the economic performance indicators that were evaluated for retrofit and greenfield.

For each cost or economic performance category in the Tables the option which displays a superior cost or economic outcome has its cell shaded.

Table 3-II. **Summary of operating and capital costs of each option.**

		Option					
	Units	**1**	**2**	**3**	**4**	**5**	**6**
Operating costs							
Energy	AUD/batch	420	423	419	413	282	331
Chemicals	AUD/batch	374	5457	903	1421	410	580
Labour	AUD/batch	719	911	1011	1083	1212	1022
Consumables	AUD/batch					139	3160
Wine loss	AUD/batch	3295	6294	4611	6175	5931	5753
Wine downgrades	AUD/batch	7838	7838	7838	7838	7838	7838
Maintenance	AUD/batch	258	335	361	361	541	928
Total	Thousands AUD/batch	12.9	21.3	15.1	17.3	16.4	19.6
	Millions AUD/yr	4.4	5.8	5.2	5.8	5.6	5.6
Cost savings							
By-product recovery	AUD/batch	59	470	470	470	235	0
Total capital costs							
Greenfield	Millions AUD	9.02	9.27	9.77	8.93	14.82	21.26
Retrofit	Millions AUD	0	1.28	1.50	1.96	5.45	10.29

Table 3-III. Estimated economic performance of each option for different winery capacity (10 and 106.5 ML/year): a) greenfield and b) retrofit scenarios.

(a) Greenfield scenario

	NPV_{10}, millions of AUD		**UOC, AU¢/L**		**UPC, AU¢/L**	
Scale (ML/yr)	10	106.5	10	106.5	10	106.5
Option						
1	- 7.3	- 54.1	5.1	5.1	7.1	6.5
2	- 9.2	- 73.3	7.5	7.5	9.6	9.0
3	- 7.7	- 56.7	5.3	5.3	7.4	6.8
4	- 8.0	- 61.4	6.0	6.0	8.0	7.4
5	- 10.3	- 69.0	5.6	5.6	9.3	8.3
6	- 13.9	- 87.8	6.5	6.5	12.0	10.5

(b) Retrofit scenario

	NPV_{10}, millions of AUD		**UOC, AU¢/L**		**UPC, AU¢/L**	
Scale (ML/yr)	10	106.5	10	106.5	10	106.5
Option						
1	- 4.0	- 37.9	4.5	4.5	5.5	5.2
2	- 6.7	- 65.3	7.5	7.5	8.9	8.5
3	- 5.2	- 48.5	5.3	5.3	6.7	6.2
4	- 5.8	- 54.5	6.0	6.0	7.4	7.0
5	- 7.3	- 59.6	5.6	5.6	8.3	7.5
6	- 9.9	- 76.8	6.5	6.5	10.2	9.1

3.4.3 Retrofit scenario

For retrofit situation, retaining Option 1 – Cold stabilisation – requires almost near zero capital cost, as it was assumed all equipment for this option already exists at Berri Estates Winery.

Options 2 and 3 – Seeding and Westfalia process – require additional capital investments of roughly 1.5 million (Australian) dollars for installing additional centrifuges.

Option 4 – Fluidisation – requires a capital investment of roughly 2 million dollars; nanofiltration involves a capital investment of approximately 5.5 million dollars; whilst electrodialysis is the most expensive in excess of 10 million dollars. An important feature is that the nanofiltration plant can be used for other processes (e.g. clarification of juice) whereas electrodialysis and fluidised bed are only used for tartrate stabilisation.

For operating costs, Option 1 – Cold stabilisation - incurs the lowest annual operating cost at only 4.4 million dollars. Westfalia process has the next lowest annual operating cost, approximately 0.8 millions more then Option 1. Investigation of operating cost categories reveal that the main driver of operating cost will be wine loss. In this respect, Option 1 had the least wine loss of all the options and this has ultimately converted into a lower overall operating cost despite higher costs in several other operating cost categories.

Option 1 – Cold stabilisation - produces the lowest NPV_{10} value as shown in Table 3-III. Options 3 and 4 –Westfalia process and Fluidisation – are the next most economic processing options. Electrodialysis has the highest NPV_{10} value of all the options.

UPC produces an identical ranking of options as NPV_{10}. It also clearly indicates that cold stabilisation is the most economic processing option for tartrate stabilisation at Berri Estates Winery.

The effect of each option on waste effluent treatment cost at the Winery was not included in the economic analysis. However, it is unlikely that inclusion of these charges would change the outcome of the current analysis. Nearly all of the alternative methods especially electrodialysis, would likely increase effluent volume when compared with cold stabilisation. This would increase process demands on and hence current costs for screening, pH correction and woodlot disposal. Where more cleaning chemicals were required or tartrate is not recovered, this would cause higher salt loads which may complicate and increase cost for woodlot disposal. Those options (e.g. nanofiltration and seeding) where COD load is decreased through increased tartrate recovery might improve performance and reduce costs of biological treatment, whilst options (e.g. electrodialysis) that decreased tartrate recovery would have the opposite effect.

3.4.4 Greenfield scenario

Under a greenfield scenario, the options have equivalent rankings to the retrofit scenario for both NPV_{10} and UPC. Option 1 – Cold stabilisation – continues to present as the cheapest option, closely followed by Option 3 and 4 – Westfalia process and Fluidisation. However, the values of NPV_{10} and UPC are much closer which makes a clear demarcation difficult given the accuracy of cost estimation.

3.4.5 Implications for other HWC wineries

Berri Estates Winery is the largest of the wineries owned and operated by HWC in Australia. Scale of winery may obviously affect the above results. To consider whether this would change the results, a brief analysis was conducted to assess how winery capacity would affect cost estimates and economic performance indicators as follows. Capital costs were scaled down by the “six-tenths” rule. Operating cost estimates were divided into fixed and variable components. Fixed operating costs were adjusted in proportion to capital cost. Variable operating cost was reduced according to capacity. Economic performance indicators were then re-calculated. A winery capacity of 10 ML of wine per annum was assumed for the analysis, which was performed for both retrofit and greenfield scenarios. The results are included in Table 3-III.

This analysis indicates that cold stabilisation is still the best option for a smaller winery under either a retrofit or greenfield scenario regardless of which economic indicator is used. Options 3 and 4 – Westfalia process and Fluidisation – also remain the next most affordable options. Electrodialysis continues to be the most expensive option.

3.5 Conclusions

Suitability and cost of various tartrate stabilisation technologies for commercial implementation at Berri Estates Winery has been considered for retrofit and greenfield scenarios. A key cost driver that differentiates available options is product loss. This study suggests that alternative methods may not provide significant technical and economical advantages over cold stabilisation. This is principally because the alternative methods require separate bentonite fining and additional processing and transfers. Furthermore, equipment used in cold stabilisation (e.g. tank and heat exchanger) has multiple functions whereas electrodialysis and fluidised bed would be single purpose. Cold stabilisation therefore remains the best tartrate removal method based on analysis of unit operating and production costs. Furthermore, other chilling methods such as Westfalia process and fluidisation appear to be the next most competitive options. Electrodialysis was found to be the most expensive option. The influence of effluent treatment was not included in this study but it is unlikely this factor would alter these findings.

Next, it is essential to combine this economic data with other important criteria in order to decide which alternative option is most suitable. Traditional economic or cost evaluation paradigms are widely employed by the wine industry. However, this approach does not allow any consideration of important intangible or non-monetary related criteria. To overcome this deficiency, a new approach known as multi-criteria decision analysis (MCDA) will be applied to analyse the alternative technologies for tartrate stabilisation at a HWC winery. This MCDA analysis is presented in Chapter 4.

CHAPTER 4 CHOOSING AN ALTERNATIVE TARTRATE STABILISATION PROCESS USING MCDA METHODS

4.1 Introduction

A comprehensive review of technical, economic and operation merits of alternative tartrate stabilisation processes, including contact stabilisation, nanofiltration and electrodialysis has been performed and presented in the previous chapter. For comparison purposes, a multi-criteria decision analysis (MCDA) was applied to determine the suitability of various technologies and to assess their relative merits for commercial implementation. MCDA permits values and weights to be assigned to evaluation criteria, so they can be combined in a systematic manner to produce a rank order. The most preferred alternative deduced from MCDA assessment is then selected for further evaluation. This work represents the first application of MCDA as a tool for process decision making in wine industry. This work will explore its applicability for wine industry decision making using Berri Estates Winery as the case study.

This chapter will summarise results from the three most widely employed MCDA methods: namely, the weighted average method (WAM), and the outranking algorithms - elimination and (et) choice translating algorithm (ELECTRE) and preference ranking organization method for enrichment evaluations (PROMETHEE).

4.2 Structuring the Problem

4.2.1 Current practise and the alternatives

Alternative technologies will be examined to replace cold stabilisation by Hardy Wine Company. As noted earlier, conventional cold stabilisation requires long processing time, incurs high energy consumption and produces large volumes of saline wastes with high disposal costs.

In this chapter, cold stabilisation is alternative 1 (**A1**). The potential replacement technologies included are listed below (designated as alternative (A), followed by a numerical identifier).

A2: Contact process with seeding of potassium bitartrate (KHT)

A3: Contact process using seeding and recycling crystals through centrifugal separation

A4: Contact process with fluidised-bed crystalliser

A5: Membrane technology - Cross-flow filtration

A6: Membrane technology – Electrodialysis

4.2.2 Definition of objectives and criteria

The objectives of the overall task must be defined prior to outlining the criteria required for comparison purposes. The classification of objectives for this case study involved technical, economic and environmental considerations.

Selected criteria were defined following detail analyses of all major aspects. At the same time, the number of criteria was minimized to ensure a manageable problem. The goal was to define unique criterion and to minimize overlap. In most cases, some overlap was unavoidable and removing a criterion with strong correlation with another could obscure important information that the decision maker may wish to consider. Clearly, the objectives of the study had to be clearly defined to avoid ambiguity. Shepard (1964) noted that humans possess limited capabilities for handling large numbers of concepts simultaneously. Shafer and Davis (1989) recommended that no more than ten items be considered at any instant. For the paired comparison method, the number of comparisons required is readily calculated using Eq. (4-1).

$$f = \frac{n\left(n-1\right)}{2} \qquad \textbf{(4-1)}$$

where f is the total number of paired comparisons required and n is the number of items being compared.

In this work, a maximum of ten criteria were considered for the pair-wise comparison. The list of objectives (O_1 – O_3) and criteria (g_1 - g_{10}) used to measure performance of each alternative is presented in Table 4-I. Evaluation of the criteria has been discussed in Chapter 3.

Table 4-I: Classification of objectives and criteria for assessing the alternatives.

Objective	**Criteria**	**Target**	**Units**
O_1, Technical performance			
g_1	Processing time	min	h
g_2	Energy Consumption	min	$\text{kWh/kL}_{\text{treated wine}}$
g_3	Labour requirement	min	$\text{h/275 kL}_{\text{treated wine}}$
g_4	Wine loss	min	%
O_2, Economic Factors			
g_5	Total unit operating cost	min	AUD¢/L wine
g_6	Capital costs	min	Millions AUD
g_7	Cost savings	max	$\text{AUD/275 kL}_{\text{treated wine}}$
O_3, Environmental impacts			
g_8	Volume of liquid waste	min	$\text{L/ kL}_{\text{treated wine}}$
g_9	Solid waste produced	min	$\text{kg/ kL}_{\text{treated wine}}$
g_{10}	Effluent quality	min	$\text{kg COD /kL}_{\text{treated wine}}$

4.2.3 Selection of decision makers

The decision makers were selected based on their knowledge and experience in tartrate stabilisation of wines. These experts were invited to make informed judgements about the relative importance of the processes and criteria to be evaluated. In this study, the selected panel of decision makers was complemented by winery site managers, cellar managers, winemakers and process improvement engineer from Hardy Wine Company wineries as well as wine industry researchers. A total of twelve decision makers were recruited.

4.2.4 Determination of weights and scores by conducting survey

A survey to obtain the opinion of a wide range of experts or stakeholders regarding the selected alternative technologies was forwarded to each decision maker. A copy of the survey form used in this study is presented in Appendix B. Individual assessment of the alternatives and criteria is preferred to ensure independent decisions. However, broad discussion amongst other decision makers prior to completing the survey was encouraged. The hope was that important issues which might otherwise be neglected could be highlighted during such discussions (Fleming, 1992).

The survey was divided into two sections:

- Part I: Assessment – the individual decision maker was required to enter a score [minimum 1 (least preferred) to maximum 10 (most preferred)] rating the performance of each alternative based on values already established for important design, operating and cost or economic evaluation criteria. The decision maker was also asked to indicate the indifference and preference thresholds for each performance criterion. Such threshold values were necessary for application of outranking methods.

- Part II: Ranking – the decision maker must evaluate the relative importance or priority of the criteria. The results were determined from a preference comparison matrix, as shown in Table 4-II. This enables the decision maker to perform a pair-wise comparison between the criteria. For each criterion in the base criteria column, the decision maker was asked to work across each row comparing the base criterion against the comparison criterion listed in the column. For each pair-wise comparison, the decision maker was required to assign a value of 1, 0 or –1. A value of 1 indicates that the decision maker prioritizes the comparison criteria as more important than the base criteria; 0 indicates the individual regard each criterion to be equal; and -1 suggests that the base criterion is more important.

Table 4-II: The preference criteria comparison matrix.

	Comparison Criteria	Processing time	Energy consumption	Labour requirement	Wine loss	Operating costs	Capital costs	Cost savings	Liquid waste volume	Solid waste	Liquid effluent quality
Base Criteria	**Item**	g_1	g_2	g_3	g_4	g_5	g_6	g_7	g_8	g_9	g_{10}
Processing time	g_1	0									
Energy consumption	g_2		0								
Labour requirement	g_3			0							
Wine loss	g_4				0						
Operating costs	g_5					0					
Capital costs	g_6						0				
Cost savings	g_7							0			
Liquid waste volume	g_8								0		
Solid waste	g_9									0	
Liquid effluent quality	g_{10}										0

After the survey forms were collected from each decision makers, the score for each alternatives and weight for each criterion were determined. Basically, the score allocated by a decision maker for each alternative on their performance on each criterion was summed and divided by the total number of decision makers. The average value yielded the preference score. A similar method was used to determine the preference and threshold value for each criterion. The performance of each tartrate stabilisation method against each criterion is summarised in Table 4-III.

In determining the weight of a criterion, the initial assigned value was modified to avoid negative values. Zero value which indicates no significant preference was replaced by 0.5; whilst -1 (indicating the base criterion is more important) was replaced with 0. The value from the same cell on Part II of each of the survey was summed and an average value is determined. The cell on the diagonal opposite to the left of the dashed diagonal line became 1 and was subtracted from the corresponding value to the right of the diagonal. The performance matrix values were summed for each column and a total was obtained. These values were normalised so that the criteria weights sum to 100.

Table 4-III: Summary of the criteria value of alternatives based on retrofit scenario.

				Alternative methods					
Objective	**Criteria**	**Units**	**Target**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
O_1, Technical Performance									
g_1	Processing time	h/275kL$_{wine}$	min	188	52	56	41	48	44
g_2	Energy consumption	kWh/ kL$_{wine}$	min	10.19	10.26	10.16	10.01	6.84	8.03
g_3	Labour requirement	h/275kL$_{wine}$	min	24	30	34	36	40	34
g_4	Wine loss	%	min	0.40	0.76	0.56	0.75	0.72	0.70
O_2, Economical Factors									
g_5	Operating costs	AU¢/ L$_{wine}$	min	4.7	7.7	5.5	6.3	5.9	7.1
g_6	Capital costs	*millions AUD*	min	0	1.28	1.50	1.96	5.45	10.29
g_7	Cost savings								
	By-product recovery	*AUD/ 275kL$_{wine}$*	max	59	470	470	470	235	0
O_3, Environmental effects									
g_8	Liquid wastes	L/ kL$_{wine}$	min	46.2	75.3	73.2	91.1	85.8	215.9
g_9	Solid wastes	kg/ kL$_{wine}$	min	2.42	2.42	2.42	2.42	2.42	2.42
g_{10}	Effluent quality								
	COD	*kg COD/ kL$_{wine}$*	min	1.08	1.82	1.35	1.78	1.70	2.01

4.3 Selection of MCDA Methods

Multi-criteria analysis was employed to convert the decision maker's judgements on the relative importance of a set of evaluation criteria into a universal preference for the alternative scenarios. Several methods for solving such problems were considered and finally, the weighted average method (WAM) and various outranking methods (ELECTRE I, PROMETHEE I and II) were chosen for this study.

For the weighted average method, a simple rating procedure was used to develop multi-attribute utilities for the decision criteria (Eqs. (2-1) and (2-2)). A criterion's weight was deduced from pair-wise comparisons and each alternative was scored on a scale from 1 – 10. Ten represents the most preferred option and 1 represents the least preferred. For a given alternative, the total value was determined by multiplying each criterion's weight by the rating of the alternative's ability to meet the criterion, then summing these over all criteria. The alternative with the highest total utility was selected.

As well, outranking methods were studied simultaneously to determine if their ranking of alternatives differed from those of the weighted average method. This class of methods present results as outranking graphs indicating preferences, indifferences and incomparability. The dominant outranking methods were used in this case study namely ELECTRE I developed by Roy (1991) and PROMETHEE developed by Brans et al. (1986).

ELECTRE I is the simplest method from the ELECTRE group. Concordance and discordance indices were calculated using Eqs. (2-6) and (2-7). The threshold values required were allocated by the decision makers in Part I of the survey form.

The second outranking method was PROMETHEE. As mentioned earlier, the threshold values were defined by the decision makers. The outranking degrees, $\prod$ were used to calculate for each alternative the leaving flow, the entering flow and the net flow using Eqs. (2-9), (2-10) and (2-11), respectively. In PROMETHEE I the alternatives are ranked based on both the leaving and entering flows. In PROMETHEE II a complete ranking was constructed based on the net flow.

4.4 Results and Discussion

4.4.1 Weights and scores

Survey forms were distributed to a range of experts and twelve responses were obtained. The responses were analysed to determine the weight for each criterion and the score of each alternative follow up the procedure described in Section 4.2.4.

The weights for the ten criteria are summarised in Table 4-IV.

Table 4-IV. Ranking of criteria.

Rank	Criteria		Weight
1	Wine loss	g_4	13.1
2	Capital costs	g_6	13.1
3	Effluent quality	g_{10}	12.0
4	Operating costs	g_5	11.2
5	Cost savings	g_7	10.9
6	Liquid waste generated	g_8	10.1
7	Energy consumption	g_2	7.9
8	Labour Requirement	g_3	7.9
9	Operating time	g_1	7.6
10	Solids waste generated	g_9	7.4

Wine loss (g_4) is the key operating cost driver and the dominant contributor to effluent quality. Capital cost (g_6) namely the upfront investment required achieved the highest weighting by decision makers. Effluent quality (g_{10}) was next. This reflects the current awareness of the decision makers when choosing alternative tartrate stabilisation method to minimise adverse environmental effects. Technical criteria such as operating time (g_1), energy consumption (g_2) and labour requirement (g_3) were of lower priority (weights in the range of 7.9 to 7.6) when compared to economic criteria (range - 13.1 to 10.9). According to the respondents, the quantity of solid waste generated (g_9), principally diatomaceous earth from filtration, was assigned the lowest weight.

The average scores for the alternative processing sequences are summarized in Table 4-V. The technology that achieved the highest score for each criterion is highlighted in the table by shading the relevant cell. These scores were used in weighted average method and ELECTRE I to determine the ranking of the alternatives.

Table 4-V. Scores of alternatives.

		Alternative methods					
Criteria		**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
g_1	Operating time	2.7	6.8	6.2	9.4	8.0	8.6
g_2	Energy consumption	4.6	4.1	4.9	5.3	9.7	8.2
g_3	Labour Requirement	9.8	7.2	5.0	4.1	5.0	8.0
g_4	Wine loss	9.5	3.4	7.7	3.9	4.8	5.3
g_5	Operating costs	9.6	3.0	7.7	5.8	6.8	3.8
g_6	Capital costs	10.0	7.4	6.8	5.6	3.1	1.3
g_7	Cost savings	3.8	8.8	8.7	8.3	5.5	1.3
g_8	Liquid waste generated	8.9	6.6	6.3	5.3	5.3	1.2
g_9	Solids waste generated	6.9	6.9	6.9	6.9	6.9	6.9
g_{10}	Effluent quality	9.8	4.1	7.8	4.9	5.6	2.5

4.4.2 Analysis using weighted average method

In this section, the weighted average method was used to select the most preferred alternative. The criterion’s weight, w_j (Table 4-IV) and the score of the alternative’s ability to meet the criterion, r_{ij} (Table 4-V) are both incorporated to determine the overall value of each alternative using Eq. (2-1). The most preferred alternative achieved the highest overall value. The evaluation matrix is presented in Table 4-VI and the final ranking of the alternatives are shown in Table 4-VII.

Table 4-VI. Evaluation matrix of Weight Average Method.

			A1		A2		A3		A4		A5		A6	
	Criteria	**Weight, w_j**	**r_{ij}, (1-10)**	**Combined Rating**	**r_{ij}, (1-10)**	**Combined Rating**	**r_{ij}, (1-10)**	**Combined Rating**	**r_{ij}, (1-10)**	**Combined Rating**	**r_{ij}, (1-10)**	**Combined Rating**	**r_{ij}, (1-10)**	**Combined Rating**
g1	Processing time	6.7	2.7	17.8	6.8	45.0	6.2	41.1	9.4	62.8	8.0	53.3	8.6	57.2
g2	Energy consumption	7.6	4.6	34.7	4.1	30.9	4.9	37.2	5.3	39.8	9.7	73.2	8.2	61.9
g3	Labour requirement	7.9	9.8	76.8	7.2	56.5	5.0	39.4	4.1	32.2	5.0	39.4	8.0	63.0
g4	Wine Loss	13.1	9.5	124.7	3.4	44.9	7.7	100.7	3.9	51.4	4.8	62.4	5.3	68.9
g5	Operating costs	11.2	9.6	107.4	3.0	33.6	7.7	86.0	5.8	65.4	6.8	76.6	3.8	42.0
g6	Capital costs	13.1	10.0	131.3	7.4	97.4	6.8	88.6	5.6	73.3	3.1	40.5	1.3	16.4
g7	Cost savings	10.9	3.8	40.9	8.8	95.5	8.7	94.5	8.3	90.0	5.5	60.0	1.3	13.6
g8	Liquid waste volume	10.1	8.9	90.1	6.6	66.5	6.3	64.0	5.3	53.0	5.3	53.0	1.2	11.8
g9	Solid waste	7.4	6.9	51.0	6.9	51.0	6.9	51.0	6.9	51.0	6.9	51.0	6.9	51.0
g10	Liquid effluent quality	12.0	9.8	118.2	4.1	49.1	7.8	94.2	4.9	59.1	5.6	67.1	2.5	30.1
	Total desirability rating, V_i			**793.0**		**570.3**		**696.7**		**578.0**		**576.6**		**416.0**

Table 4-VII. Rank of alternatives based on weighted average method.

Rank	Alternative	Total value, V_i
1	A1	793.0
2	A3	696.7
3	A4	578.0
4	A5	576.6
5	A2	570.3
6	A6	416.0

In summary, cold stabilisation (A1) achieved the highest overall value. This was closely followed by Westfalia process (A3). Fluidisation (A4) was ranked slightly above nanofiltration (A5). However, the percentage difference in total value between these alternatives was less than 0.5 %. Hence, it is reasonable to conclude that A4 and A5 are equally preferred. The alternative achieving the lowest preference was electrodialysis (A6).

4.4.3 Analysis using ELECTRE I

ELECTRE I involves five basic steps:

1) determine the weight of each criterion;

2) calculate the concordance index using Eq. (2-3);

3) calculate the discordance index with the assigned value of each level for each criterion using Eq. (2-4);

4) define outranking relation based on the defined preference (*p*) and indifference (*q*) threshold values and construct a composite graph; and

5) determine the kernel of the graph.

Each criterion’s weight as assigned by the decision makers is presented in Table 4-IV. The total weights assigned sums to 100.

The concordance index was calculated using Eq. (2-3). The resulting concordance matrix is presented in Table 4-VIII.

Table 4-VIII. The complete concordance matrix.

$C(a_i,a_k)$	A1	A2	A3	A4	A5	A6
A1	-	0.79	0.71	0.71	0.71	0.82
A2	0.21	-	0.37	0.40	0.46	0.50
A3	0.29	0.63	-	0.77	0.78	0.74
A4	0.29	0.60	0.23	-	0.34	0.68
A5	0.29	0.54	0.22	0.66	-	0.69
A6	0.18	0.50	0.26	0.32	0.31	-

To calculate discordance index, each criterion was assigned a maximum scale of 100. The value attributed to each level of a criterion was then calculated based on number of levels of that particular criterion. For instance, processing time (g_1) possessed five levels; hence, each level is worth $\frac{100}{5} = 20$ points. A summary of the point values used for calculating the discordance index is presented in Table 4-IX.

Table 4-IX. Point values used for calculating the discordance matrix.

Criteria		Levels	Value
g_1	Processing time	≤ 45	100
		46 - 50	80
		51 - 55	60
		56 - 60	40
		> 60	20
g_2	Energy consumption	≤ 5.0	100
		5.01 – 6.0	80
		6.01 – 7.0	60
		7.01 – 8.0	40
		> 8.0	20
g_3	Labour requirement	≤ 25	100
		26 - 30	75
		31 - 35	50
		> 35	25
g_4	Wine Loss	≤ 0.5	100
		0.51 - 0.6	75
		0.61 - 0.7	50
		> 0.7	25
g_5	Operating costs	< 5.0	100
		5.1 – 6.0	80
		6.1 – 7.0	60
		7.1 – 8.0	40
		> 8.0	20
g_6	Capital costs	≤ 1.0	100
		1.1 - 1.5	80
		1.6 – 2.0	60
		2.1 - 2.5	40
		> 2.5	20
g_7	Cost savings	> 500	100
		251 - 500	75
		101 - 250	50
		≤ 100	25
g_8	Liquid waste volume	≤ 50	100
		50.1 – 70.0	80
		70.1 – 90.0	60
		90.1 – 110.0	40
		> 110.0	20
g_9	Solid waste	≤ 0.5	100
		0.5 - 1.5	75
		1.5 - 2.5	50
		> 2.5	25
g_{10}	Liquid effluent quality	≤ 1.5	100
		1.51 - 1.75	75
		1.76 – 2.0	50
		> 2.0	25

Next, the discordance index was calculated using Eq. (2-7). The respective discordance indices were combined to generate a discordance matrix as tabulated in Table 4-X.

Table 4-X. The discordance matrix.

$D(a_i,a_k)$	A1	A2	A3	A4	A5	A6
A1	-	0.75	0.75	0.80	0.60	0.80
A2	0.60	-	0.50	0.40	0.40	0.40
A3	0.40	0.20	-	0.60	0.40	0.60
A4	0.75	0.25	0.50	-	0.40	0.25
A5	0.80	0.60	0.60	0.50	-	0.25
A6	0.80	0.75	0.75	0.75	0.50	-

After the concordance and discordance indices were established, the outranking relation was defined and used to form a composite graph. A directed arc connecting a_i to a_k in this composite graph indicates that alternative i is preferred to alternative k provided that $C(a_i, a_k) \geq y$ and $D(a_i,a_k) \leq z$ where y and z represent the respective concordance and discordance threshold values. For simplicity, y and z were set to be 0.50 and 0.25, respectively. The set of indices that satisfied these conditions are: (A3, A2), (A4, A2), (A4, A6) and (A5, A6). The resulting composite graph is presented in Figure 4-1.

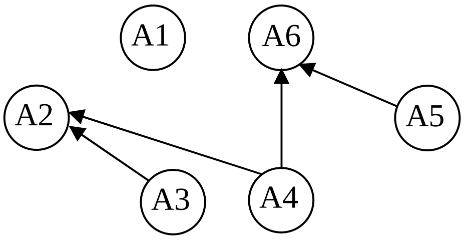


Figure 4-1. The composite graph for $y = 0.5$ and $z = 0.25$.

Finally, the kernel of the graph which contains the nodes corresponding to those alternatives which are preferred on the basis of the outranking relation was determined. This step was essential as those nodes that are not in the kernel will be removed for further consideration.

Figure 4-1 confirms that alternatives A1, A3, A4 and A5 did not dominate each other; alternative A3 dominates alternative A2; alternative A4 dominates alternatives A2 and A6; and alternative A5 dominates alternative 6. Therefore, the kernel was now composed of alternatives A1, A3, A4 and A5. As a result, the decision set could be reduced in size to four options.

4.4.4 Analysis using PROMETHEE

PROMETHEE, the second of the outranking methods, requires the input of weights and the selection of the criteria type for each criterion. Based on chosen criteria type, corresponding indifference and/or preference thresholds were specified. A summary of threshold values for the problem is presented in Table 4-XI.

Using the preference functions suggested by Brans et al. (1986) and the weights shown in Table 4-IV, a preference index may be computed using Eq. (2-8). The outgoing and entering flows (Φ^+ and Φ^-) were determined using Eqs. (2-9) and (2-10), respectively. The calculated preference index and preference flows are presented in Table 4-XII.

Table 4-XI. Types of criteria and the corresponding threshold values.

Criteria		**Type of Criterion**	**Threshold**	
			Indifference, q	**Preference, p**
g_1	Operating time	V	10	25
g_2	Energy consumption	V	2.17	4.28
g_3	Labour Requirement	V	4	9
g_4	Wine loss	IV	0.27	0.46
g_5	Operating costs	IV	0.4	0.8
g_6	Capital costs	V	0.23	0.52
g_7	Cost savings	III	-	65
g_8	Liquid waste generated	II	9.1	-
g_9	Solids waste generated	II	0.92	-
g_{10}	Effluent quality	V	0.21	0.48

Table 4-XII. Preference index.

$\prod(a_i,a_k)$	A1	A2	A3	A4	A5	A6	$\Phi^+(a_i)$
A1	-	0.457	0.349	0.508	0.51	0.528	2.351
A2	0.277	-	0.000	0.159	0.24	0.240	0.917
A3	0.277	0.226	-	0.314	0.36	0.473	1.648
A4	0.277	0.219	0.124	-	0.24	0.362	1.222
A5	0.345	0.283	0.168	0.117	-	0.397	1.310
A6	0.193	0.185	0.180	0.199	0.15	-	0.903
$\Phi^-(a_i)$	1.368	1.371	0.821	1.297	1.494	2.000	

4.4.4.1 PROMETHEE I

This algorithm is designed to provide a partial ranking based on the flows $\Phi^{+}(a_i)$ and $\Phi^{-}(a_i)$. Clearly, cold stabilisation (A1) had the largest outflow. However, its entering flow exceeds that for Westfalia process (A3) and fluidisation (A4). Thus, A1, A3 and A4 were incomparable.

The Westfalia process (A3) has a better outflow than any remaining alternative and outranks the remaining four alternatives. Fluidisation (A4) and nanofiltration (A5) were incomparable as A5 had a better outflow than the remaining three alternatives whereas A4 had a lower entering flow. Both alternatives outrank the two remaining alternatives - seeding (A2) and electrodialysis (A6). Finally, A2 with a larger outflow and entering flow than those for A6 clearly outranked A6.

The partial order determined by PROMETHEE I for the six alternatives is presented in Figure 4-2.

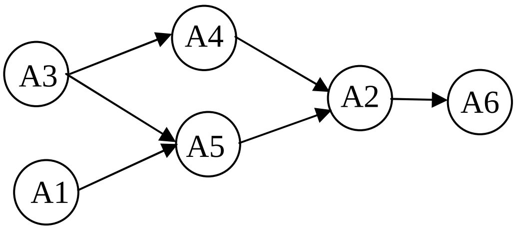


Figure 4-2. Partial ranking of the six alternatives of PROMETHEE I.

4.4.4.2 PROMETHEE II

The complete order deduced by application of PROMETHEE II is based on the net flows calculated using Eq. (2.8). In the case, the ranked order suggested by Table 4-XIII is summarised in Figure 4-3.

Table 4-XIII. Net flows of all alternatives.

	A1	A2	A3	A4	A5	A6
$\Phi(a_i)$	0.98	-0.45	0.83	-0.08	-0.18	-1.10

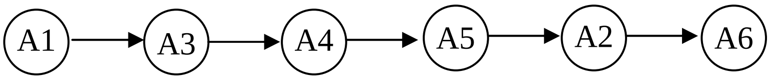


Figure 4-3. Complete ranking of PROMETHEE II.

The ranking shown in Figure 4-3 is identical to the ranking deduced by the weighted average method (Table 4-VII).

4.5 Sensitivity Analysis

The ranking of alternatives is dependent on the various threshold values and indices of importance (Hokkanen and Sakminen, 1997a). Hence, following the completion of the initial solution, a sensitivity analysis was performed. The aim of such an analysis was twofold:

1) to discover how the changes in the weights may influence the ranking of the alternatives; and

2) to determine the effect of changes in the preference and indifference threshold values.

4.5.1 Changes in weights

Since the criteria weights are critical determinants of the final ranking of the alternatives, the stability of the rank order under different weighting schemes must be tested by a sensitivity analysis.

The sensitivity of the selected MCDA methods to changes in weights allocated for each alternative was evaluated. In this case, all criteria were assigned an equal weight of 10.

The new ranking of alternatives obtained from the weighted average method is presented in Table 4-XIV. This ranking is almost identical to the ranking obtained based on the weights assigned by the decision makers. However, one rank reversal occurred and nanofiltration (A5) was ranked above fluidisation (A4).

The effect of changes in weights on the evaluation of concordance and discordance indices for ELECTRE I was undertaken and results are presented in Table 4-XV and Table 4-XVI. It is evident that despite slight changes in the value of the indices, the final kernel of the composite graph with the initial threshold values of $C(a_i, a_k) \geq 0.5$ and $D(a_i,a_k) \leq 0.25$ remains the same. Alternatives A1, A3, A4 and A5 were the four options identified for further consideration.

Table 4-XIV. The changes in the ranking of alternatives determined from weighted average method.

Rank	Alternative	Total value, V_i
1	A1	755.0
2	A3	679.2
3	A5	605.8
4	A4	594.2
5	A2	581.7
6	A6	468.3

Table 4-XV. The concordance matrix of equal criteria weights.

C(a_i,a_k)	A1	A2	A3	A4	A5	A6
A1	-	0.75	0.65	0.65	0.65	0.75
A2	0.25	-	0.40	0.40	0.45	0.45
A3	0.35	0.60	-	0.70	0.70	0.65
A4	0.35	0.60	0.30	-	0.35	0.65
A5	0.35	0.55	0.30	0.65	-	0.65
A6	0.25	0.55	0.35	0.35	0.35	-

Table 4-XVI. The discordance matrix of equal criteria weights.

D(a_i,a_k)	A1	A2	A3	A4	A5	A6
A1	-	0.75	0.75	0.80	0.60	0.80
A2	0.60	-	0.50	0.40	0.40	0.40
A3	0.40	0.20	-	0.60	0.40	0.60
A4	0.75	0.25	0.50	-	0.40	0.25
A5	0.80	0.60	0.60	0.50	-	0.25
A6	0.80	0.75	0.75	0.75	0.50	-

The changes in criteria weights produced no effect on the PROMETHEE I partial order for the six alternatives (as shown in Table 4-XVII). The partial ranking is identical to that shown in Figure 4-2. However, the overall ranking determined from PROMETHEE II which was based on net flows (Φ) did change as illustrated in Table 4-XVII and Figure 4-4. A reversal in ranking between alternatives 1 and 3 and between alternatives A4 and A5 was observed.

Table 4-XVII. Preference flows of all alternatives with equal criteria weights.

	A1	A2	A3	A4	A5	A6
$\Phi^+(a_i)$	2.048	0.835	1.457	1.150	1.338	1.006
$\Phi^-(a_i)$	1.52	1.27	0.85	1.20	1.31	1.69
$\Phi(a_i)$	0.53	-0.43	0.61	-0.05	0.03	-0.68

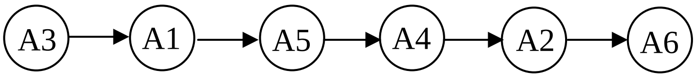


Figure 4-4. The complete ranking of PROMETHEE II with equal criteria weights.

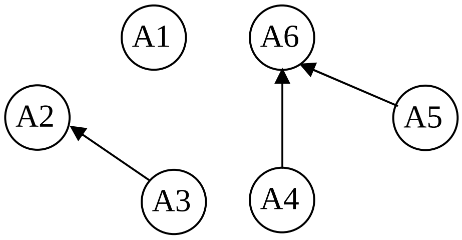
4.5.2 Changes in thresholds

4.5.2.1 Effect on ELECTRE I outcome

The sensitivity of the ELECTRE I solution to changes in the values of y and z was determined. Increments of the concordance requirement with z fixed at 0.25 did not change the solution when y is increased to 0.6. As shown in Figure 4-5 (a), the kernel still consisted of alternatives A1, A3, A4 and A5, however, the outranking relation between alternatives A4 and A2 had vanished. Reduction of the concordance requirement to $y = 0.4$ produced no effect on the alternatives in the kernel or the outranking relation (as shown in Figure 4-5 (b)).

By contrast, changes in the discordance requirement did result in changes in the kernels (Figure 4-5 (c), (d) and (e)). For instance, when z was increased to 0.4, alternatives A1, A3 and A4 no longer dominated each other; alternative A3 dominated alternatives A2 and A5; alternative A4 dominated alternatives A2 and A6; and alternative A5 dominated alternative A6. Hence, the kernel was composed of alternatives A1, A3 and A4. Consequently, only three options required further consideration. However, when z was reduced to 0.2, the ranking relation between alternatives A3 and A2 became the sole outranking relationship. Five options (except alternative A2 - eliminated) remained for further consideration. If the allowable discordance was increased to $z = 0.5$, it can be seen that outranking relations between alternatives A5 and A4 and between alternatives A3 and A5 were introduced. The kernel was now composed of alternative A1 and A3.

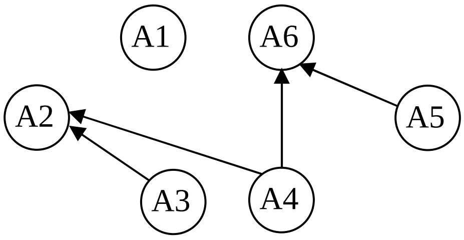
The results of these sensitivity studies confirm that alternatives A1 and A3 were consistently retained in most of the reduced decision sets.



(*y*,z) = (0.6, 0.25)

Kernel = {A1, A3, A4, A5}

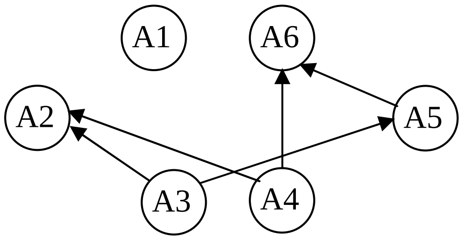
(a)



(*y*,z) = (0.4, 0.25)

Kernel = {1, 3, 4, 5}

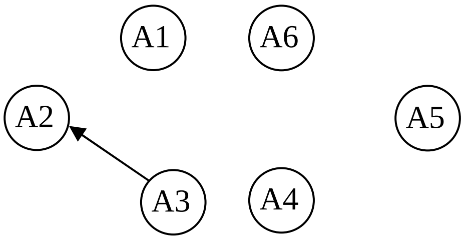
(b)



(*y*,z) = (0.5, 0.4)

Kernel = {A1, A3, A4}

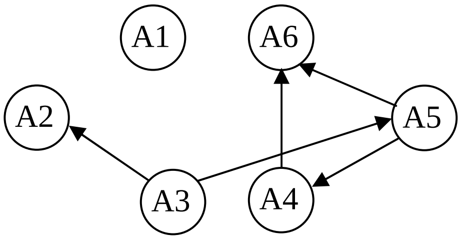
(c)



(*y*,z) = (0.5, 0.2)

Kernel = {A1, A3, A4, A5, A6}

(d)



(*y*,z) = (0.5, 0.5)

Kernel = {A1, A3}

(e)

Figure 4-5. The composite graphs and associated kernels corresponding to various *p* and *q*.

4.5.2.2 Effect on PROMETHEE outcome

According to Lahdelma et al. (2000), the demand for preference information from the decision makers should be minimal because of time and money constraints. Hence, Haralambopoulos and Polatidis (2003) proposed an alternative method for determining the preference threshold, p using Eq. (4-1).

$$p = {}^{1}\!/_{n}\left(V_i\big|_{max} - V_i\big|_{min}\right)$$

(4-1)

where $V_i|_{max}$ and $V_i|_{min}$ are the maximum and minimum performance values for each criterion, a_i; and n is the total number of alternatives. For simplicity reasons, these authors suggested the indifference threshold to be set to zero for all cases. A summary of the threshold values obtained by applying Eq. (4-1) is tabulated in Table 4-XVIII.

Compared to the threshold values obtained from the survey, the calculated threshold values were significantly higher for certain criteria, including processing time (g_1), capital costs (g_6) and liquid waste generated (g_8). The effects of changes in the threshold values on the PROMETHEE solutions are summarized in Table 4-XIX.

Referring to Table 4-XIX, the changes in preference and indifference values did not affect the partial ranking of the alternatives. However, the changes in threshold values did affect the overall ranking of PROMETHEE II. Rank reversal between alternatives A4 and A5 was observed. Alternative A1 retains at the highest rank followed by alternative 3.

Table 4-XVIII. New threshold values based on Haralambopoulos and Polatidis (2003) proposed equation.

Criteria		Type of Criterion	Threshold	
			Indifference, q	**Preference, p**
g_1	Operating time	V	25	0
g_2	Energy consumption	V	0.69	0
g_3	Labour Requirement	V	2	0
g_4	Wine loss	IV	0.06	0
g_5	Operating costs	IV	0.5	0
g_6	Capital costs	V	1.72	0
g_7	Cost savings	III	-	0
g_8	Liquid waste generated	II	28.3	0
g_9	Solids waste generated	II	0.00	0
g_{10}	Effluent quality	V	0.16	0

Table 4-XIX. The preference flows of PROMETHEE with changes in threshold values.

	A1	A2	A3	A4	A5	A6
$\Phi^+(a_i)$	2.909	1.295	2.284	1.664	1.896	1.630
$\Phi^-(a_i)$	1.45	2.27	1.41	1.84	2.06	2.65
$\Phi(a_i)$	1.46	-0.97	0.87	-0.18	-0.16	-1.02

4.6 Conclusions

In this study, the application of MCDA as a useful tool for the selection of alternative tartrate stabilisation method(s) for the Australian wine industry was successfully demonstrated. There were no substantial differences between the solutions derived from the weighted average method, ELECTRE I and PROMETHEE I and II methods. If a single method is to be recommended for further implementation, PROMETHEE I is strongly recommended. This method accounts for threshold values and allows the decision makers to assign criteria type for more precise evaluation. PROMETHEE I provides partial ranking which means that incomparability between any alternatives is revealed. As suggested by Salminen et al. (1998), more than one MCDA method should be used if time and resources permit. If all methods provide identical results, then the analyst and decision makers may be very confident of the choice. In the case where the results differ, the decision makers are encouraged to choose between the two most competitive alternatives.

All of the selected MCDA methods confirm that the current method – cold stabilisation remains the best practice for large winery like Berri Estates. However, the results also suggest that the Westfalia process (A3), nanofiltration (A5) and fluidisation (A4) merit further consideration. These findings have been presented to Hardy Wine Company and extensively discussed to decide which alternative should be selected for further evaluation. Clearly, the Westfalia process and fluidisation are attractive alternatives. However, a concern on the potential risk of contamination with the reuse of seeds subsequently eliminated these alternatives as feasible options. As well, the Westfalia process is a fully developed industrial-scale process with little potential for improvement at this stage. Nanofiltration with potential for other applications in wine industry seemed a logical focus to achieve improved performance in tartrate removal provided that fundamental technical knowledge for industrial design and operation of the process could be obtained. Unfortunately, there is limited reliable data currently available regarding the technical feasibility and operation of nanofiltration for tartrate stabilisation. Hence, it was agreed that this would be the objective of further research, in particular to investigate the relationship between feed pressure, recovery and crystallisation rates for different commercial nanofiltration membranes. This investigation was conducted in two phases, initially as a laboratory study, then by field test at a winery. Both of these phases are separately described in the following chapters.

CHAPTER 5 BENCH SCALE EXPERIMENTAL STUDY: NANOFILTRATION

5.1 Introduction

As noted in Section 2.1, the most recent pilot-scale study on the use of membranes to stabilize tartrate in wine was performed by Mannapperuma (2001). In this case study, nanofiltration (NF) was employed to concentrate the wine and the crystals formed in NF retentate were then removed by microfiltration (MF). Permeates from NF and MF were blended to reconstitute wine. However, the NF system was operated at an elevated pressure of 62 bar, typical of a reverse osmosis system. KHT crystals were observed and reported at recovery rates exceeding 40 %. However, at such a high operating pressure there would be negligible energy savings compared with cold stabilisation. Usually, NF systems operate at much lower pressures (approximately 10 - 15 bar). Under these conditions, energy savings could be significant and make the process an attractive and cost effective alternative. To achieve low pressures, the NF membrane must be permeable to ethanol and water but still retain tartrate salts so they can be concentrated to induce crystallisation, and hence, achieve removal to stabilise the wine.

The molecular weights of potassium, tartaric acid and KHT are 39, 150 and 188 Daltons (Da), respectively. Consequently the ideal NF membrane should possess a nominal molecular weight cut-off (MWCO) less than 500 Da. Such NF membranes exist and are already widely used for desalination and/or softening of water. According to Domnick Hunter representatives, these NF membranes should be able to remove tartrate salts from the wine. However, no permeability data for ethanol with these membranes is available.

Hence, the aims of this work were to:

1. use current industrial NF membranes to evaluate feasibility of NF operating at modest pressure as a potential tartrate stabilisation method;
2. select the optimal membrane based on consideration of flux, KHT crystallization rate and overall rejection rate; and
3. study the need of addition of KHT crystal seeds into NF retentate to enhance crystallisation.

A custom-built laboratory NF stirred cell was employed for conducting this work.

5.2 Materials and Methods

The experimental protocol involved in this study is summarized and presented in Figure 5-1. In essence, new membranes were cleaned and stored ready for evaluation. The performance of different membranes was initially investigated with an unstable *Semillon* wine. Tests with *Colombard* and *Shiraz* wines were subsequently conducted to evaluate membrane performance for achieving tartrate stability with and without seeding.

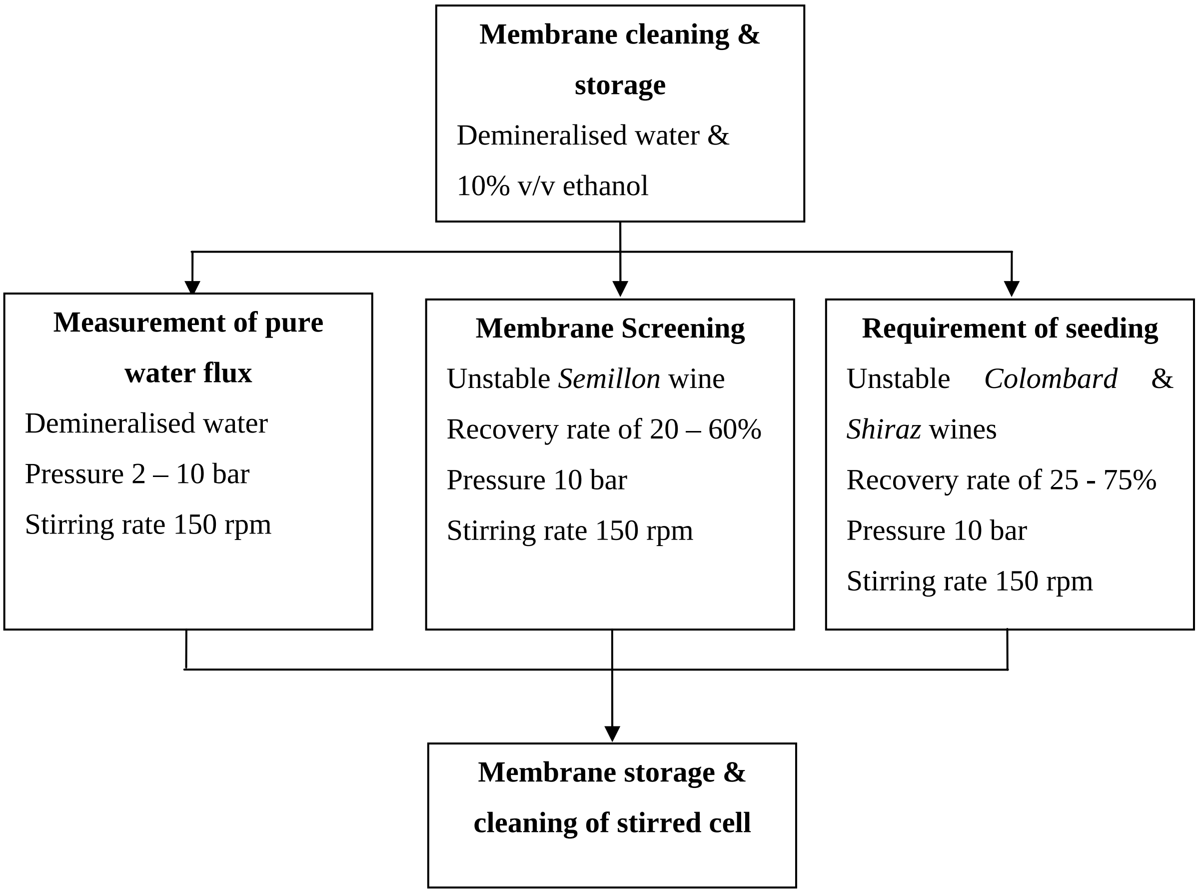


Figure 5-1. NF experimental protocol.

5.2.1 Lab-scale NF stirred cell

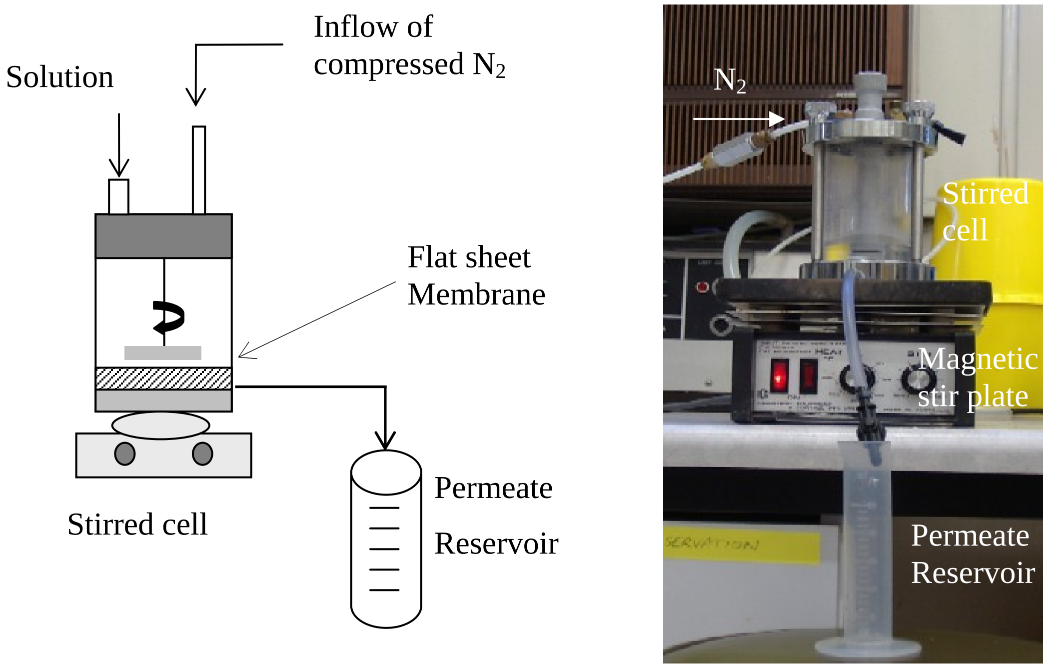
The maximum operating pressure of commercial stirred cells currently available including those from PALL and MILLIPORE is approximately 7 bar. However, a higher operating pressure was required for this work in order to achieve higher output.

As a consequence, a custom-built cell was designed and constructed which could safely operate at up to 20 bar. Table 5-I shows the specifications of the stirred cell custom built by the Chemical Engineering Workshop, The University of Adelaide. Drawings showing dimensions of different part of the stirred cell are presented in Appendix C. Figure 5-2 shows a photo and schematic of the stirred cell as was set up for testing in this study.

The maximum capacity of the cell was 300 mL. The cell was pressurized using compressed nitrogen gas. A circular flat sheet membrane with an effective membrane area of 38.5 cm^2 was employed. The filtration study was conducted in a constant temperature (15 ± 0.5 ^oC) room. Magnetic stirring at 150 rpm was employed to minimize concentration polarization.

Table 5-I. Specifications of the custom-built stirred cell.

Description	**Material**
Top and bottom plate	PTFE-coated stainless steel
Cylinder	Borosilicate glass
Stirring bar	PTFE
O-ring	Fluorocarbon
Pressure tube	Polyethylene
Permeate tube	Silicone rubber
Membrane support disc	Porous polypropylene



(a) (b)

Figure 5-2. Stirred cell pressurised by nitrogen gas: (a) schematic and (b) photograph.

5.2.2 Preparation of wine samples

Tartrate unstable wines from Berri Estates Winery were used in this study. The wines included a *Semillon*, *Colombard* and *Shiraz*. *Semillon* wine was used for membrane screening study whilst *Colombard* and *Shiraz* were used for subsequently investigating the effect of KHT seed addition.

The wines were pre-clarified by centrifugation at 3000 rpm for 10 min, then filtered through PALL 0.45 µm, 47mm GN-6 Metricel Grid sterile membrane filter (Pall Co., Michigan, USA). The analyses of key variables (including content of potassium, calcium and tartaric acid, alcohol level and tartrate instability) for the wines used in this study were performed by Berri Estates Winery using standard methods. Table 5-II summarises values for key wine properties in each case.

Table 5-II. Physical and chemical properties of tartrate unstable *Semillon*, *Colombard* and *Shiraz* used in this study.

Property		***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	0.07	0.04	0.07
Tartaric acid	g/L	2.560	2.601	2.550
Tartrate stability test*		SD^	HD#	SD^

*: Refer to Section 5.4.5

^: Slight deposits observed

#: Heavy deposits observed

5.3 Selection of Membranes

Two different NF membranes – Filmtec *NF70* (supplied by Filmtec, Michigan, USA) and Desal *DK* (supplied by Osmonics, California, USA) were used by Mannapperuma (2001) in his pilot scale tartrate stabilisation study. In this study, four membranes including Filmtec *NF70* (now known as Filmtec *NF*) were used. The relevant properties, as provided by Filmtec and Domnick Hunter (California, USA) of the four membranes are summarized in Table 5-III.

All new membranes were cut into circles of 72 mm in diameter. Before use, the membrane was placed in a stirred cell and 250 mL of demineralised water was filtered through at constant pressure of 10 bar. This step was essential to compress the membrane as well as to rinse off any remaining protective materials (Grandison et al., 2002). Following each experimental run, the membrane was stored in 10 %v/v ethanol solution to prevent any microbial growth.

Table 5-III. Description of membranes used (supplied by Filmtec and Domnick Hunter).

Membrane (Supplier)	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%

5.3.1 Screening study: Investigation of membrane performance with Semillon wine

The following studies were performed using each membrane.

The water fluxes were measured over a pressure range of 2 to 10 bar to check if any damage or fouling had occurred.

Subsequently, the *Semillon* wine was filtered through the membrane at a constant applied pressure of 10 bar to determine the tartrate, K^+ and Ca^{2+} ions' and ethanol permeability, and the flux at various recovery rates (20 to 60%). [Recovery rate, r was defined as the ratio of permeate produced to feed wine expressed as a percentage (Eq. (2-26)). The volumetric flux of permeate, J_V (L/m^2/h) was calculated using Eq. (2-24). Membrane permeability of rejection rate for each species, R_i was calculated using Eq. (2-25).] Ethanol concentration in permeate and retentate were measured by refractive index (RI). The K^+ and Ca^{2+} ion concentrations were quantified using an atomic absorption spectrophotometer. The tartrate ion concentration was determined by measurement of tartaric acid using High Performance Liquid Chromatography (HPLC). All analyses were performed in duplicate.

At the conclusion of each run using the wine, the water permeate flux was measured (at 10 bar) to determine if fouling had occurred.

5.3.2 Evaluation of tartrate stability and seeding requirement

The initial conductivities of *Colombard* and *Shiraz* wines were measured prior to 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 placed on a stirrer plate. Gentle stirring was commenced immediately and conductivity changes were recorded after 10 seconds. As noted in Chapter 2, measurement of conductivity can be used to monitor KHT precipitation rate. Therefore, conductivity was continually recorded at one minute intervals during the most rapid crystallization period, and subsequently at gradually longer intervals until equilibrium was reached (up to 2 hours). A small amount of retentate was filtered through PALL 0.45 μm, 25mm Acrodisc syringe filter (Part no. 4614, Pall Co., Michigan, USA) and then blended with permeate to make up 20 mL of reconstituted wine. 500 mg/L of commercial KHT powder (Australian Tartaric Product, Victoria, Australia) was added to the remaining unfiltered retentate. Conductivity changes for the unfiltered retentate were recorded. Once the conductivity approached equilibrium, the retentate was filtered and blended with permeate to make up 250 mL of reconstituted wine. The remaining permeate and retentate were set aside for other analyses. The reconstituted wine’s conductivity was recorded and compared to the initial (raw wine) value. Tartrate stability of the reconstituted wine was checked by a stability test. All experiments were duplicated.

5.4 Analytical Methods

5.4.1 Metal ions

The K^+ and Ca^{2+} ion concentrations were measured by flame photometry using a Varian SpectrAA-100 atomic absorption spectrophotometer (Varian, Inc., California, USA) in the 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 7.8mm was employed. The column was equilibrated in 0.005 M sulfuric acid and held at 60^{o}C. 10 μL of sample was injected. The flow rate of the eluent was 0.6 mL/min and peaks were detected at 210 nm. H_2T concentration was quantified by comparing the measured peak areas with H_2T standards (i.e. 0.5, 2.0, 5.0 and 10.0 g/L H_2T).

5.4.3 Ethanol

Ethanol concentration was measured using two different instruments: 1) ATAGO DR-A1 Digital Abbe Refractometer (ATAGO Co., Ltd., Tokyo, Japan); and 2) Anton Paar's Alcolyzer Wine (Anton Paar Gmbh, Graz, Austria).

The refractive index, RI (nD) was measured at 20^{o}C (with an accuracy of ± 0.0002 nD). The ethanol concentration was inferred from RI values using refractometer.

The Anton Paar Alcolyzer Wine was employed to verify the accuracy of RI measurements. This instrument measures the amount of light absorbed by the sample across the NIR spectrum at 920 nm in a 30 mm cell. The ethanol concentration was inferred from these absorbance measurements by comparison with known standards. The accuracy of measurement was ± 0.1% v/v ethanol (Anton Paar Alcolyzer Wine, 2007).

5.4.4 pH and conductivity

pH and conductivity were determined with a TPS pH/conductivity meter WP-81 (T.P.S Pty Ltd, Brisbane, Australia). WP-81 was calibrated with pH buffers of 4.0 and 6.88 (T.P.S. Pty Ltd, Brisbane, Australia) and a conductivity standard of 2.76 mS/cm (T.P.S. Pty Ltd, Brisbane, Australia) before each run.

5.4.5 Tartrate stability test

Approximately 100 mL of the reconstituted wine was filtered through 0.45 μm membrane, and placed in 200 mL medical flat glass bottle. The sample was then placed in a refrigerator at -3^{o}C for 72 hours. After the incubation period, the sample was checked while still cold for the presence of crystals. The sample was then allowed to warm to 20^{o}C. If crystals were still present, the sample was considered unstable (Cold Stabilities Wine Instruction, 2004).

5.5 Results and Discussion

5.5.1 Membrane characteristics

5.5.1.1 Fluxes and ethanol permeability

All membranes produced a linear relationship between the water flux and the applied pressure (Figure 5-3). The order in the magnitude of fluxes was:

NF270 > NFA > NF > ATF

This sequence correlates with the MWCO of the membranes. This would be expected as a higher MWCO usually means that pore size of a NF membrane will be larger and thus the permeate flux should be greater.

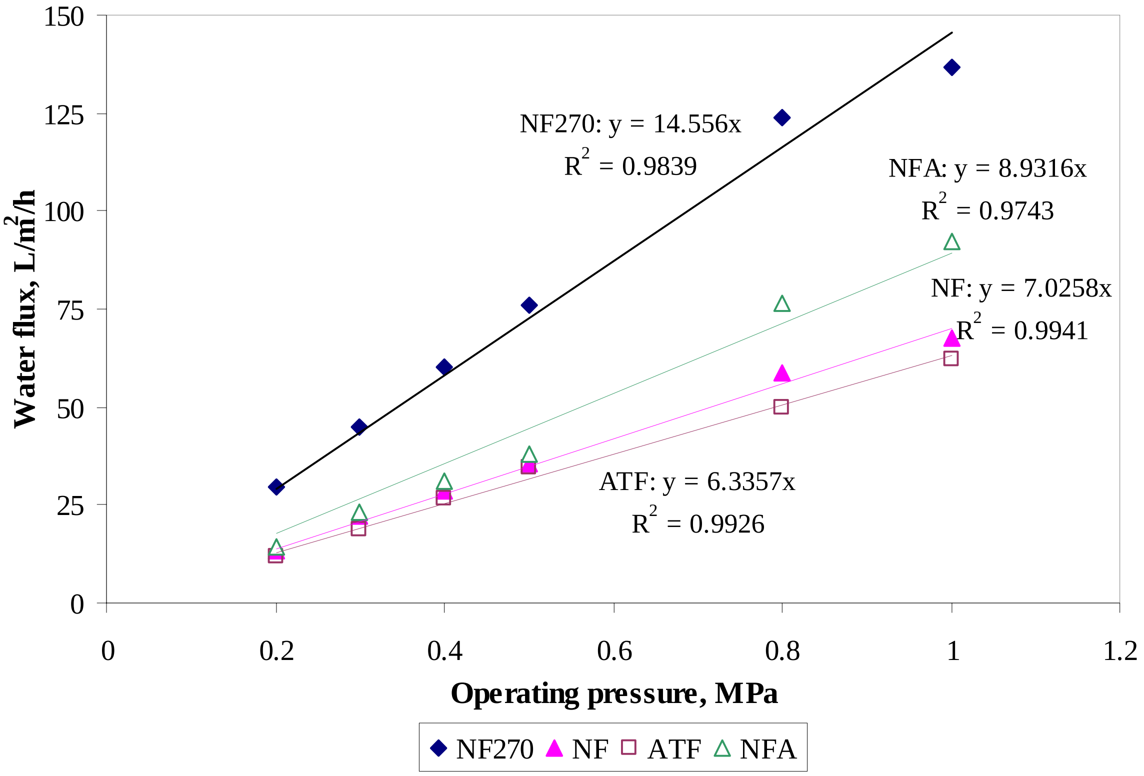


Figure 5-3. Water fluxes of four different membranes at various applied pressure.

The *Semillon*'s permeate flux rates recorded at different recovery rates (at 10 bar feed pressure) are presented in Figure 5-4. The magnitudes of the wine's fluxes are approximately one tenth of water fluxes at the same operating pressure. Figure 5-4 shows that permeate flux decreased as the recovery rate increased. This trend is consistent with the findings by Gonçalves et al. (2001). These authors conducted a study on white wine clarification by micro and ultrafiltration. They observed that permeation flux declined as the concentration factor rose. Furthermore, they attributed the reduction in permeate flux to increasing osmotic pressure differences between the retentate and permeate as the recovery rate was increased, thus reducing the driving force for permeate flow through the membrane.

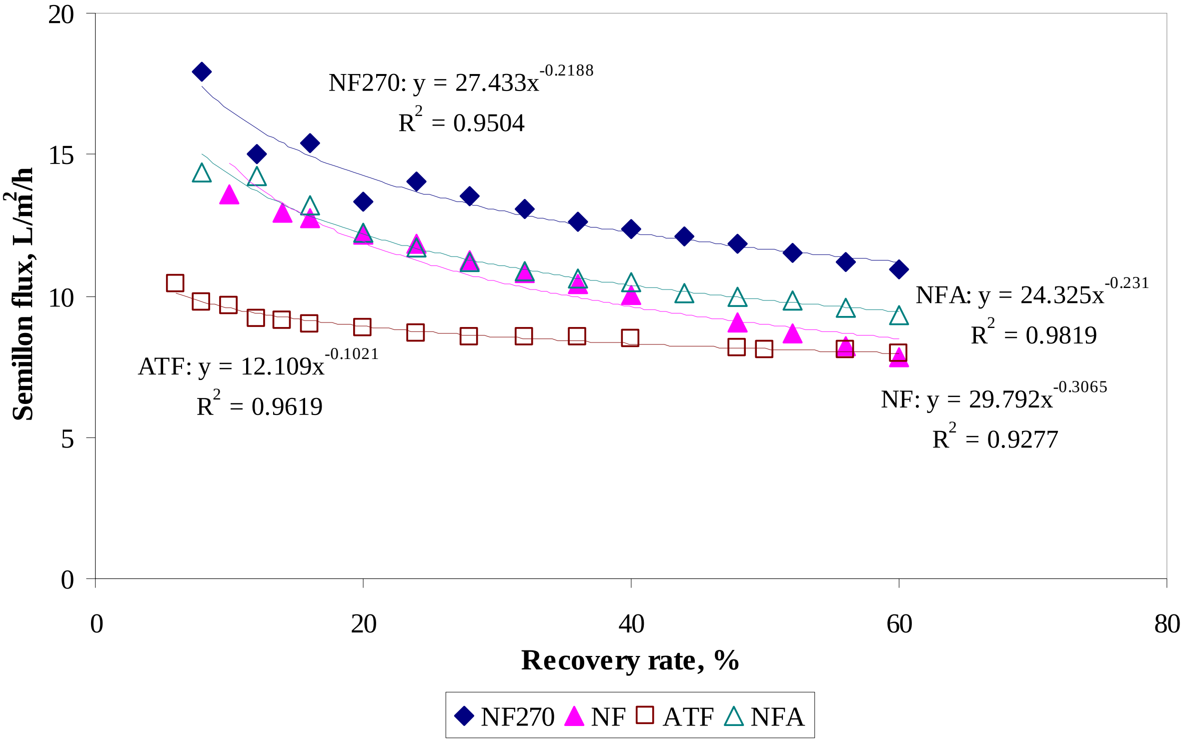


Figure 5-4. Fluxes of *Semillon* wine at different recovery rates.

For the purposes of illustration, the extent by which osmotic pressure may increase during NF of a wine can be estimated as follows. To quantify osmotic pressure differences between feed (retentate) and permeate solutions induced by each component in wine, $\Delta\pi_i$, the following equation (Geankoplis, 2005) may be used.

$$\Delta\pi_i = \Delta C_i \; RT \qquad \textbf{(5-1)}$$

where $\Delta\pi_i$ is osmotic pressure differences between retentate and permeate of *i* component in wine (kPa), ΔC_i is the concentration of *i* component differences between retentate ($C_{r,i}$) and permeate ($C_{p,i}$) (mol/L), *R* is the ideal gas constant (8.314 kPa.L/mol/K) and *T* is the absolute temperature (K). Using Eq. (5-1), the osmotic pressure differences induced by potassium ion at recovery rates of 20 and 50 % of *NFA* membrane at 15 ^{o}C are compared and summarised in Table 5-IV. Table 5-IV showed osmotic pressure induced by potassium ion increased by approximately 8 kPa (0.08 bar) as the recovery rate rises from 20 to 50 %.

Table 5-IV. Osmotic pressure differences induced by potassium ion at 20 and 50 % recovery rate of *NFA* membrane.

Recovery rate, %	**[K$^+$], mol/L** **C_r**	**C_p**	**ΔC**	**$\Delta\pi$, kPa**
20	0.021	0.006	0.015	35.24
50	0.028	0.010	0.018	43.65

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 from alcolyzer (% v/v ethanol) and refractometer (nD) are presented in Table 5-V (a) and (b). In Table 5-V (a), ethanol content determined by alcolyzer indicated a slight decrease in retentate with maximum reduction of 0.5 % v/v. Reduction in ethanol content may have arose from the long experimental period during which evaporation of ethanol to atmosphere may have occurred. According to the RI versus ethanol content calibration curve presented in Figure D-1 (b) in Appendix D, a reduction of 0.5% v/v ethanol should have produced a 0.0002 nD reduction in R.I value. However, Table 5-V (b) shows only a slight increment in RI was observed as the recovery rate increased. This is explicable as RI does not solely measure of ethanol content but also the other soluble solids in wine (e.g. sugar) (Zoecklein et al., 1995). The greater the concentration of soluble solids in the solution, the more the light passing through the solution is refracted. In this work, the soluble solids were concentrated during the filtration process and hence could have produced the higher R.I readings.

Therefore, on the basis of alcolyzer measurements, it is reasonable to conclude that all membranes tested possessed high levels of ethanol permeability such that the rejection rate was negligible.

Table 5-V. Comparison of ethanol content between NF retentate and initial *Semillon* feed using (a) values from alcolyzer (% v/v); and (b) refractive index value (nD) from refractometer.

(a) Percent ethanol by volume as determined by 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) as determined by refractometer (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

5.5.1.2 Ion rejection characteristics

The rejection characteristics of tested membranes using tartrate unstable *Semillon* wine are summarised in Figure 5-5. At pH 3 to 4, 50 - 70 % of tartaric acid exists as bitartrate ion and 2 – 7 % exists as tartrate ion (Boulton et al., 1996). Hence, the overall rejections of tartrate and bitartrate ions are expressed as rejection of tartaric acid in this work. All membranes showed highest rejection of the calcium ions (98 - 99%), followed by tartaric acid (75 - 81 %) with lowest rejection of the potassium ion (62 - 70 %). This excellent rejection of the dissociated tartaric acid and calcium ions was expected as NF membranes have high selectivity for the charge of the dissolved components. The membranes normally retain divalent and multivalent ions whilst passing monovalent ions.

Overall, the *NF* membrane provided the highest rejection of tartaric acid, followed by the *ATF* membrane. The *NFA* membrane had a better tartaric acid rejection rate compared to the *NF270* membrane.

For potassium ion rejection, the *NF* membrane performed the best followed by the *ATF* membrane. The *NFA* membrane produced the lowest rejection for the potassium ion.

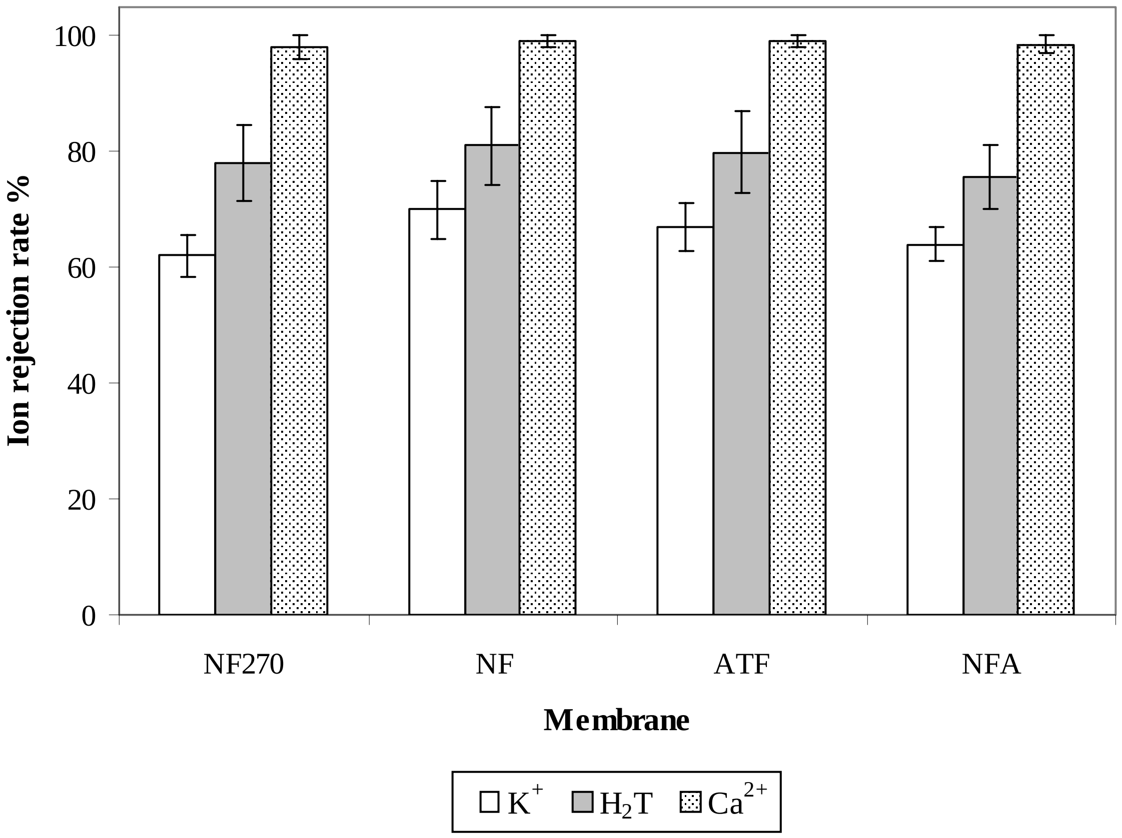


Figure 5-5. Ion rejection characteristics of four different membranes (standard deviation of each measurement is expressed as error bar).

5.5.2 Tartrate stability and requirement of seeding

The results of tartrate stability of the reconstituted wine from different recovery rates (25, 50 and 75%) using the tartrate unstable *Colombard* and *Shiraz* are summarised in Table 5-VI (a) and (b). All the reconstituted wines were stable following treatment by NF except for the *Colombard* wine treated by *NF270* and *NFA* at 25% recovery rate without seeding. This suggests that both wines could be tartrate stabilised by NF without seeding at a recovery rate of at least 50 %. Furthermore, the results suggests, in the case of the *Colombard* wine that seeding can reduce the recovery rate necessary for tartrate stability to be achieved.

The effectiveness of NF in stabilising the wine can be explained by analysis of the degree of supersaturation that each wine would have experienced as it was concentrated by the process. Table 5-VII (a) and (b) shows the estimated degree of supersaturation, S (Eq. (2-13)) of the NF retentate of *Colombard* and *Shiraz* attained at a series of recovery rates (25, 50 and 75 %) with and without seeding. The method of calculations used for estimating S is presented in Appendix E. In brief, Eq. (2-13) and Eq. (2-23) were used. The ion rejection rates of each membrane (shown in Figure 5-5) were used to estimate the ions' concentrations in the retentate in order to calculate the value of concentration product (*CP*).

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

NF > ATF > NFA > NF270

By adding 0.5 g/L of KHT crystal seeds, the degree of supersaturation of both *Colombard* and *Shiraz* is actually 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. Referring to Eq. (2-13) and Eq. (2-23), such increment contributed to the rise in the *CP* value and subsequently increased value of S.

Table 5-VI. Tartrate stability of the reconstituted wine: (a) *Colombard* and (b) *Shiraz*.

(a) Colombard

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

(b) Shiraz

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

✓: No crystals visible during the -3°C/3days test – wine was stable

✗: Crystals formed during the -3°C/3days test – wine was unstable

Table 5-VII. Estimated degree of supersaturation of the retentate obtained at different recovery rate: (a) *Colombard* and (b) *Shiraz*.

(a) Colombard

	Degree of Supersaturation at 15°C, *S*						
	Without seeding				Seeding		
	Recovery rate %				Recovery rate %		
Membrane	**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

	Degree of Supersaturation at 15°C, *S*						
	Without seeding				Seeding		
	Recovery rate %				Recovery rate %		
Membrane	**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

According to Rhein and Neradt (1979) and Gerbaud et al. (1996a), spontaneous crystallisation occurred in highly supersaturated wine with the relative KHT supersaturation level greater than 3. In this study, all the retentate obtained from 50 and 75 % recovery rates should exceed the degree of supersaturation of 3. Hence, spontaneous crystallisation should have occurred under these conditions. The results in Table 5-VII show that this must have been achieved. As tartrate stability was also achieved at 25 % recovery in some cases, this suggests that these conditions also favoured some form of nucleation. According to Gerbaud et al. (1996a), the lower the degree of supersaturation the longer the KHT induction time will be. Hence, even though in some cases where degree of supersaturation is less than 3, nucleation may still occur but very slowly and given the time of experiment (i.e. an average of 1 to 4 hours to achieve 25% recovery; more than 4 hours to achieve 50% recovery; and more than 8 hours to achieve 75% recovery) this may explain why stability was achieved.

Therefore, it is difficult to accurately extrapolate the requirement for recovery rate and holding time of an industrial scale NF process implementation from this experimental data. This information would ideally be obtained from field test at likely production scale conditions to determine the optimum operating conditions.

Nucleation rate, J is dependent on degree of saturation as shown in Eq. (2-14). The effect of changes in degree of saturation on nucleation rate was calculated where K_J and B in Eq. (2-14) were assumed to be constant. Eq. (2-14) is simplified as:

$$J = \frac{S}{-(ln\,S)^2} \qquad \textbf{(5-2)}$$

Figure 5-6 presents the normalised changes of nucleation rate dependent on S, $\frac{J(S)-J(S_0)}{J(S_0)}$ as the degree of saturation in *Colombard* and *Shiraz* increased. The initial degree of saturation of *Shiraz* (S_0 = 3.37) was higher than *Colombard* (S_0 = 2.39). It is therefore expected that with the same increment in degree of saturation, *Colombard* has significantly higher nucleation rate changes (at least 2.5 times more) compared to *Shiraz*.

Real time measurement of conductivity changes during filtration was impossible as the membrane stirred cell was pressurised at 10 bar and hence, a conductivity probe was not able to be placed in the cell. Consequently, the crystallisation kinetics cannot be estimated from this data.

Percent conductivity changes at steady state of the reconstituted wines (with and without seeding) relative to the initial untreated wine are tabulated in Table 5-VIII (a) and (b). The magnitude of the conductivity changes for both *Colombard* and *Shiraz* was:

NF > ATF > NFA > NF270

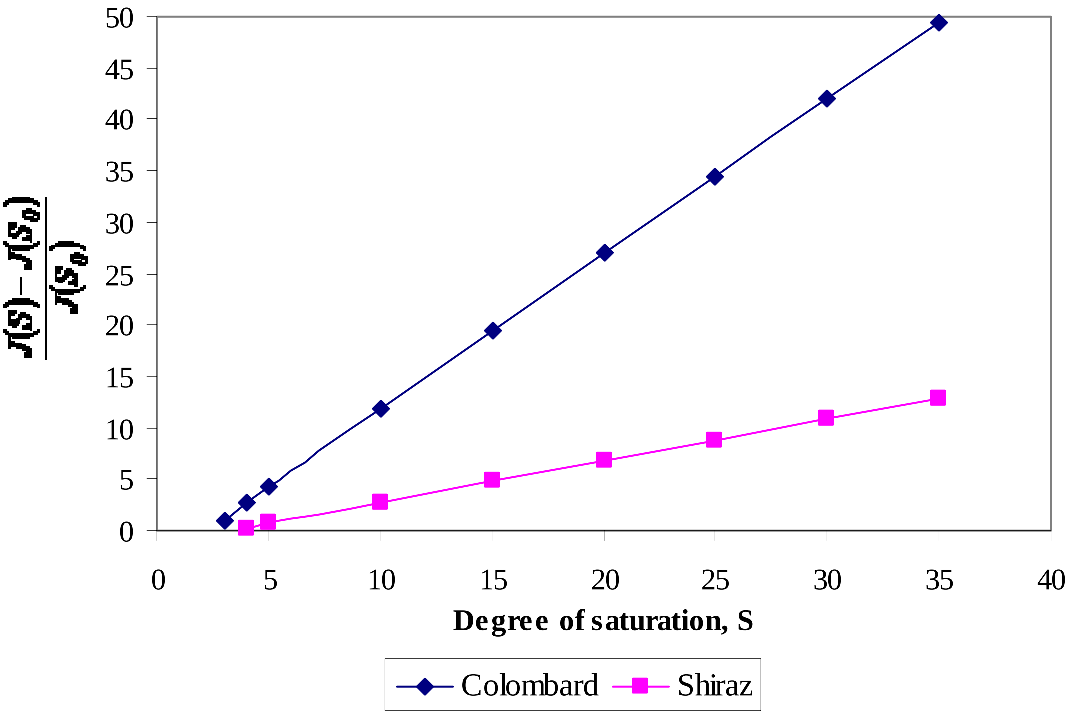


Figure 5-6. Dependence of nucleation rate on the degree of saturation in nucleation of KHT crystals in *Colombard* and *Shiraz* at 15°C.

This result corresponds with the estimated degree of supersaturation. Rapid crystallisation is expected at higher recovery rate with higher degree of saturation. Greatest conductivity reduction was measured for both *Colombard* and *Shiraz* filtered through the *NF* membrane and reconstituted at recovery rate of 75% without addition of KHT seed.

In Table 5-VIII, conductivity changes in the reconstituted wine with seeding were noticeable slightly less than the reconstituted wine without seeding. This suggested possible dissolution of KHT seeds in retentate occurred. Rodriguez-Clemente et al. (1990) who proposed tartrate stabilisation method by passing wine through an adsorption column filled with KHT seeds before chilling the wine in order to extract any inhibitor component before precipitation process has raised the concern on possible dissolution of KHT crystals and suggested such excess dissolved will be removed during the chilling process. Hence, addition of 0.5 g/L KHT seeds to retentate before reconstituting the wine might increase the risk of wine tartrate instability.

Table 5-VIII. 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 Recovery rate %			Seeding 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 Recovery rate %			Seeding 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

Overall, *Colombard* had greater conductivity reduction compared to *Shiraz* for all cases. A possible explanation for such differences was the presence of higher proportion of colloidal and organic compounds in red wine compared to white wine which might inhibit KHT nucleation and/or crystallisation (Vernhet et al., 1999b; Gerbaud et al., 1996a; Tanahashi et al, 1992).

5.6 Conclusions

A dead-end membrane stirred cell was custom-built to withstand internal pressures of up to 20 bar. This stirred cell was used to investigate the feasibility of using NF to stabilise wine.

The permeate fluxes, ethanol permeability and rejection characteristics of four commercial NF membranes were studied using tartrate unstable *Semillon* wine. The *ATF* (Domnick Hunter) and *NF* (Filmtec) membranes provided good rejection characteristics. However, low permeate fluxes ca. 10 L/m^2/h were achieved at the test pressure of 10 bar.

Evaluation of tartrate stability and the need for addition of crystal seeds was undertaken using tartrate unstable *Colombard* and *Shiraz* wines. The same membranes were employed. For all membrane types, both wines treated passed the tartrate stability test at recoveries of 50 to 75 % or supersaturation levels of greater than 3. Crystal seeding at 0.5 g/L did not appear to significantly influence the recovery required or time to achieve tartrate stability.

Therefore, it was successfully demonstrated that NF could be used to tartrate stabilise a wine.

In these laboratory studies, the nature of the experiment arrangement involved a long processing period for concentration of the wine. It was not possible to accurately observe crystallisation kinetics.

In the following chapter, results and analysis from field testing of NF is presented. The field tests were performed at Berri Estates Winery using the existing membrane system on-site. The field testing included simulation of industrial scale conditions to confirm the technical feasibility of NF for tartrate stabilising wines; and chemical and sensory analysis to compare NF stabilised wines with those achieve by cold stabilisation.

CHAPTER 6   FIELD TRIALS: NANOFILTRATION

6.1 Introduction

In the preceding chapter, tartrate unstable wines were treated using a laboratory dead-end nanofiltration (NF) stirred cell. This study demonstrated that NF was feasible for tartrate stabilisation of wine.

This chapter documents and presents the results of field tests to investigate application of NF for tartrate stabilisation at Berri Estates Winery under production-scale conditions. The field tests were conducted on tartrate unstable *Colombard* and *Shiraz* wines using an existing NF system at the winery. The principal goals of the tests were to:

1. confirm the feasibility of NF for tartrate stabilisation of wine (without chilling);
2. further investigate and evaluate seeding requirements following NF concentration of wine;
3. establish whether there was any significant difference in the chemical or sensory properties NF stabilised wine and wine stabilised by cold stabilisation (the existing process at the winery); and
4. determine whether there is a need to refine previous economic evaluation of NF 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 and 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 NF 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.

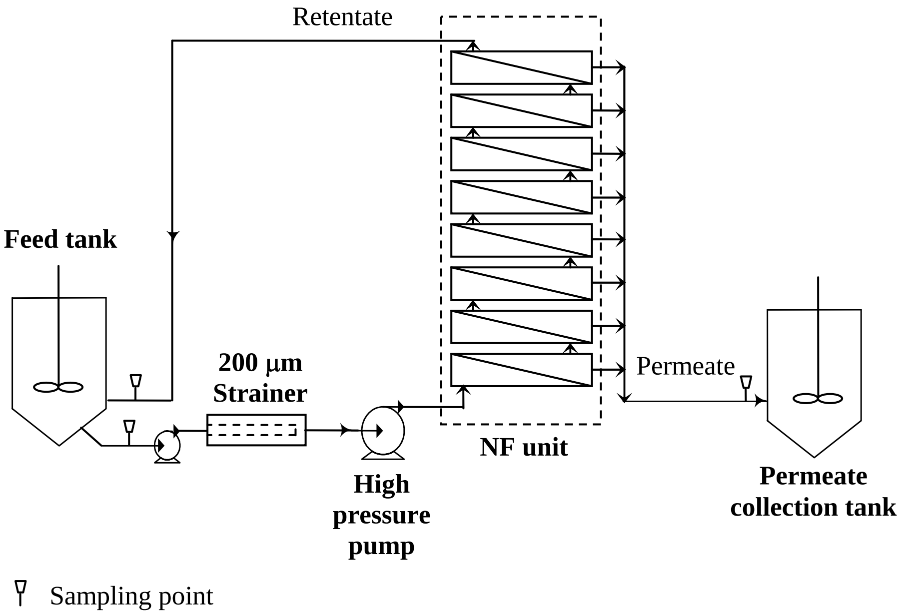


Figure 6-1. Process flowsheet illustrating the field testing arrangement.

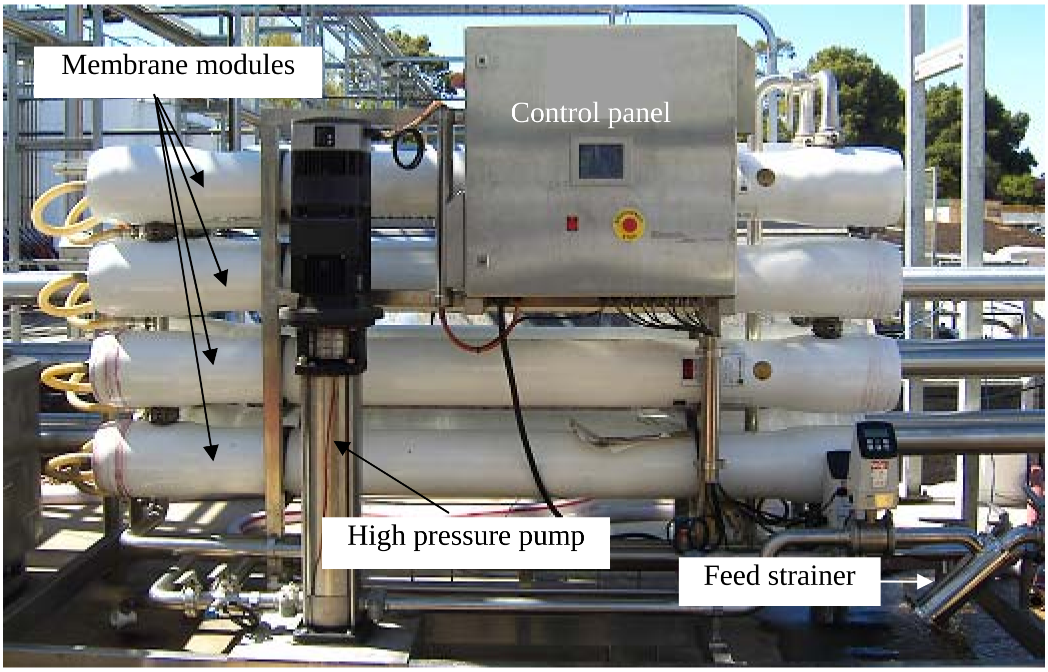


Figure 6-2. Picture of the membrane filtration system at Berri Estates Winery.

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 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 oxygen 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 NF 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 four 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.

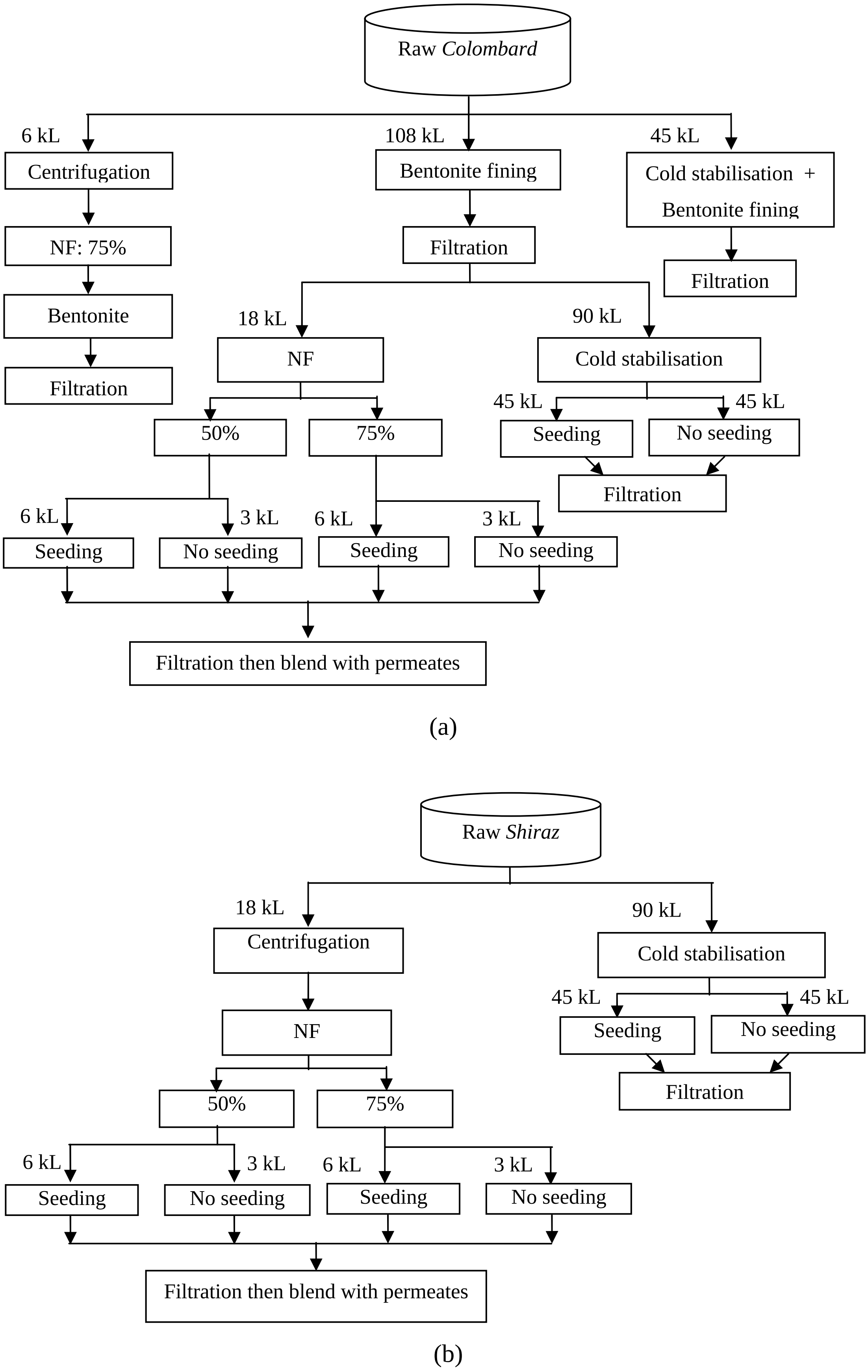


Figure 6-3. Summary of field testing performed for; (a) *Colombard*; and (b) *Shiraz* wines.

6.2.3.4 Cold stabilisation

Cold stabilisation testing of the wines was conducted at the same time as the NF 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 (KHT).

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 ^{o}C until testing. Table 6-I shows the samples codes applied to each testing permutation.

The ambient temperature during NF of wines was variable during and between tests. Thus, measurement of permeate flux were normalised:

$$J_{V\,@\,25^{o}C} = \frac{V_p}{A \times t} \times TCF \tag{6-1}$$

where V_p is volume of permeate collected (L), A is membrane effective area (m^2), t is time required for the collection of V_p (h) and TCF is temperature correction factor as tabulated in APPENDIX F.

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 & 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 acid (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). The sampling codes employed for the sensory test are given in Table 6-I. 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.

Table 6-I. Details of sample collected from *Colombard* and *Shiraz* NF trials for sensory evaluation.

***Colombard* trial**		***Shiraz* trial**	
Sample Label	**Description**	**Sample Label**	**Description**
1A	Raw *Colombard*	2A	Raw *Shiraz*
1B	Bentonite fined raw *Colombard*	2C	Conventional cold stabilisation *Shiraz*
1C	Conventional cold stabilisation *Colombard* with bentonite fining	2CS	Cold stabilisation with seeding *Shiraz*
1DS	Bentonite fined *Colombard* then cold stabilisation with seeding	2A75B	*Shiraz* undergo NF at 75% recovery
1B75B	Bentonite fined raw *Colombard* undergo NF at 75% recovery		

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-II. 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-II. 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	1.05	1.08
Ca^{2+}	g/L	0.04	0.07
H_2T	g/L	2.78	2.55
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[^]

*: Refer to Section 5.4.5

#: Heavy deposits observed

^: Slight deposits observed

6.4.2 Performance of NF system during trials

Tables 6-III and 6-IV 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 shown in Figure 6-4). 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.

Table 6-III. 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/h	T, °C	Flow, L/h	Flux, $L/m^2/h$	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

Table 6-III ***cont.***

(b) Bentonite fined *Colombard* at 50% recovery

	Feed		**Permeate**			
Time, min	Flow, L/h	T, °C	Flow, L/h	Flux, $L/m^2/h$	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

(c) Bentonite fined *Colombard* at 75% recovery

	Feed		**Permeate**			
Time, min	Flow, L/h	T, °C	Flow, L/h	Flux, $L/m^2/h$	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

Table 6-IV. NF operating conditions and performance during *Shiraz* trials: (a) Raw *Shiraz* at 50 % recovery; (b) Raw *Shiraz* at 75 %.

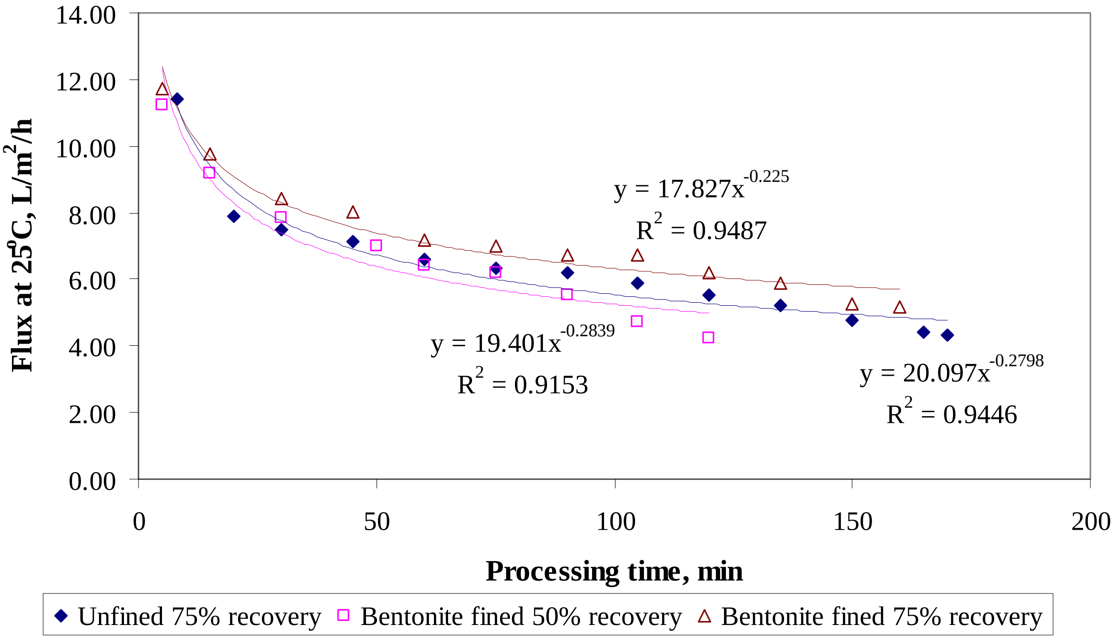
(a) Raw *Shiraz* at 50 % recovery

	Feed		**Permeate**			
Time, min	Flow, L/h	T, ^oC	Flow, L/h	Flux, $L/m^2/h$	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

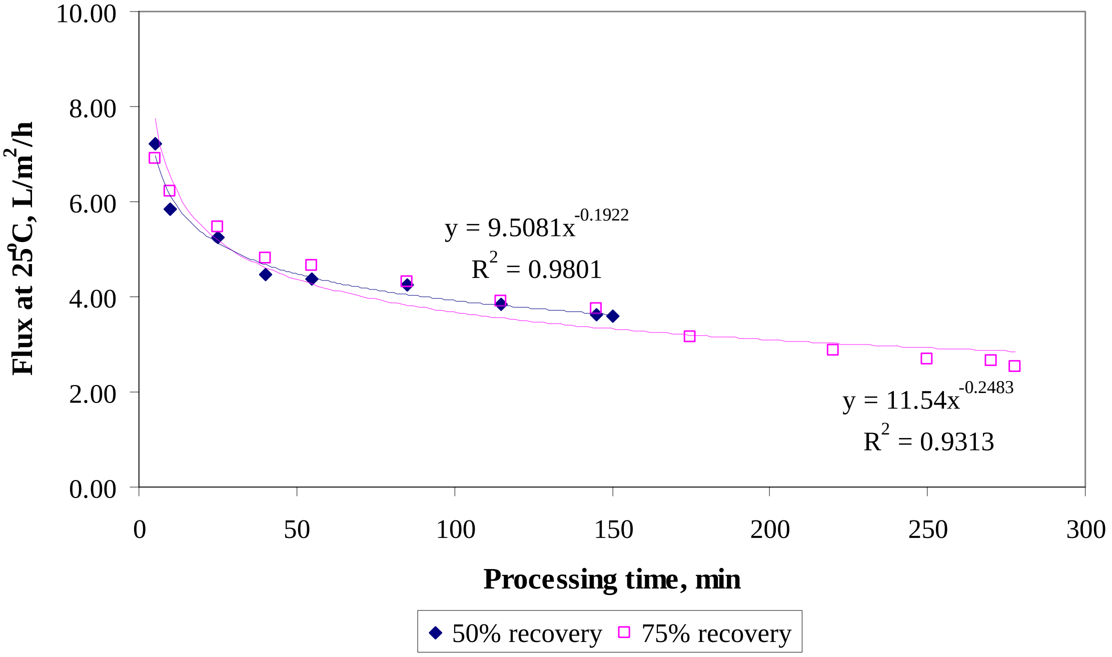
Table 6-IV *Cont.*

(b) Raw *Shiraz* at 75 % recovery

	Feed		Permeate			
Time, min	Flow, L/h	T, °C	Flow, L/h	Flux, L/m^2/h	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



(a)



(b)

Figure 6-4. Fluxes of wines at different recovery rate: (a) *Colombard*; and (b) *Shiraz*.

6.4.3 Membrane rejection

Table 6-V gives values from chemical analysis of retentate and permeate taken during at the commencement of a NF field test with *Colombard* wine. Similarly, values from chemical analyses of the retentate and permeate at the commencement of a NF field test with *Shiraz* wine is presented in Table 6-VI. 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. Such excellent rejection characteristic was expected as majority of phenolics compound have molecular weights ranging from 300 to over 4000 Da (Haslam, 1998) whilst the cut off of the NF membrane was 300 Da.

Additionally, there was nearly total rejection of flavonoid compounds in *Colombard* trials and anthocyanins in *Shiraz* trials. Generally, flavonoids have molecular weights ranging from 220 Da and anthocynanins have molecular weights exceeding 400 Da. However, both compounds can be polymerized or linked to other macromolecules (Cheynier et al., 2006; Mazzaracchio et al., 2004) and hence likely to be retained by NF membrane.

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 SO_2 in permeate were 7 and 11 mg/L, respectively.

Table 6-V. Composition of permeate and retentate of *Colombard* wine and the estimated rejection characteristics of the membrane.

Property		***Colombard***			
		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-VI. Composition of *Shiraz*'s permeate and retentate and the estimated rejection characteristics of the membrane.

Property		***Shriaz***			
		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

6.4.4 Effect of differing treatments on composition and tartrate stability

The effects of differing treatment on physical, chemical and tartrate stability characteristics for the *Colombard* and *Shiraz* wines are presented in Tables 6-VIII and 6-IX, respectively. The data presented in both tables is the mean value of duplicate measurements. The sampling codes used for the analyses are provided in Table 6-VII.

Table 6-VII. Details of all treated samples collected for physical and chemical analysis.

***Colombard* trial**		***Shiraz* trial**	
Sample Label	**Description**	**Sample Label**	**Description**
1A	Raw *Colombard*	2A	Raw *Shiraz*
1B	Bentonite fined raw *Colombard*	2C	Conventional cold stabilisation *Shiraz*
1C	Conventional cold stabilisation *Colombard* with bentonite fining	2CS	Cold stabilisation with seeding *Shiraz*
1D	Bentonite fined *Colombard* then cold stabilisation	2A50B	*Shiraz* undergo NF at 50% recovery
1DS	Bentonite fined *Colombard* then cold stabilisation with seeding	2A50BS	*Shiraz* undergo NF at 50% recovery with seeding
1A75B	Raw *Colombard* undergo NF at 75% recovery then bentonite fined	2A75B	*Shiraz* undergo NF at 75% recovery
1B50B	Bentonite fined raw *Colombard* undergo NF at 50% recovery	2A75BS	*Shiraz* undergo NF at 75% recovery with seeding
1B50BS	Bentonite fined raw *Colombard* undergo NF at 50% recovery with seeding		
1B75B	Bentonite fined raw *Colombard* undergo NF at 75% recovery		
1B75BS	Bentonite fined raw *Colombard* undergo NF at 75% recovery with seeding		

There were noticeable changes in some characteristics. Thus, Tables 6-X and 6-XI present the percentage change for each property for the cold stabilisation and NF treatment that appeared to produce the greatest difference in wine quality.

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. Such improvement is expected as free tartaric acid can be complexed with proteins, polyphenolics, and other compounds which may inhibit precipitation of KHT (Zoecklein, 1988a). However, bentonite able to remove of a portion of these complexing compounds which then can enhance tartrate stability (Zoecklein, 1988b).

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. Unfortunately, no comparison of such observation can be made as no other studies investigated the affect of bentonite fining prior and 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. Such greater precipitation may be induced by provision of external nuclei and may be also due to ability of bentonite to remove some complexing compounds which act as crystallisation inhibitors (Zoecklein, 1988b).

All NF 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 NF 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 NF (see Figure 6-3). Sulfited 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 sulfited water. This could have also produced the lower values recorded for other wine properties.

Despite this, NF treatments did not appear to produce significant differences in free and total sulfur dioxide 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, NF seemed to consistently produce lower values of total flavonoids and phenolics when compared with cold stabilisation and which is unlikely to be attributable to dilution effects. [The values of total flavonoids and phenolics for 1B50FS look aberrant and probably cannot be considered reliable.] This may have been a result of differences in adsorption by KHT crystals produced by each process, which may have varied in size and concentration. It is known that adsorption of phenolic components on the KHT crystal faces can account for 0.2 – 0.8 % of the crystal dry weight (Vernhet et al., 1999a). Alternatively, it may have arisen from added phenolics adsorption by NF membranes, with this effect on final phenolics concentration exacerbated by the relatively small volume of wine processed. It was not possible to further investigate or elucidate the reasons for these apparently lower values in phenolics produced by NF during the field tests.

6.4.4.2 *Shiraz* wine

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

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

Slightly lower ethanol concentrations during NF were also recorded, again suggesting a dilution may have occurred. Again this is the likely explanation for some of the slight reductions in observed for other wine properties.

Nevertheless, a noticeable decrease in the total anthocyanins and total phenolics by NF treatment (relative to cold stabilisation) and unlikely to be attributable to dilution were again observed. However, this decrease was not accompanied by a reduction in coloured (ionized) anthocyanins or colour density. It may be that the coloured (ionized) anthocyanins were not as readily adsorbed by crystals or the membranes, or that their original concentration was restored in equilibrium reactions with other anthocyanin compounds.

Clearly, these observed changes in anthocyanin and phenolic compounds (for both *Colombard* and *Shiraz* wines), which can contribute to wine colour, flavour and aroma, arising from NF treatment warrant future investigation outside of this current study.

Table 6-VIII. The physical and chemical properties of *Colombard* wines treated by different technologies.

		Colombard									
Property		**1A**	**1B**	**1C**	**1D**	**1DS**	**1A75B**	**1B50B**	**1B50BS**	**1B75B**	**1B75BS**
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
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-IX. The physical and chemical properties of *Shiraz* wines treated by different technologies.

		Shiraz						
Property		**2A**	**2C**	**2CS**	**2A50B**	**2A50BS**	**2A75B**	**2A75BS**
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
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$^{\#}$	✓$^{\wedge}$	✓$^{\wedge}$	✓$^{\wedge}$	✓$^{\wedge}$	✓$^{\wedge}$	✓$^{\wedge}$

#: Slight deposits observed ^: No deposits observed and wine was considered stable

Table 6-X. Percentage change of characteristics of *Colombard* treated by different treatments.

			Changes in property, %								
Property		**1A**	**1B**	**1C**	**1D**	**1DS**	**1A75B**	**1B50B**	**1B50BS**	**1B75B**	**1B75BS**
Ethanol	% v/v	12.57	-0.56	-0.48	-0.72	-0.64	-9.55	-12.97	-12.97	-8.91	-11.22
Titrable acidity	g/L as H_2T	7.57	-5.42	-14.80	-11.62	-15.32	-20.87	-12.95	-31.57	-18.76	-17.57
Free SO_2	mg/L	28	-10.71	-14.29	-17.86	-17.86	-46.43	-3.57	-14.29	0.00	-10.71
Total SO_2	mg/L	144	-2.08	5.56	5.56	5.56	-15.97	-8.33	-11.81	-8.33	-6.25
K^+	g/L	1.05	-1.19	-22.09	-5.94	-24.94	-23.99	-7.84	-13.54	-24.94	-23.99
Ca^{2+}	g/L	0.07	-2.78	11.11	-2.78	-2.78	-2.78	11.11	-30.56	-2.78	11.11
H_2T	g/L	2.79	-2.63	-27.69	-8.36	-30.55	-28.41	-5.49	-12.30	-20.17	-26.62
Total flavonoids	a.u.	35	-2.86	-5.71	-2.86	-5.71	-22.86	-11.43	-48.57	-22.86	-14.29
Total phenolics	a.u.	4.52	-11.50	-14.16	-12.39	-12.61	-34.29	-15.93	-68.36	-38.05	-25.22
Relative brownness	a.u	0.16	-30.82	-37.11	-37.11	-18.24	-11.95	-24.53	-37.11	-37.11	-24.53

Table 6-XI. Percentage change of characteristics of *Shiraz* treated by different treatments.

			Changes in property, %					
Property		**2A**	**2C**	**2CS**	**2A50B**	**2A50BS**	**2A75B**	**2A75BS**
Ethanol	% v/v	13.98	-1.22	0.00	-6.87	-7.22	-5.87	-8.37
Titrable acidity	g/L as H_2T	6.32	-1.58	0.16	-12.66	-3.80	-6.01	-7.44
Free SO_2	mg/L	37	-18.92	-21.62	-27.03	-21.62	-24.32	-21.62
Total SO_2	mg/L	82	-14.63	-17.07	-23.17	-17.07	-20.73	-14.63
K^+	g/L	1.08	-1.94	-2.87	-1.94	-4.72	-9.34	-11.19
Ca^{2+}	g/L	0.07	-4.11	-4.11	-31.51	-17.81	-17.81	-4.11
H_2T	g/L	2.55	-0.41	-1.20	-0.41	-1.59	-18.45	-18.06
Color density		8.30	0.00	14.46	-1.20	22.89	1.20	13.25
Hue		0.70	0.00	-4.29	-5.71	-2.86	-7.14	-8.57
Total phenolics	a.u.	39	-2.56	-2.56	-12.82	-2.56	-17.95	-7.69
Total anthocyanins	a.u	280	-0.71	-2.14	-18.93	-15.36	-20.36	-16.79
Colored anthocynanins	mg/L	55.80	-7.48	25.01	1.57	25.13	-0.10	19.10

6.4.5 Conductivity measurement

Figures 6-5 and 6-6 show conductivity changes recorded in the feed tank and retentate hold tank for *Colombard* and *Shiraz* wines during the concentration and holding periods of NF 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 NF treatment.

Consider Figure 6-5(a): raw wine concentrated to a 75 % recovery with no seeding. Between 0 and 170 minutes, the conductivity increases proportionally as the wine is concentrated. During this period, supersaturation of KHT 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, 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 minutes from commencement of the holding phase.

The behaviour of the un-fined *Colombard* wine in Figure 6-5(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 6-5(b) shows the conductivity changes of the un-fined *Colombard* wine at a recovery rate of 50 %, where the concentration phase was shorter (120 minutes). The same type of behaviour can also be observed. However, a longer time, approximately 80 minutes, 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 6-6 except that even longer times, in the order of 100 to 150 minutes, are required for the wine to achieve a new steady state during the holding phase. Such findings are expected as red wines generally have higher inhibition of KHT crystallisation than white wines (Vernhet et al., 1999a; Gerbaud et al., 1997; Tanahashi et al., 1992).

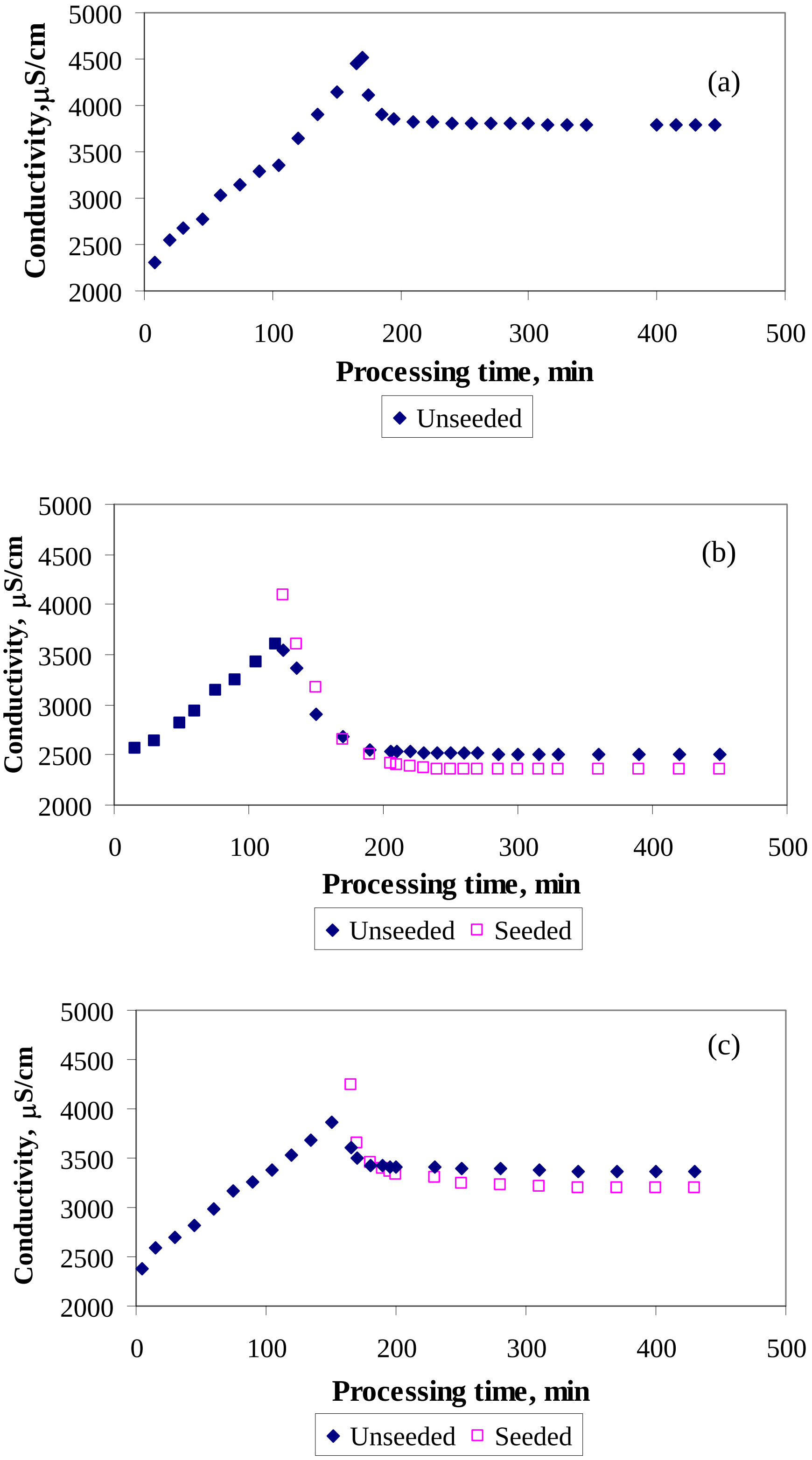
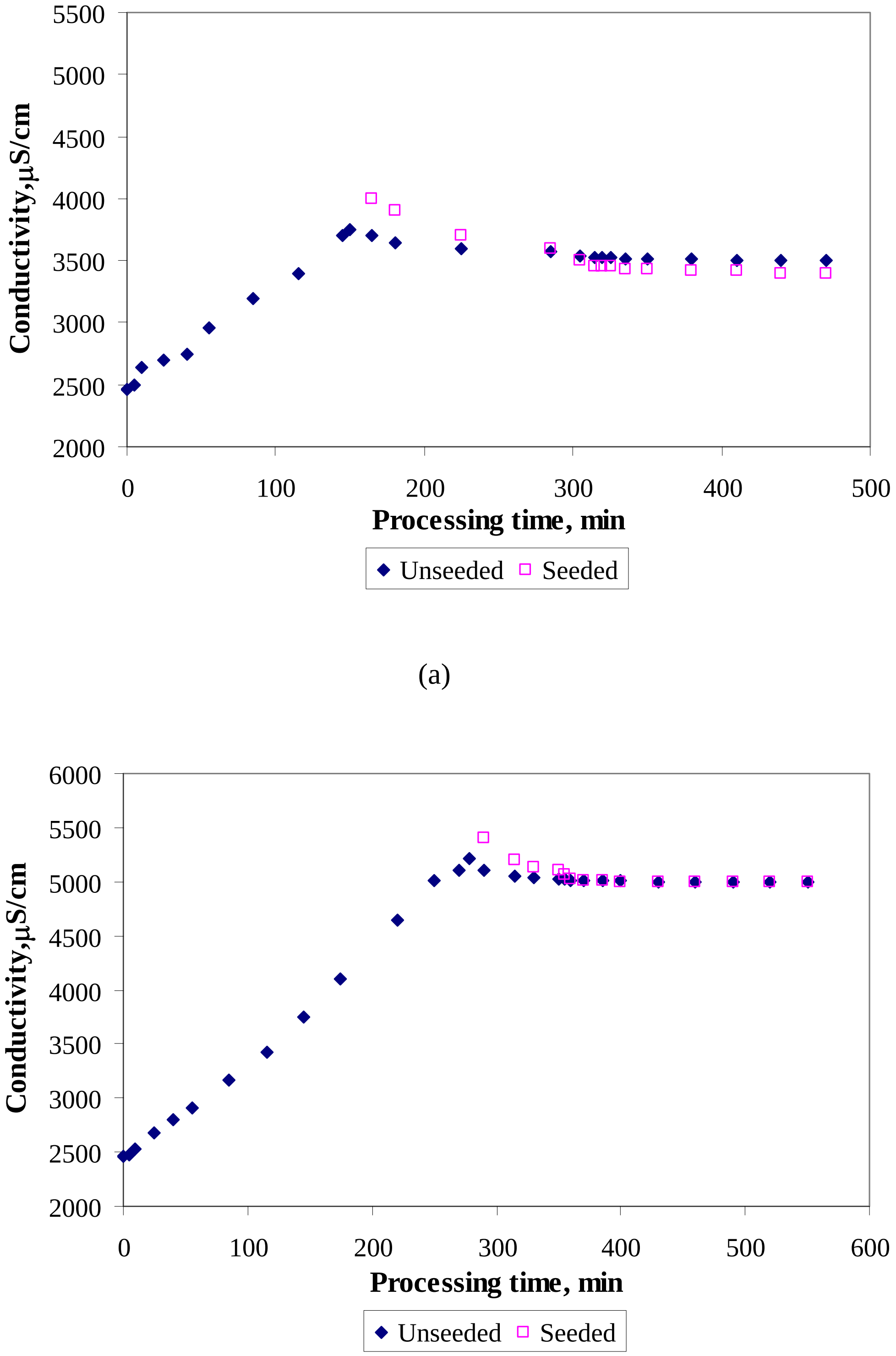


Figure 6-5. Evolution of *Colombard* conductivity during nanofiltration process: (a) Raw wine treated at 75 % recovery; (b) bentonite fined wine treated at 50 % recovery; and (c) bentonite fined wine treated at 75 % recovery,



(a)

(b)

Figure 6-6. Evolution of *Shiraz* conductivity during nanofiltration process: (a) treated at 50 % recovery; and (b) treated at 75 % recovery.

6.4.6 Analysis of crystallisation kinetics

6.4.6.1 Theory

According to Mullin (1972), the mechanism for crystal growth involves a diffusion step followed by a surface integration step where nucleation is not limiting. A generalised equation for crystallisation can be expressed as

$$-\frac{ds}{dt} = k_G A(c - c^*)^n \qquad \textbf{(6-1)}$$

where k_G is an overall crystal growth coefficient (made up of two individual component coefficients, k_D and k_S for diffusion and surface integration, respectively); A is the surface area of crystal; c is solute concentration in supersaturated solution; c^* is equilibrium concentration; and n is an overall growth rate order. Generally, the diffusional step is considered to be first order and most of the surface interactions are second order (Karpinski, 1980). Crystallisation in which both steps are limiting factors will have values of n between one and two.

According to Abguéguen and Boulton (1993), if a plot of ln $(c\text{-}c^*)$ versus time displays linearity, that means diffusion step is limiting step (first order kinetics). However, if a plot of $1/(c\text{-}c^*)$ shows linearity then surface integration step is controlling step (second order kinetics).

For the purpose of analysis in this section, it will be assumed that conductivity is an accurate surrogate for KHT concentration in the wine. (This same strategy for analysis of crystallisation kinetics was employed by Dunsford and Boulton (1981a and b)). Furthermore, c^* is the final equilibrium value of conductivity during holding period of field testing.

ln $(c\text{-}c^*)$ versus holding time observed during the holding period for the *Colombard* and *Shiraz* wines were plotted and are presented in Figures 6-7 and 6-9. Trendlines to illustrate the general behaviour of ln $(c\text{-}c^*)$ with time are included in the figures. In particular, these trendlines are employed to highlight the perceived distinction between linear and non-linear behaviour. Plot of $1/(c\text{-}c^*)$ versus time for the *Colombard* and *Shiraz* wines to estimate second order regions are presented in Figures 6-8 and 6-10.

Finally, the lumped kinetic constants for the first and second order regions of both wines obtained at different recovery rates are presented in Table 6-XII.

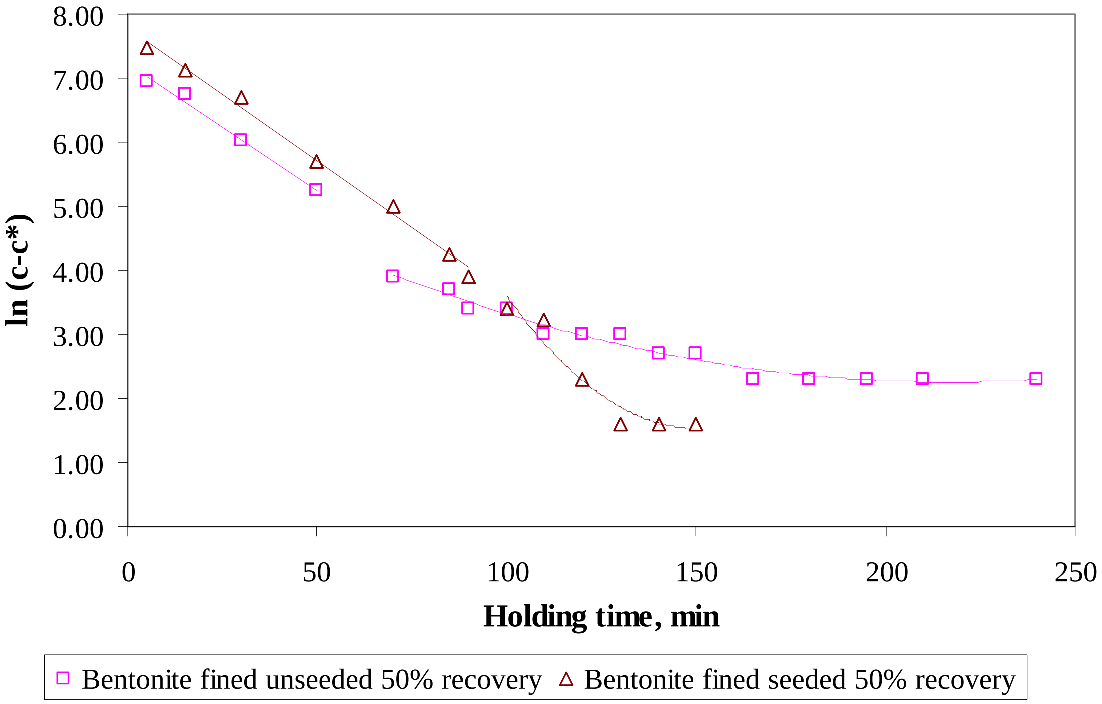
6.4.6.2 *Colombard* wine

Figure 6-7 showed that at recovery rate of 50 % the first order regions were reached within 5 minutes. However, there was no sign of first order regions for recovery rate at 75 %. According to Dunsford and Boulton (1981b), concentration of KHT or level of supersaturation governed the progression of the surface reaction regime. At 50 % recovery the degree of supersaturation was much lower than that at 75 % recovery. Hence, at 50 % recovery, a period of at least first 50 minutes was under diffusion control.

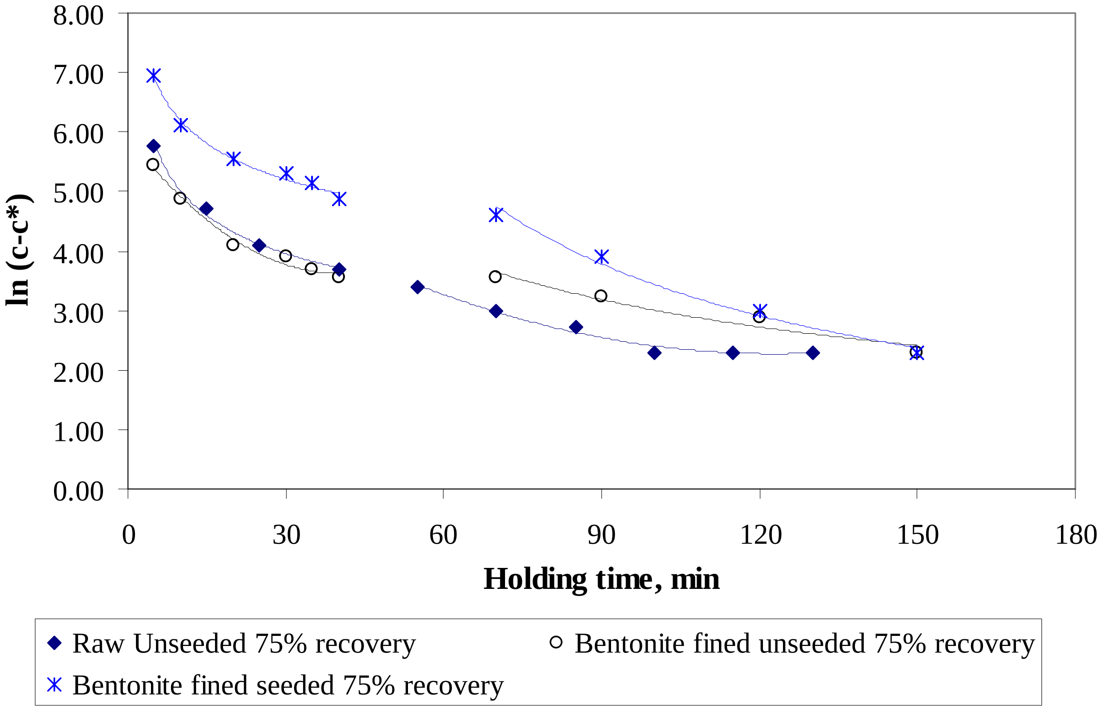
Evidence of a second order reaction as the rate controlling stage in *Colombard* wines was found after 70 to 100 minutes for 50 % recovery but noticeable within 5 minutes for 75 % recovery (Figure 6-8). Interestingly, non-linear trendlines were observed in Figure 6-8 (b) after a period of 40 minutes for *Colombard* wines treated by NF at 75 % recovery. Such findings indicated that the highly supersaturated wines experienced higher growth order of surface reaction than two. This phenomenon is possible as the order of surface reaction can be in the range between 2 and 5 (Nyvlt, 1971).

6.4.6.3 *Shiraz* wine

Similarly, *Shiraz* treated at 50 % recovery is controlled by diffusion then surface reaction steps. *Shiraz* treated at 75 % recovery is controlled by surface reaction step instead. Transition from diffusion to surface reaction regime at 50 % recovery was much slower compared to *Colombard*– after period of 150 minutes (Figure 6-9 (a)). Figure 6-10 (b) showed that *Shiraz* treated at 75 % recovery displayed two second-order kinetics regions where the second began after approximately 75 minutes of crystallisation. This has been interpreted as an evidence of complexing occurred.



(a)



(b)

Figure 6-7. First order regions of *Colombard* crystallisation treated at recovery rate of: (a) 50 %; and (b) 75 %.

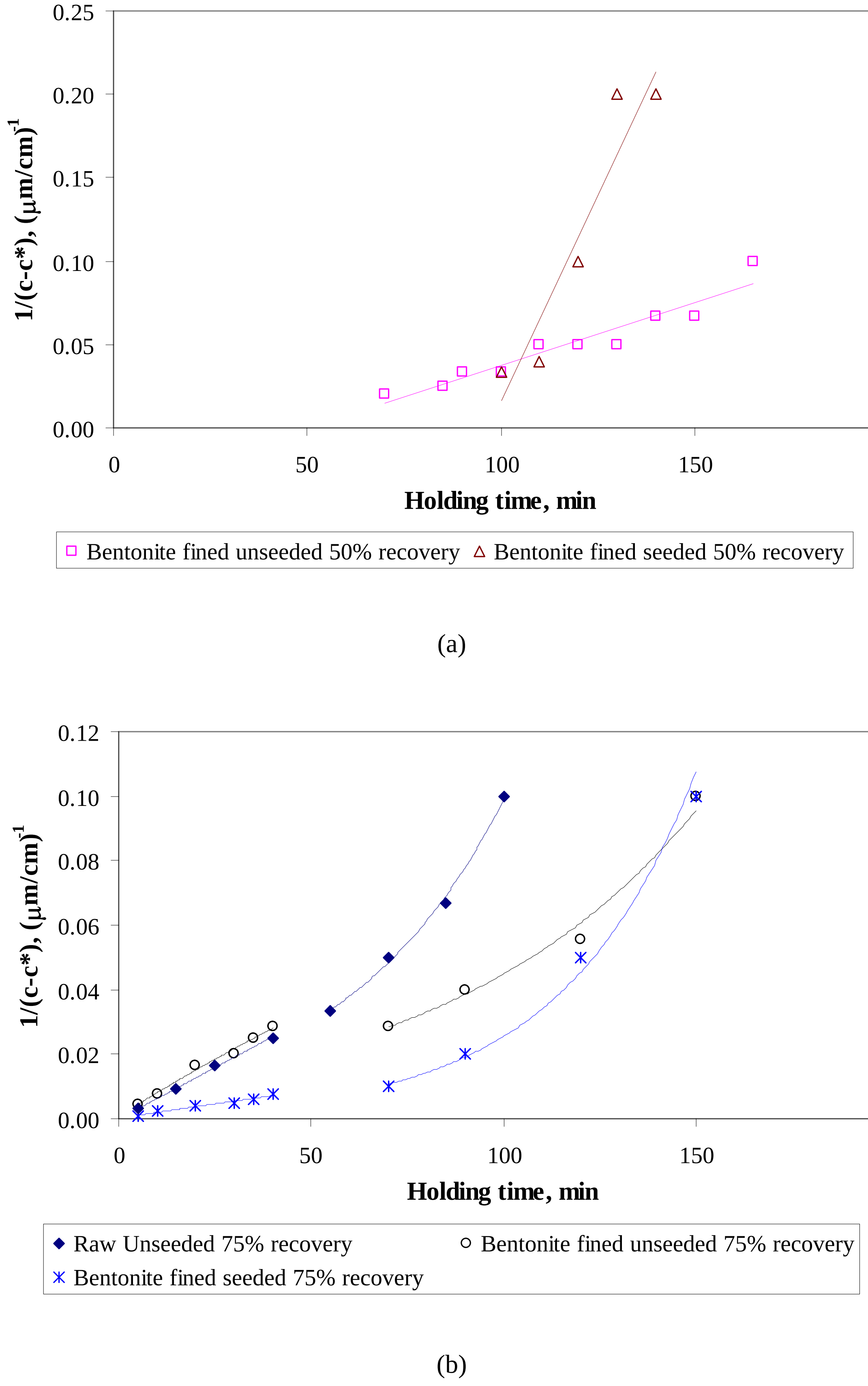
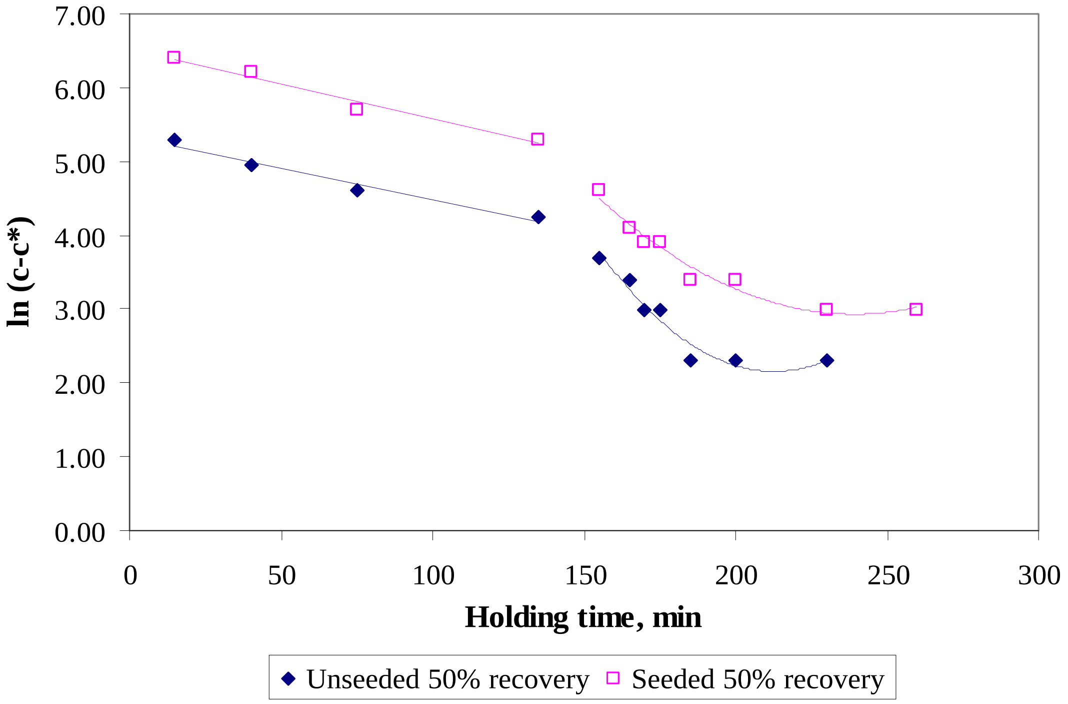
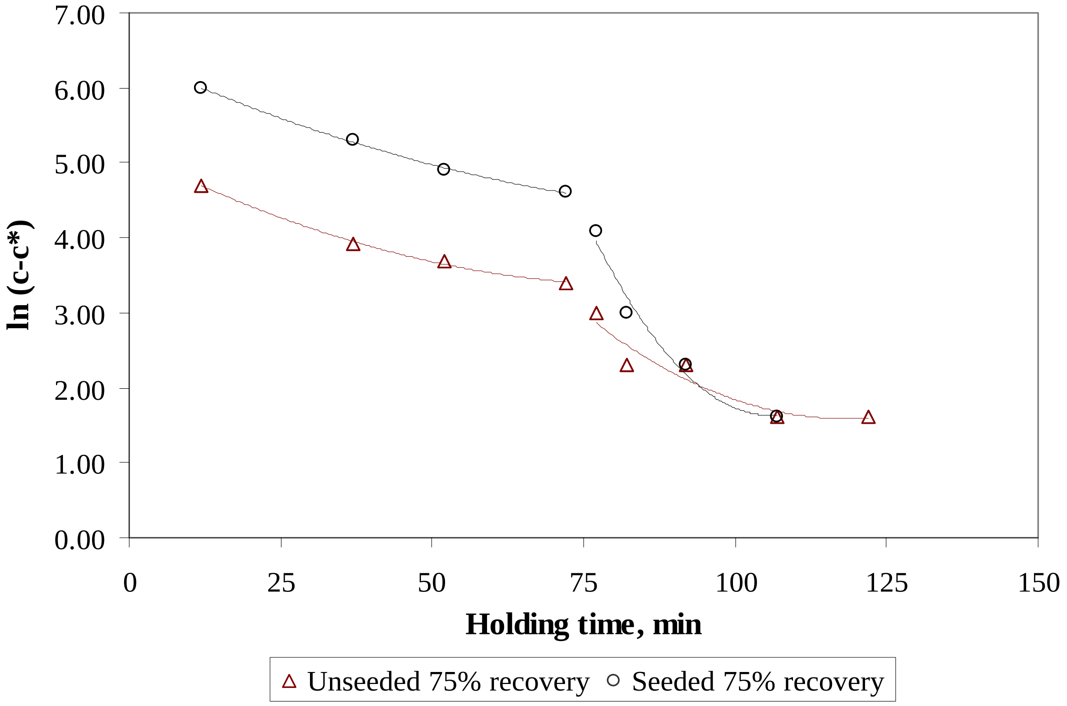


Figure 6-8. Second order regions of *Colombard* crystallisation treated at recovery rate of: (a) 50 %; and (b) 75 %.

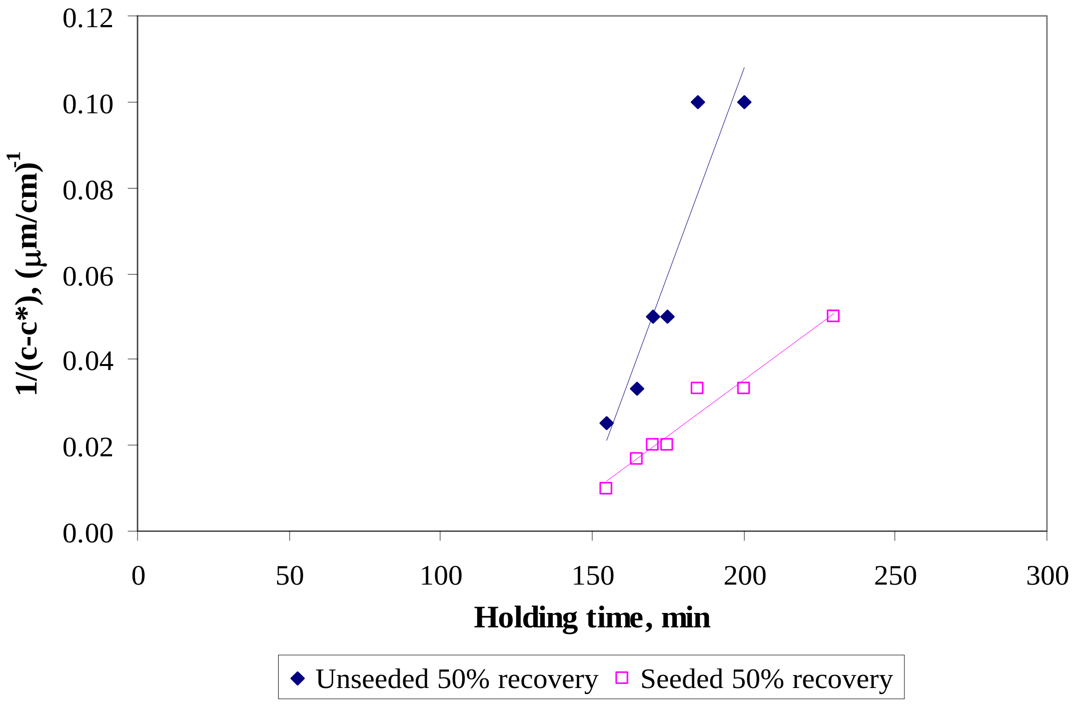


(a)

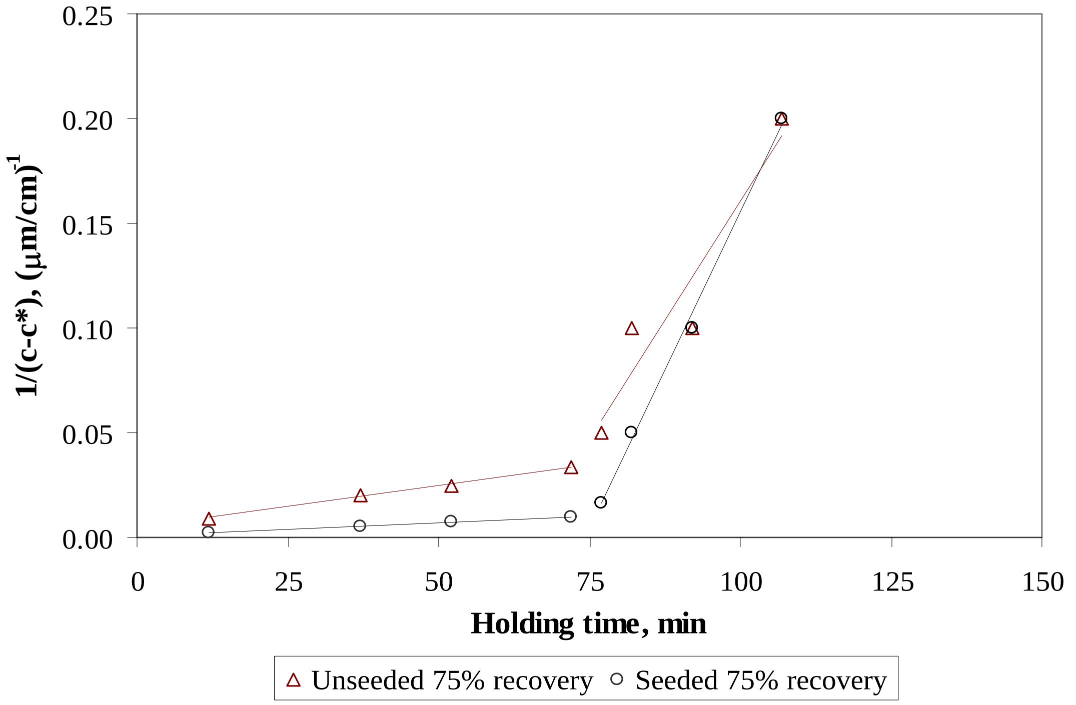


(b)

Figure 6-9. First order regions of *Shiraz* crystallisation treated at recovery rate: (a) 50 %; and (b) 75 %.



(a)



(b)

Figure 6-10. Second order regions of *Shiraz* crystallisation treated at recovery rate: (a) 50 %; and (b) 75 %.

Table 6-XII. Lumped kinetic constants for first and second order regimes of KHT crystallisation in different wine retentate.

	First Order $(k_D A)$		***Second order*** $(k_S A)$	
Treatment	min^{-1} x 10^{-3}	R^2	(µm/cm)$^{-1}$min^{-1} x 10^{-3}	R^2
Colombard				
50 % recovery				
Bentonite-fined unseeded	39.5	0.989	0.7	0.913
Bentonite-fined seeded	41.6	0.994	0.49	0.902
75 % recovery				
Raw unseeded	-	-	0.6	0.996
Bentonite-fined unseeded	-	-	0.7	0.986
Bentonite-fined seeded	-	-	0.2	0.974
Shiraz				
50 % recovery				
Unseeded	8.5	0.962	1.9	0.876
Seeded	9.5	0.974	0.5	0.957
75 % recovery				
Unseeded	-	-	0.4	0.998
			4.5	0.905
Seeded	-	-	0.1	0.991
			6	0.997

6.4.7 Outcome of sensory evaluation

The results of selected comparisons obtained by the duo-trio difference tests are presented in Table 6-XIII.

Table 6-XIII. Results of duo-trio difference tests for (a) *Colombard* wines; and (b) *Shiraz* wines.

(a) *Colombard* trials

Test	Wine 1		Wine 2	No. correct responses/ No. total responses	*P*-value
1	1A	vs	1C	17/25	0.032*
2	1A	vs	1B75B	18/25	0.014*
3	1A	vs	1B	10/25	0.097
4	1C	vs	1B75B	20/25	0.002*
5	1C	vs	1DS	13/25	0.155

(b) *Shiraz* trials

Test	Wine 1		Wine 2	No. correct responses/ No. total responses	*P*-value
1	2C	vs	2A	20/25	0.002**
2	2C	vs	2A75B	20/25	0.002**
3	2C	vs	2CS	14/25	0.133
4	2A	vs	2A75B	23/25	$8.94 \times 10^{-6**}$

* denotes significance at $P < 0.05$

** denotes significance at $P < 0.01$

6.4.7.1 *Colombard* wine

Table 6-XIII(a) shows results for the *Colombard* wine. These results suggest that

- bentonite fining of the wine did not have a significant sensory effect (e.g. 1A vs. 1B);
- both cold stabilisation and NF had an effect on the raw wine (e.g. 1A vs. 1C and 1A vs. 1B75B);
- there was a difference between the effect of cold stabilisation and NF (e.g. 1C vs. 1B75B); and
- seeding of wine during cold stabilisation did not have an effect (e.g. 1C vs. 1DS).

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 NF on the raw wine was considered negative;
- furthermore, the effect of NF on the sensory quality of the wine was also negative when compared with cold stabilisation.

Whilst these informal comments may not be scientifically quantitative or reliable, they do provide a valuable description from the panellists of what the differences, where occurring, were and what they might be attributed to.

An obvious reason for the nature of the above negative effects observed with NF 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. According to Ribéreau-Gayon et al. (2000), reduction in ethanol content might cause flatness in wine sensory which as noticed in wine 1B75B.

This study showed no significant difference was detected between raw wine (1A) and bentonite fined raw wine (1B). This result concurred with the findings summarised by Parent and Welsh (1986), Leske et al.(1995) and Muhlack et al. (2006). However, Miller et al. (1985) found that bentonite-treated wine was distinguishable and untreated wine was preferred instead. The most recent study by Nordestgaard et al. (2007) showed that there was a significant difference between the untreated and batch-fined Chardonnay, but not between the untreated and batch-fined Semillon-Chardonnay. Such contradicting findings add to commonly questionable data on the effect of bentonite on wine quality.

6.4.7.2 *Shiraz* wine

Table 6-XIII(b) shows results of the sensory evaluation for the *Shiraz* wine. These suggest that

- both cold stabilisation and NF had an effect on the raw wine (e.g. 2C vs. 2A and 2A vs. 2A75B);
- the effect of cold stabilisation was different to that of NF (e.g. 2C vs. 2A75B); and
- seeding of wine during cold stabilisation did not produce any effect (e.g. 2C vs. 2CS).

Likewise, the informal notes from the sensory panel suggested

- the effect of cold stabilisation on the wine was not adverse;
- but the effect of NF on the raw wine was considered negative; and
- the effect of NF 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 (2A) and cold stabilised (2C) wines had higher burnt rubber aroma and had more fruit flavour and acidity, whilst the nano-filtered wine (2A75B) appeared to possess off-notes of plastic, smoky and sweaty characters. Higher burnt rubber aroma in both wines 2A and 2C might be due to the presence of higher content of sulphur dioxide possibly caused by excessive addition of copper metabisulphite prior bottling, whilst sweaty character noted in wine 2A75B might be due to contamination of equipment by the surface yeast (i.e. *Brettanomyces spp*.) which produced tetrahydropyridines (Gibson and Farkas, 2007).

6.5 Implication of Field Testing on Cost Estimation

In Chapter 3 of this thesis, a cost comparison between differing tartrate stabilisation technologies, including NF was performed. One of the objectives of undertake field testing for NF was to collect design and operating data that could be used to validate assumptions made in preparing the cost estimate. The key uncertainties in assumptions which were made included the feed pressure and flux rate which could be achieved. These two parameters influenced the sizing on the NF plant and the energy consumption that would be required. The field tests has indicated that the feed pressure and flux rate data assumed for the cost estimate were achievable: pressure between 15 – 20 bar and flux rates of ca. 5 L/m^2/h. This serendipitous outcome means that revision of earlier cost estimates is unnecessary. Furthermore, the economic comparison or ranking at NF relative to other tartrate stabilisation technologies which was obtained is valid.

6.6 Conclusions

The existing NF system at Berri Estates Winery was operated in a batch mode to confirm the feasibility of NF for tartrate stabilisation of wine in large scale. During operation of the NF system, flux rates of between 5 and 12 L/m^2/h for *Colombard* wine, and between 2 and 6 L/m^2/h 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.

These field tests demonstrated that NF operated at moderate pressure could successfully tartrate stabilise *Colombard* and *Shiraz* wines at recoveries exceeding 50 %. The holding time required for completion of the crystallisation phase following concentration was between 30 and 150 minutes depending on the wine and recovery rate. The results suggested 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.

The membrane (nominal cut off of 300 Da) displayed similar rejection characteristics for potassium and calcium ions and tartaric acid as to membranes used during the laboratory experiments. Complete rejection of phenolics in both wines was also achieved.

Conductivity changes in the treated wines were monitored in order to study the crystallisation kinetics. Crystallisation of KHT of wines treated at 50 % recovery (with and without seeding) displayed rate limitation by diffusion (first-order regime) followed by surface reaction (second-order regime). On the other hand, a surface reaction step was the sole crystallisation rate controlling factor for wines treated at 75 % recovery.

In this study, sensory evaluation was also performed on selected wine samples collected from *Colombard* and *Shiraz* trials. The 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.

Based on the field testing data, reconsideration of previous estimated process cost estimates presented in Chapter 3 is unnecessary.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

This study has found that cold stabilisation likely remains the most cost effective tartrate stabilisation technology for the Australian wine industry. This finding was made by performing a comprehensive side-by-side comparison between six different tartrate stabilisation technologies based on engineering calculations and conceptual cost estimates as well as through the application of selected multi-criteria decision analysis methods. In the economic analysis, a key observation was that product loss was identified as a key cost driver or differentiating factor between alternative technologies. It was also concluded that the Westfalia process, nanofiltration and fluidisation merit further consideration and evaluation for future application or where cold stabilisation is not preferred.

As a consequence, nanofiltration was then selected for further evaluation because of its potential to be used for other or multiple applications in wine industry. This included laboratory experimentation and field testing. It was demonstrated that nanofiltration can successfully tartrate stabilise wine. This was achieved; using membranes with a MWCO of approximately 300 Da; at moderate feed pressures of less than 20 bar and flux rates of between 5 and 10 $L/m^2/h$; recoveries of at least 50 %; and without the need to add seed crystals.. Furthermore, this study has also provided the first ever insight into crystallisation kinetics of wine following concentration by nanofiltration. This includes the requirement to achieve relatively high degrees of supersaturation and that crystallisation rates are generally dictated by surface integration. Furthermore, the design and operating data collected during the field testing validated the assumptions made in earlier cost estimates.

Unfortunately, adverse sensory outcomes were observed in nano-filtered wines produced during field testing. The cause of these negative outcomes has not yet been determined and requires additional studies.

Nevertheless, if the problem with the adverse sensory outcomes can be satisfactorily resolved, this study has confirmed that tartrate stabilisation is a technically viable process that can be used by the Australian wine industry as an alternative to cold stabilisation.

To further develop nanofiltration for industrial application, further field testing and sensory evaluations are recommended to investigate effects of nanofiltration on wine quality.

Apart from focusing on nanofiltration, if cold stabilisation is to be retained the following areas should be addressed:

- As identified in this study, product loss is a key cost driver. Hence, further investigation on ways to minimise product loss would be beneficial to the wine industry.
- Cleaning the tartrate encrusted tank is another issue related to tartrate stabilisation process. Development of a more efficient tank cleaning method is essential to reduce generation of high salinity wastewater resulting from caustic cleaning. Use of alternative cleaning chemicals and exploration of the feasibility of ultrasonic disruption of deposits for tank cleaning should be undertaken.

APPENDIX A SUMMARY OF TECHNICAL & ECONOMIC EVALUATION OF SELECTED TARTRATE STABILISATION TECHNOLOGIES

This appendix summarises the assumptions and calculations made to evaluate technical and economic performances of selected tartrate stabilisation technologies under retrofit and greenfield scenarios as discussed in Chapter 3.

A.1 Calculation of Technical Performance and Operating Costs

Operating costs for maintenance, labour, consumables (i.e. membranes, filters, etc.), chemicals, electricity and water were based on material and energy balances and market or internal HWC data and discussions with equipment suppliers and HWC operating personnel.

Table A-I. Summary of estimation of operating costs of Option 1 –cold stabilisation: (a) wine loss; (b) energy consumption; (c) chemical usage; and (d) labour requirements.

(a) Wine loss (%/batch)		
Wine->tank	0.06	* 0.06 % (2 x 15 sec @ 20 kL/hr) assumed
Red: Tank->centrifuge	0.25	* 0.42 % assumed (2 x 30 sec @ 20 kL/hr + 0.3 % solids loss), 40/60 White/Red split
White: Tank -> DE	0.05	*(2 x 30 sec @ 20 kL/hr= 0.12 % transfer loss), 5 % lees
White: Tank lees -> RDV	0.02	* 1 % (pipe+processing) loss assumed
RDV	0.02	
Total (%/batch)	**0.40**	
Value ($/batch)	**3295.00**	
Value (c/bottle)	**0.90**	* $3/L
Wine (final product) value loss (%/batch)	**1.90**	* 40 % white * 5 % lees * 95 % RDV recovery
Value ($/batch)	**7837.50**	
Value (c/bottle)	**2.14**	* Value halved

Table A-I (*cont.*)

(b) Energy consumption (kWh/batch)		
Pump: Wine->tank	8.73	* 275 kL @ 100 kPa (Berri Estates operating data; Estimate 30 kPa x 2 for HE + 20 kPa pipe + fittings = 80 kPa, OK), 70 % eff.
Energy recovery + Chilling	1283.33	* ER: 8 -> 3 [50 % of time], Ultrachiller 3 -> -4; COPref. = 2.5
Hold period: Convective (-4 C)	576.58	* U=1 W/m2.K,A=275 m2, dT=23.3-4, COP=2.5, max=8d; Note, radiative losses negligible, solar radiation process neutral & not included
Hold period: Convective (8 C)		* Now at 8 C
Hold period: Solar insolation	440.00	* Assume 18 MJ/m2/d, 20 % ave. area, absorptivity ~ 0.5
Pump: Red: Tank->centrifuge	22.92	* 275 kL @ 350 kPa (Berri Estate operating data), 70 % eff.
Centrifuge: Red	270.00	* Westfalia SC150: 30 kW (ave. actual operating data) for 15 hr
Pump: White: Tank -> DE	8.73	* 275 kL @ 200 kPa (Berri Estates operating data
DE	168.00	* 14 hr @ 30 kW
Pump: White: Tank lees -> RDV tank	0.44	* 5 % of 275 kL @ 200 kPa, 18 kL/hr
Pump: RDV tank -> RDV	0.22	* 5 % of 275 kL @ 100 kPa, 4 kL/hr
RDV	24.00	4 hr @ 15 kW
Total (kWh/batch)	**2802.94**	
kWh/kL	**10.19**	
Value ($/batch)	**420.44**	
Value (c/bottle)	**0.11**	*15 c/kWh

Table A-I (*cont.*)

(c) Chemicals (inc. water) ($/batch)		
Tartrate consumption (kg/batch)	0.00	
$/batch	0.00	* 4.60/kg
Tartrate resale (kg/batch)	39.60	* 1 kg/kL precipitate, 40 % recovery unseeded, 95 % seeded
$/batch	59.40	$ 1.50/kg
Tartrate recovered (kg/batch)	39.60	
$/batch	59.40	$ 1.50/kg
Waterfill & flush lines pre-process		
Chillers	0.04	1000 L ($0.04/kL)
Centrifuge	0.02	1000 L
DE filter	0.02	600 L
RDV	0.01	500 L
Clean Chillers		Water -> Caustic -> Water -> Sanitise
Water	0.04	1000 L, 4 c/kL
Caustic	13.44	1000 L, 2 % Caustic, 20 L 50 % wt Caustic, 67c/L
Water	0.04	
Citric/sulfur	2.63	1000 L, 500 g citric $5/kg, 50 g Potassium Metabisuplhite $1.74/kg
Clean tank	4.84	Same protocol, but 300 L
Clean centrifuge	9.69	Same protocol, identical volume
Bentonite	74.25	0.5 g/L $0.78/kg
DE	23.68	80 kg [22 kg/hr for 4 hr, 45 kL/hr process rate] $0.74/kg
Clean DE filter equipment & associated lines	1.85	Same protocol, except caustic performed weekly
Perlite	243.20	800 kg perlite required @ $0.76/kg
Clean lees tank, RDV	0.74	Assume same as DE filter
Total chemicals(ex tartrate) ($/batch)	**374.49**	
Total chemicals(in tartrate) ($/batch)	**374.49**	
Net chemical cost ($/batch)	**315.09**	

Table A-I (*cont.*)

(d) Labour requirements (h/batch)		
Plumb chillers/transfer lines	1.00	1 person x 1 h
Flush & fill product lines	0.50	2 person x 15 min
Catch wine	0.50	2 person x 15 min
Monitor fill operation	0.33	1 person x 5 min x 4
Flush lines with water & catch	0.50	2 person x 15 min
Clean & sanitise line	0.50	1 person x 1 h (50%)
Monitor cold stabilisation	1.17	1 person x 10 min x 1 d
Clean tank	1.00	1 person x 2 h (50%)
Red wine (60% of production):		
Prepare for & initiate mixing	0.15	1 person x 15 min
Flush & prepare centrifuge & lines	0.60	2 person x 30 min
Catch wine	0.30	2 person x 15 min
Monitor centrifuge	8.40	1 person x 14 h
Flush lines with water & catch	0.30	2 person x 15 min
Clean & sanitise centrifuge & lines	0.60	1 person x 1 h
White wine (40% of production):		
Prepare bentonite slurry	0.30	1 person x 1.5 h (50%)
Transfer slurry to contact tank	0.20	2 person x 15 min
Clean bentonite tank & line	0.20	1 person x 30 min (50%)
Prepare DE & flush lines	0.40	1 person x 1 h
Catch wine	0.20	2 person x 15 min
Monitor DE	3.20	1 person x 8 h
Flush with water & catch wine	0.20	2 person x 15 min
Clean & sanitise DE	0.20	1 person x 1 h (50%)
Rack off bentonite lees	0.40	1 person x 1 h
Flush line with water	0.20	2 person x 15 min
Clean & sanitise lines	0.20	1 person x 1 h (50%)
Prepare RDV	0.40	1 person x 1 h
Operate & monitor RDV	1.60	1 person x 8 h (50%)
Flush lines with water & catch	0.20	2 person x 15 min
Clean-up RDV & lines	0.20	1 person x 1 h (50%)
Total (h/batch)	**23.95**	
Labour cost ($/batch)	**718.50**	* $30/h for cellar hand
Labour cost (c/bottle)	**0.20**	

Table A-II. Summary of estimation of operating costs of Option 2 –cold stabilisation with seeding: (a) wine loss; (b) energy consumption; (c) chemical usage; and (d) labour requirements.

(a) Wine loss (%/batch)		
Wine->tank	0.06	* 0.06 % (2 x 15 sec @ 20 kL/hr) assumed
White: Tank -> DE	0.05	*(2 x 30 sec @ 20 kL/hr= 0.12 % transfer loss), 5 % lees
White: Tank lees -> RDV	0.02	* 1 % (pipe+processing) loss assumed
RDV	0.02	* 1 % (pipe+processing) loss assumed
Tank -> centrifuge	0.62	* 0.18 % additional occluded in seed crystals (4 kg/kL * 275 kL / 2000kg/kL * 0.9 = 0.5 kL = 0.18 %) + 0.42 % normally observed
Total (%/batch)	**0.76**	
Value ($/batch)	**6293.93**	
Value (c/bottle)	**1.72**	* $3/L
Wine (final product) value loss (%/batch)	**1.90**	* 40 % white * 5 % lees * 95 % RDV recovery
Value ($/batch)	**7837.50**	
Value (c/bottle)	**2.14**	* Value halved

Table A-II (*cont.*)

(b) Energy consumption (kWh/batch)		
Pump: Wine->tank	8.73	* 275 kL @ 100 kPa (Berri Estates operating data; Estimate 30 kPa x 2 for HE + 20 kPa pipe + fittings = 80 kPa), 70 % eff.
Energy recovery (ER) + Chilling	1283.33	* ER: 8 to 3 [50 % of time], Ultrachiller 3 to -4; COPref. = 2.5
Hold period: Convective (-4 C)	144.10	* U=1 W/m2.K,A=275 m2, dT=23.3-4, COP=2.5, max=8d; Note: radiative losses negligible, solar radiation process neutral & not included
Hold period: Convective (8 C)	242.35	* Now at 8 C
Hold period: Solar insolation	440.00	* Assume 18 MJ/m2/d, 20 % ave. area, absorptivity ~ 0.5
Pump: White: Tank -> DE	8.73	* 275 kL @ 200 kPa (Berri Estates operating data
DE	180.00	* 15 h @ 30 kW
Pump: White: Tank lees -> RDV tank	0.44	* 5 % of 275 kL @ 200 kPa, 18 kL/h
Pump: RDV tank -> RDV	0.22	* 5 % of 275 kL @ 100 kPa, 4 kL/h
RDV	24.00	4 h @ 15 kW
Tank->centrifuge	38.20	* 275 kL @ 350 kPa (Berri Estate operating data), 70 % eff.
Centrifuge	450.00	* Westfalia SC150: 30 kW (ave. actual operating data) for 15 hr
Total (kWh/batch)	**2820.10**	
kWh/kL	**10.21**	
Value ($/batch)	**423.00**	
Value (c/bottle)	**0.11**	*15 c/kWh

Table A-II (*cont.*)

(c) Chemicals (inc. water) ($/batch)		
Tartrate consumption (kg/batch)	1100.00	
$/batch	5060.00	* 4.60/kg
Tartrate resale (kg/batch)	1413.50	* 1 kg/kL precipitate, 40 % recovery unseeded, 95 % seeded
$/batch	2120.25	$ 1.50/kg
Tartrate recovered (kg/batch)	313.50	
$/batch	470.25	$ 1.50/kg
Waterfill & flush lines pre-process		
Chillers	0.04	1000 L ($0.04/kL)
Centrifuge	0.04	1001 L ($0.04/kL)
DE filter	0.02	600 L ($0.04/kL)
RDV	0.01	500 L ($0.04/kL)
Clean Chillers		Water -> Caustic -> Water -> Sanitise
Water	0.04	1000 L, 4 c/kL
Caustic	13.44	1000 L, 2 % Caustic, 20 L 50 % wt Caustic, 67c/L
Water	0.04	
Citric/sulfur	2.63	1000 L, 500 g citric $5/kg, 50 g Potassium Metabisuplhite $1.74/kg
Clean tank	4.84	Same protocol, but 300 L
Clean centrifuge	16.15	Same protocol, identical volume
Bentonite	74.25	0.5 g/L $0.78/kg
DE	23.68	80 kg [22 kg/hr for 4 hr, 45 kL/hr process rate] $0.74/kg
Clean DE filter equipment & associated lines	1.85	Same protocol, except caustic performed weekly
Perlite	243.20	800 kg perlite required @ $0.76/kg
Clean lees tank, RDV	0.74	Assume same as DE filter
Total chemicals(ex tartrate) ($/batch)	**397.19**	
Total chemicals(in tartrate) ($/batch)	**5457.19**	
Net chemical cost ($/batch)	**3336.94**	

Table A-II (*cont.*)

(d) Labour requirements (h/batch)		
Plumb chillers/transfer lines	1.00	1 person x 1 h
Flush & fill product lines	0.50	2 person x 15 min
Catch wine	0.50	2 person x 15 min
Monitor fill operation	0.33	1 person x 5 min x 4
Flush lines with water & catch	0.50	2 person x 15 min
Clean & sanitise line	0.50	1 person x 1 h (50%)
Monitor cold stabilisation	0.20	1 person x 10 min x 1 d
Clean tank	1.00	1 person x 2 h (50%)
Red wine (60% of production):		
Prepare for & initiate mixing	0.15	1 person x 15 min
Flush & prepare centrifuge & lines	0.60	2 person x 30 min
Catch wine	0.30	2 person x 15 min
Monitor centrifuge	8.40	1 person x 14 h
Flush lines with water & catch	0.30	2 person x 15 min
Clean & sanitise centrifuge & lines	0.60	1 person x 1 h
White wine (40% of production):		
Prepare bentonite slurry	0.30	1 person x 1.5 h (50%)
Transfer slurry to contact tank	0.20	2 person x 15 min
Clean bentonite tank & line	0.20	1 person x 30 min (50%)
Prepare DE & flush lines	0.40	1 person x 1 h
Catch wine	0.20	2 person x 15 min
Monitor DE	3.20	1 person x 8 h
Flush with water & catch wine	0.20	2 person x 15 min
Clean & sanitise DE	0.20	1 person x 1 h (50%)
Rack off bentonite lees	0.40	1 person x 1 h
Flush line with water	0.20	2 person x 15 min
Clean & sanitise lines	0.20	1 person x 1 h (50%)
Prepare RDV	0.40	1 person x 1 h
Operate & monitor RDV	1.60	1 person x 8 h (50%)
Flush lines with water & catch	0.20	2 person x 15 min
Clean-up RDV & lines	0.20	1 person x 1 h (50%)
White centrifugation	6.90	
Seed addition	0.50	2 person x 1 h (50%)
Total (h/batch)	**30.38**	
Labour cost ($/batch)	**911.00**	* $30/h for cellar hand
Labour cost (c/bottle)	**0.25**	

Table A-III. Summary of estimation of operating costs of Option 3 –cold stabilisation by Westfalia process: (a) wine loss; (b) energy consumption; (c) chemical usage; and (d) labour requirements.

(a) Wine loss (%/batch)		
Wine->contact tank	0.04	* 0.04 % (2 x 10 sec @ 20 kL/hr) assumed
Contact tank -> hydrocyclone	0.24	* 0.25 % (2 x 1 min res. Time x 20 kL/hr x 100 % dispersion)
Hydrocyclone -> centrifuge	0.19	* 0.24 % Centrifuge/pipe loss - 0.05 % crystals
White: Tank -> DE	0.05	*(2 x 30 sec @ 20 kL/hr= 0.12 % transfer loss), 5 % lees
White: Tank lees -> RDV	0.02	* 1 % (pipe+processing) loss assumed
RDV	0.02	* 1 % (pipe+processing) loss assumed
Total (%/batch)	**0.56**	
Value ($/batch)	**4610.83**	
Value (c/bottle)	**1.26**	* $3/L
Wine (final product) value loss (%/batch)	**1.90**	* 40 % white * 5 % lees * 95 % RDV recovery
Value ($/batch)	**7837.50**	
Value (c/bottle)	**2.14**	* Value halved

Table A-III (*cont.*)

(b) Energy consumption (kWh/batch)		
Wine->contact tank	8.73	* 275 kL @ 100 kPa (Berri Estates operating data; Estimate 30 kPa x 2 for HE + 20 kPa pipe + fittings = 80 kPa, OK), 70 % eff.
Pump: Contact tank -> hydrocyclone -> centrifuge	43.65	* 275 kL @ 400 kPa (Berri Estate operating data + 50 kPa hydrocyclone), 70 % eff.
Energy recovery (ER) + Chilling	1283.33	* ER: 8 -> 3 [50 % of time], Ultrachiller 3 -> -4; COPref. = 2.5
Hold period: Convective (-4 C)	72.10	* U=1 W/m2.K,A=275 m2, dT=23.3-4, COP=2.5, max=8d; Note, radiative losses negligible, solar radiation process neutral & not included
Hold period: Convective (8 C)	282.74	* Now at 8 C
Hold period: Solar insolation	440.00	* Assume 18 MJ/m2/d, 20 % ave. area, absorptivity ~ 0.5
Seeding	0.22	* 4 g/L dosing rate
Centrifuge	450	* Westfalia SC150: 30 kW (ave. actual operating data) for 15 hr
Pump: White: Tank -> DE	8.73	* 275 kL @ 200 kPa (Berri Estates operating data
DE	180.00	* 15 hr @ 30 kW
Pump: White: Tank lees -> RDV tank	0.44	* 5 % of 275 kL @ 200 kPa, 18 kL/hr
Pump: RDV tank -> RDV	0.22	* 5 % of 275 kL @ 100 kPa, 4 kL/hr
RDV	24.00	4 hr @ 15 kW
Total (kWh/batch)	**2793.94**	
kWh/kL	**10.16**	
Value ($/batch)	**419.09**	
Value (c/bottle)	**0.11**	*15 c/kWh

Table A-III (*cont.*)

(c) Chemicals (inc. water) ($/batch)		
Tartrate consumption (kg/batch)	110.00	
$/batch	506.00	* 4.60/kg
Tartrate resale (kg/batch)	423.50	* 1 kg/kL precipitate, 40 % recovery unseeded, 95 % seeded
$/batch	635.25	$ 1.50/kg
Tartrate recovered (kg/batch)	313.50	
$/batch	470.25	$ 1.50/kg
Waterfill & flush lines pre-process		
Chillers	0.04	1000 L ($0.04/kL)
Centrifuge	0.04	1001 L ($0.04/kL)
DE filter	0.02	600 L ($0.04/kL)
RDV	0.01	500 L ($0.04/kL)
Clean Chillers ($/batch)		Water -> Caustic -> Water -> Sanitise
Water	0.04	1000 L, 4 c/kL
Caustic	13.44	1000 L, 2 % Caustic, 20 L 50 % wt Caustic, 67c/L
Water	0.04	1000 L ($0.04/kL)
Citric/sulfur	2.63	1000 L, 500 g citric $5/kg, 50 g Potassium Metabisuplhite $1.74/kg
Clean tank	4.84	Same protocol, but 300 L
Clean centrifuge	16.15	Same protocol, identical volume
Bentonite	74.25	0.5 g/L $0.78/kg
DE	23.68	80 kg [22 kg/hr for 4 hr, 45 kL/hr process rate] $0.74/kg
Clean DE filter equipment & associated lines	1.85	Same protocol, except caustic performed weekly
Perlite	243.20	800 kg perlite required @ $0.76/kg
Clean lees tank, RDV	0.74	Assume same as DE filter
Total chemicals(ex tartrate) ($/batch)	**397.19**	
Total chemicals(in tartrate) ($/batch)	**903.19**	
Net chemical cost ($/batch)	**267.94**	

Table A-III (*cont.*)

(d) Labour requirements (h/batch)		
Cold stabilisation		
Plumb chillers/transfer lines	1.00	1 person x 1 h
Flush & fill product lines	0.50	2 person x 15 min
Catch wine	0.50	2 person x 15 min
Monitor fill operation	0.33	1 person x 5 min x 4
Flush lines with water & catch	0.50	2 person x 15 min
Clean & sanitise line	0.50	1 person x 1 h (50%)
Monitor cold stabilisation	0.17	1 person x 10 min x 1 d
Clean tank	1.00	1 person x 2 h (50%)
Red wine (60% of production):		
Prepare for & initiate mixing	0.15	1 person x 15 min
Flush & prepare centrifuge & lines	0.60	2 person x 30 min
Catch wine	0.30	2 person x 15 min
Monitor centrifuge	8.40	1 person x 14 h
Flush lines with water & catch	0.30	2 person x 15 min
Clean & sanitise centrifuge & lines	0.60	1 person x 1 h
White wine (40% of production):		
Prepare bentonite slurry	0.30	1 person x 1.5 h (50%)
Transfer slurry to contact tank	0.20	2 person x 15 min
Clean bentonite tank & line	0.20	1 person x 30 min (50%)
Prepare DE & flush lines	0.40	1 person x 1 h
Catch wine	0.20	2 person x 15 min
Monitor DE	3.20	1 person x 8 h
Flush with water & catch wine	0.20	2 person x 15 min
Clean & sanitise DE	0.20	1 person x 1 h (50%)
Rack off bentonite lees	0.40	1 person x 1 h
Flush line with water	0.20	2 person x 15 min
Clean & sanitise lines	0.20	1 person x 1 h (50%)
Prepare RDV	0.40	1 person x 1 h
Operate & monitor RDV	1.60	1 person x 8 h (50%)
Flush lines with water & catch	0.20	2 person x 15 min
Clean-up RDV & lines	0.20	1 person x 1 h (50%)
White centrifugation	6.90	
Flush seed tank with wine & catch	1.00	2 person x 0.5 h
Settle seed tank & rack	1.00	2 person x 0.5 h
Flush & sanitise seed tank	2.00	2 person x 1 h (50%)
Total (h/batch)	**33.70**	
Labour cost ($/batch)	**1011.00**	* $30/h for cellar hand
Labour cost (c/bottle)	**0.28**	

Table A-IV. Summary of estimation of operating costs of Option 4 –cold stabilisation by fluidisation: (a) wine loss; (b) energy consumption; (c) chemical usage; and (d) labour requirements.

(a) Wine loss (%/batch)		
White: Tank -> DE	0.05	*(2 x 30 sec @ 20 kL/hr= 0.12 % transfer loss), 5 % lees
White: Tank lees -> RDV	0.02	* 1 % (pipe+processing) loss assumed
RDV	0.02	* 1 % (pipe+processing) loss assumed
Wine -> fluidised bed -> centrifuge	0.66	* 0.24 % Fluidised bed (20min/60 min * 20 kL/hr * 10 % dispersion) + 0.42 % [Centrifuge/pipe transfer] losses
Total (%/batch)	**0.75**	
Value ($/batch)	**6,175.00**	
Value (c/bottle)	**1.68**	* $3/L
Wine (final product) value loss (%/batch)	**1.90**	* 40 % white * 5 % lees * 95 % RDV recovery
Value ($/batch)	**7,837.50**	
Value (c/bottle)	**2.14**	* Value halved

(b) Energy consumption (kWh/batch)		
Energy recovery + Chilling	1,283.33	* ER: 8 -> 3 [50 % of time], Ultrachiller 3 -> -4; COPref. = 2.5
Hold period: Convective (8 C)	323.14	* Now at 8 C
Hold period: Solar insolation	440.00	* Assume 18 MJ/m2/d, 20 % ave. area, absorptivity ~ 0.5
Centrifuge	450.00	* Westfalia SC150: 30 kW (ave. actual operating data) for 15 hr
Pump: White: Tank -> DE	8.73	* 275 kL @ 200 kPa (Berri Estates operating data
DE	180.00	* 15 hr @ 30 kW
Pump: White: Tank lees -> RDV tank	0.44	* 5 % of 275 kL @ 200 kPa, 18 kL/hr
Pump: RDV tank -> RDV	0.22	* 5 % of 275 kL @ 100 kPa, 4 kL/hr
RDV	24.00	4 hr @ 15 kW
Pump: Wine -> fluidised bed -> centrifuge	43.65	* 275 kL @ 400 kPa (Berri Estate operating data + 50 kPa fluidised bed pressure drop), 70 % eff.
Total (kWh/batch)	**2,753.51**	
kWh/kL	**10.01**	
Value ($/batch)	**413.03**	
Value (c/bottle)	**0.11**	*15 c/kWh

Table A-IV (*cont.*)

(c) Chemicals (inc. water) ($/batch)		
Tartrate consumption (kg/batch)	220.00	
$/batch	1,012.00	* 4.60/kg
Tartrate resale (kg/batch)	533.50	* 1 kg/kL precipitate, 40 % recovery unseeded, 95 % seeded
$/batch	800.25	$ 1.50/kg
Tartrate recovered (kg/batch)	313.50	
$/batch	470.25	$ 1.50/kg
Fluidised bed cleaning cycle ($/batch)		
Fill & flush lines with water	0.08	10000 L ($0.04/L)
Sanitise citric/sulfur	26.27	10000 L ($0.04/L)
Clean Chillers ($/batch)		
Water	0.04	1000 L, 4 c/kL
Caustic	13.44	1000 L, 2 % Caustic, 20 L 50 % wt Caustic, 67c/L
Water	0.04	1000 L ($0.04/kL)
Citric/sulfur	2.63	1000 L, 500 g citric $5/kg, 50 g Potassium Metabisuplhite $1.74/kg
Flush and perserved fluidised bed	6.69	500ppm SO2 $2.66/kg, V = 5kL
Clean Centrifuge	16.15	
Bentonite	74.25	0.5 g/L $0.78/kg
DE	23.68	80 kg [22 kg/hr for 4 hr, 45 kL/hr process rate] $0.74/kg
Clean DE filter equipment & associated lines	1.85	Same protocol, except caustic performed weekly
Perlite	243.20	800 kg perlite required @ $0.76/kg
Clean lees tank, RDV	0.74	Assume same as DE filter
Total chemicals(ex tartrate) ($/batch)	**409.06**	
Total chemicals(in tartrate) ($/batch)	**1,421.06**	
Net chemical cost ($/batch)	**620.81**	

Table A-IV (*cont.*)

(d) Labour requirements (h/batch)		
Centrifugation of wine	14.00	1 person x 14 h
Plumb chillers/transfer lines/pre centrifuge	1.00	1 person x 1 h
Flush & fill bed/centrifuge & pipework	1.00	2 person x 30 min
Catch wine	1.00	2 person x 30 min
Operate & monitor Fluidised bed	7.50	1 person x 15 h (50%)
Flush with water & catch wine	1.00	2 person x 30 min
Clean & sanitise feed lines	0.50	1 person x 1 h (50%)
Clean & sanitise centrifuge & lines	1.00	1 person x 1 h
Sanitise fluidised bed	1.00	1 person x 1 h
White wine (40% of production):		
Prepare bentonite slurry	0.30	1 person x 1.5 h (50%)
Transfer slurry to contact tank	0.20	2 person x 15 min
Clean bentonite tank & line	0.20	1 person x 30 min (50%)
Prepare DE & flush lines	0.40	1 person x 1 h
Catch wine	0.20	2 person x 15 min
Monitor DE	3.20	1 person x 8 h
Flush with water & catch wine	0.20	2 person x 15 min
Clean & sanitise DE	0.20	1 person x 1 h (50%)
Rack off bentonite lees	0.40	1 person x 1 h
Flush line with water	0.20	2 person x 15 min
Clean & sanitise lines	0.20	1 person x 1 h (50%)
Prepare RDV	0.40	1 person x 1 h
Operate & monitor RDV	1.60	1 person x 8 h (50%)
Flush lines with water & catch	0.20	2 person x 15 min
Clean-up RDV & lines	0.20	1 person x 1 h (50%)
Total (h/batch)	**36.10**	
Labour cost ($/batch)	**1,083.00**	* $30/h for cellar hand
Labour cost (c/bottle)	**0.30**	

Table A-V. Summary of estimation of operating costs of Option 5 –nanofiltration with centrifugation: (a) wine loss; (b) consumables; (c) energy consumption; (d) chemical usage; and (e) labour requirements.

(a) Wine loss (%/batch)		
White: Tank -> DE	0.05	*(2 x 30 sec @ 20 kL/hr= 0.12 % transfer loss), 5 % lees
White: Tank lees -> RDV	0.02	* 1 % (pipe+processing) loss assumed
RDV	0.02	* 1 % (pipe+processing) loss assumed
Wine -> centrifuge	0.37	* 0.42 % centrifuge - 0.05 % crystals
Nanofiltration step	0.05	* (Dia = 8 in.; L = 40 in.; Vol = pi/4*(8*2.54/100)^2*(40*2.54/100); 6 vessels x 3 membranes; 50% filled; 10% loss), 0.04% transfer loss
Retentate -> centrifuge	0.17	* 0.05 % crystals + 0.12 % Centrifuge/pipe transfer losses
Rententate/Permeate -> blend tank	0.04	* 0.04 % (2 x 10 sec @ 20 kL/hr) assumed
Total (%/batch)	**0.72**	
Value ($/batch)	**5930.63**	
Value (c/bottle)	**1.62**	* $3/L
Wine (final product) value loss (%/batch)	**1.90**	* 40 % white * 5 % lees * 95 % RDV recovery
Value ($/batch)	**7837.50**	
Value (c/bottle)	**2.14**	* Value halved

(b) Consumables		
NF membranes ($/batch)	**139.18**	4 x 2 array (6 in total), 4 x 8" elements per vessel, $1500 per element, replaced biannually, 3 plants

Table A-V (*cont.*)

(c) Energy consumption (kWh/batch)		
Hold period: Convective (8 C)	323.14	* Now at 8 C
Hold period: Solar insolation	440.00	* Assume 18 MJ/m2/d, 20 % ave. area, absorptivity ~ 0.5
Pump: Red: Tank->centrifuge		* 275 kL @ 350 kPa (Berri Estate operating data), 70 % eff.
Centrifuge: Red		* Westfalia SC150: 30 kW (ave. actual operating data) for 15 hr
Pump: White: Tank -> DE	8.73	* 275 kL @ 200 kPa (Berri Estates operating data
DE	168.00	* 14 hr @ 30 kW
Pump: White: Tank lees -> RDV tank	0.44	* 5 % of 275 kL @ 200 kPa, 18 kL/hr
Pump: RDV tank -> RDV	0.22	* 5 % of 275 kL @ 100 kPa, 4 kL/hr
RDV	24.00	4 hr @ 15 kW
Pump: Wine -> centrifuge	38.61	* 275 kL @ 350 kPa (Berri Estate operating data), 70 % eff.
Centrifuge	450.00	* Westfalia SC150: 30 kW (ave. actual operating data) for 15 hr
Pump: Nanofiltration step	163.69	* 15 Bar, 50 % recovery
Pump: Retentate -> centrifuge	19.31	* 139 kL @ 350 kPa
Centrifuge: Retentate	225.00	* Westfalia SC150: 30 kW (ave. actual operating data) for 7.5 hr
Rententate/Permeate -> blend tank	8.73	* 0.06 % (2 x 15 sec @ 20 kL/hr) assumed
Total (kWh/batch)	**1881.86**	
kWh/kL	**6.84**	
Value ($/batch)	**282.28**	
Value (c/bottle)	**0.08**	*15 c/kWh

Table A-V (*cont.*)

(d) Chemicals (inc. water) ($/batch)		
Tartrate consumption (kg/batch)	0.00	
$/batch	0.00	* 4.60/kg
Tartrate resale (kg/batch)	156.75	* 1 kg/kL precipitate, 40 % recovery unseeded, 95 % seeded
$/batch	156.75	$ 1.50/kg
Tartrate recovered (kg/batch)	235.13	
$/batch	235.13	$ 1.50/kg
Clean centrifuge	74.25	Same protocol, identical volume
Bentonite	23.68	0.5 g/L $0.78/kg
DE	1.85	80 kg [22 kg/hr for 4 hr, 45 kL/hr process rate] $0.74/kg
Clean DE filter equipment & associated lines	243.20	Same protocol, except caustic performed weekly
Perlite	0.74	800 kg perlite required @ $0.76/kg
Fill & flush centrifuge line	0.04	
Clean centrifuge	16.15	
Clean feed tank	4.84	
Fill & flush NF & lines	0.04	
Clean NF	12.04	1000 L water, 1 kg Osmoclean $12/kg
Sanitise NF& ancillary pipework	2.63	
Fill & flush centrifuge line	0.04	
Clean centrifuge	16.15	
Clean retentate tank	4.84	
Fill & flush permeate lines	0.04	
Clean permeate tank	4.84	
Fill & flush blen line	0.04	
Clean blend tank	4.84	
Total chemicals(ex tartrate) ($/batch)	**410.26**	
Total chemicals(in tartrate) ($/batch)	**410.26**	
Net chemical cost ($/batch)	**253.51**	

Table A-V (*cont.*)

(e) Labour requirements (h/batch)		
Flush & prepare centrifuge & lines	1.0	2 person x 30 min
Catch wine	0.5	2 person x 15 min
Monitor centrifuge	14.0	1 person x 14 h
Flush lines with water & catch	0.5	2 person x 15 min
Clean & sanitise centrifuge & lines	1.0	1 person x 1 h
Flush lines & NF with water	0.50	1 person x 30 min
Catch wine	0.33	2 person x 10 min
Operate & monitor process	2.80	1 person x 14 hr (20%)
Catch wine	0.33	2 person x 10 min
Clean & santise feed lines	0.38	1 person x 1.5 hr (50%) (simultaneous with cleang NF)
Clean & sanitise NF	0.38	1 person x 1.5 hr (50%)
Clean & sanitise feed tank	0.50	1 person x 1 hr (50%)
Retentate -> centrifuge		
Flush with water & catch wine	0.33	2 person x 10 min
Operate & monitor centrifuge	6.88	1 person x 7 hr (assume 50% recovery)
Clean & sanitise centrifuge & lines	1.00	1 person x 1 hr
Flush retentate & permeate lines & catch wine	0.34	2 person x 10 min (simultaneous process with catching permeate)
Monitor retentate & permeate transfer	0.66	2 person x 4 x 5 min
Catch wine retentate line	0.17	2 person x 10 min (simultaneous process with catching permeate)
Catch wine permeate line	0.17	2 person x 10 min
Clean & sanitise lines	0.50	1 person x 30 min x 2 (50%)
White wine (40% of production):		
Prepare bentonite slurry	0.3	1 person x 1.5 h (50%)
Transfer slurry to contact tank	0.2	2 person x 15 min
Clean bentonite tank & line	0.2	1 person x 30 min (50%)
Prepare DE & flush lines	0.4	1 person x 1 h
Catch wine	0.2	2 person x 15 min
Monitor DE	3.2	1 person x 8 h
Flush with water & catch wine	0.2	2 person x 15 min
Clean & sanitise DE	0.2	1 person x 1 h (50%)
Rack off bentonite lees	0.4	1 person x 1 h
Flush line with water	0.2	2 person x 15 min
Clean & sanitise lines	0.2	1 person x 1 h (50%)
Prepare RDV	0.4	1 person x 1 h
Operate & monitor RDV	1.6	1 person x 8 h (50%)
Flush lines with water & catch	0.2	2 person x 15 min
Clean-up RDV & lines	0.2	1 person x 1 h (50%)
N2 sparge to mix wine	0.05	1 person x 30 min x 2 (5%)
Total (h)	**40.41**	
Labour cost ($/batch)	**1212.25**	* $30/h for cellar hand
Labour cost (c/bottle)	**0.33**	

Table A-VI. Summary of estimation of operating costs of Option 6 –electrodialysis: (a) wine loss; (b) consumables; (c) energy consumption; (d) chemical usage; and (e) labour requirements.

(a) Wine loss (%/batch)		
White: Tank -> DE	0.05	*(2 x 30 sec @ 20 kL/hr= 0.12 % transfer loss), 5 % lees
White: Tank lees -> RDV	0.02	* 1 % (pipe+processing) loss assumed
RDV	0.02	
Wine -> centrifuge	0.37	* Same as nanofiltration pre-clarification step
Electrodialysis	0.24	* 0.12 % (10 min res. Time @ 20 kL/hr * 10 % breakthough) + 0.12 % pipe losses
Total (%/batch)	**0.70**	
Value ($/batch)	**5752.50**	
Value (c/bottle)	**1.57**	* $3/L
Wine (final product) value loss (%/batch)	**1.90**	* 40 % white * 5 % lees * 95 % RDV recovery
Value ($/batch)	**7837.50**	
Value (c/bottle)	**2.14**	* Value halved

(b) Consumables		
Electrodialysis membrane replacement & maintenance ($/batch)	**3160.00**	1.15 c/L (from unit supplier)

Table A-VI (*cont.*)

(c) Energy consumption (kWh/batch)		
Hold period: Convective (8 C)	323.14	* Now at 8 C
Hold period: Solar insolation	440.00	* Assume 18 MJ/m2/d, 20 % ave. area, absorptivity ~ 0.5
Pump: Red: Tank->centrifuge		* 275 kL @ 350 kPa (Berri Estate operating data), 70 % eff.
Centrifuge: Red		* Westfalia SC150: 30 kW (ave. actual operating data) for 15 hr
Pump: White: Tank -> DE	8.73	* 275 kL @ 200 kPa (Berri Estates operating data
DE	168.00	* 14 hr @ 30 kW
Pump: White: Tank lees -> RDV tank	0.44	* 5 % of 275 kL @ 200 kPa, 18 kL/hr
Pump: RDV tank -> RDV	0.22	* 5 % of 275 kL @ 100 kPa, 4 kL/hr
RDV	24.00	4 hr @ 15 kW
Pump: Wine -> centrifuge	38.61	* Same as nanofiltration pre-clarification step
Centrifuge	450.00	
Electrodialysis	742.50	* 2.7 kWh/kL assumed
Total (kWh/batch)	**2207.63**	
kWh/kL	**8.03**	
Value ($/batch)	**331.14**	
Value (c/bottle)	**0.09**	*15 c/kWh

Table A-VI (*cont.*)

(d) Chemicals (inc. water) ($/batch)		
Tartrate consumption (kg/batch)	0.00	
$/batch	0.00	* 4.60/kg
Tartrate resale (kg/batch)	0.00	* 1 kg/kL precipitate, 40 % recovery unseeded, 95 % seeded
$/batch	0.00	$ 1.50/kg
Tartrate recovered (kg/batch)	0.00	
$/batch	0.00	
Bentonite	74.25	0.5 g/L $0.78/kg
DE	23.68	80 kg [22 kg/hr for 4 hr, 45 kL/hr process rate] $0.74/kg
Clean DE filter equipment & associated lines	1.85	Same protocol, except caustic performed weekly
Perlite	243.20	800 kg perlite required @ $0.76/kg
Clean lees tank, RDV	0.74	Assume same as DE filter
Fill & flush centrifuge line	0.04	
Clean centrifuge	16.15	
Clean feed tank	4.84	
Cleaning electrodialysis unit		
Nitric acid	125.77	72.7 L ($1.73/ L) concentrated for electrode solutions
NaCl	1.16	1.32 kg ($0.88 /kg) concentrated for electrode solutions?
Potassium Nitrate	9.46	4.3kg ($2.2 /kg) for electrode solutions?
KCl	56.32	32kg ($1.76/ kg) for diluent solutions?
Water	1.73	Assume 1000 L for electrode solutions + 15 L/100 L for diluent?
Cleaning cycle	16.15	Same as for centrifuge
Flush & fill product lines	0.04	Assume 1000 L water
Clean product tank	4.84	
Total chemicals(ex tartrate) ($/batch)	580.23	
Total chemicals(in tartrate) ($/batch)	580.23	
Net chemical cost ($/batch)	580.23	

Table A-VI (*cont.*)

(e) Labour requirements (h/batch)		
Preclarification		
Flush & prepare centrifuge & lines	1.00	2 person x 30 min
Catch wine	0.50	2 person x 15 min
Monitor centrifuge	14.00	1 person x 14 h
Flush lines with water & catch	0.50	2 person x 15 min
Clean & sanitise centrifuge & lines	1.00	1 person x 1 h
Prepare electrodialysis electrode & collection solutions	1.00	1 person x 1 hr
Flush lines, catch, operate & monitor, flush & clean & sanitise	5.22	Same as NF
Clean & sanitise EDR	2.25	Clean after every 100kL processed (3*1.5h; 50%man hour)
White wine bentonite fining	8.10	
Dispose EDR electrode & collection solutions	0.50	1 person x 30 min
Total (h/batch)	**34.07**	
Labour cost ($/batch)	**1022.00**	* $30/h for cellar hand
Labour cost (c/bottle)	**0.28**	

A.2 Calculation of Capital Cost

Capital cost estimation under retrofit and greenfield scenarios was made by standard engineering practices, i.e. refer Peters and Timmerhaus (1991), using a combination of methods. This involved scaling and updating equipment costs from historical data, applying Lang factors and taking into account of usage of equipment for particular process as well as direct quotation from suppliers for equipment or entire plant.

For retrofit investigations, equipment already in place at Berri Estates Winery was taken into account when considering new capital investment required

Table A-VII. Summary of capital cost of Option 1- cold stabilisation.

	Derate		Lang factor		Unit Cost	No. of Equipment		Cost (10^3 of AUD)	
Equipment	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**	**(10^3 of AUD)**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Transfer centrifugal pump, 45 kL/h	60%	60%	1.5	2.3	14	0	3	0	58
Heat exchanger [energy recovery]	80%	80%	2	3.15	18	0	3	0	136
Ultracooler	80%	80%	2	3.15	50	0	3	0	378
Insulated jacketed tank, 278 kL	60%	60%	2	3.15	98	0	6	0	1111
DE filter feed pump, centrifugal, 45 kL/h	70%	70%	1.5	2.3	14	0	3	0	68
DE filtration, 35 kL/h, 80 micron	70%	70%	1.5	2.3	129	0	3	0	623
Lees pump, positive displacement, 3 kL/h	70%	70%	1.5	2.3	12	0	3	0	58
RDV filtration, $30m^2$, 2 kL/h	80%	80%	1.5	2.3	130	0	3	0	718
Centrifuge feed pump, 45 kL/h	60%	60%	1.5	2.3	14	0	4	0	77
Centrifuge SC150, 20 kL/h [inc. hydrocyclone]	60%	60%	1.5	2.3	500	0	4	0	2760
Bentonite fining tanks	60%	60%	2	3.15	98	0	3	0	556
Refrigeration system, 30 % capacity increase	100%	100%	2	3.15	95	0	1	0	299
Direct Cost Sub-totals								0	6840
Design & project management			0.1					0	680
Contractors' fees			0.1					0	680
In-direct cost Sub-total								0	8200
Contingency			0.1					0	820
Capital cost (10^3 of AUD)								**0**	**9020**

Table A-VIII. Summary of capital cost of Option 2- cold stabilisation with seeding.

	Derate		Lang factor		Unit Cost	No. of Equipment		Cost (10^3 of AUD)	
Equipment	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**	**(10^3 of AUD)**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Transfer centrifugal pump, 45 kL/h	60%	60%	1.5	2.3	14		3		58
Heat exchanger [energy recovery]	80%	80%	2	3.15	18		3		136
Ultracooler	80%	80%	2	3.15	50		3		378
Insulated jacketed tank, 278 kL	60%	60%	2	3.15	98		6		1111
DE filter feed pump, centrifugal, 45 kL/h	70%	70%	1.5	2.3	14		3		68
DE filtration, 35 kL/hr, 80 micron	70%	70%	1.5	2.3	129		3		623
Lees pump, positive displacement, 3 kL/h	70%	70%	1.5	2.3	12		3		58
RDV filtration, 30m^2, 2 kL/h	80%	80%	1.5	2.3	130		3		718
Mixing tank, 5 kL+ Agitator	100%	100%	2	0	20	3	3	120	189
Dosing pump, positive displacement, 1 kL/h	100%	100%	1.5	2.3	5	3	3	23	35
Centrifuge feed pump, 45 kL/h	60%	60%	1.5	2.3	14	1	4	13	77
Centrifuge SC150, 20 kL/h	60%	60%	1.5	2.3	500	1	4	450	2760
Bentonite fining tanks	60%	60%	2	3.15	98	3	3	353	556
Refrigeration system, 25 % capacity increase	100%	100%	2	3.15	85		1		268
Direct Cost Sub-totals								960	7030
Design & project management			0.1					100	700
Contractors' fees			0.1					100	700
In-direct cost Sub-total								1160	8430
Contingency			0.1					120	840
Capital cost (10^3 of AUD)								**1280**	**9270**

Table A-IX. Summary of capital cost of Option 3- cold stabilisation by Westfalia process.

	Derate		Lang factor		Unit Cost	No. of Equipment		Cost (10^3 of AUD)	
Equipment	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**	**(10^3 of AUD)**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Transfer centrifugal pump, 45 kL/h	60%	60%	1.5	2.3	14		3		58
Heat exchanger [energy recovery]	80%	80%	2	3.15	18		3		136
Ultracooler	80%	80%	2	3.15	50		3		378
Insulated jacketed tank, 278 kL	60%	60%	2	3.15	98		6		1111
DE filter feed pump, centrifugal, 45 kL/h	70%	60%	1.5	2.3	14		3		58
DE filtration, 35 kL/h, 80 micron	70%	80%	1.5	2.3	129		3		712
Lees pump, positive displacement, 3 kL/h	70%	70%	1.5	2.3	12		3		58
RDV filtration, 30m^2, 2 kL/h	80%	80%	1.5	2.3	130		3		718
Tartrate tank, 10 kL+ Agitator	100%	100%	2	0	30	3	3	180	284
Dosing pump, positive displacement, 1 kL/h	100%	100%	1.5	2.3	5	3	3	23	35
Centrifuge feed pump, 45 kL/h	60%	60%	1.5	2.3	14	1	4	13	77
Hydrocyclone	100%	100%	2	3.15	20	3	3	120	189
Centrifuge SC150, 20 kL/h	60%	60%	1.5	2.3	500	1	4	450	2760
Bentonite fining tanks	60%	60%	2	3.15	98	3	3	353	556
Refrigeration system, 25 % capacity increase		100%	2	3.15	85		1		268
Direct Cost Sub-totals								1140	7400
Design & project management			0.1					110	740
Contractors' fees			0.1					110	740
In-direct cost Sub-total								1360	8880
Contingency			0.1					140	890
Capital cost (10^3 of AUD)								**1500**	**9770**

Table A-X. Summary of capital cost of Option 4- cold stabilisation by fluidisation.

	Derate		Lang factor		Unit Cost	No. of Equipment		Cost (10^3 of AUD)	
Equipment	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**	**(10^3 of AUD)**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Feed centrifugal pump, 45 kL/h	60%	60%	1.5	2.3	14		3		58
Heat exchanger [energy recovery]	80%	80%	2	3.15	18		3		136
Ultracooler	80%	80%	2	3.15	50		3		378
DE filter feed pump, cent., 45 kL/h	70%	70%	1.5	2.3	14		3		68
DE filtration, 35 kL/h, 80 micron	70%	70%	1.5	2.3	129		3		623
Lees pump, positive displacement, 3 kL/h	100%	100%	1.5	2.3	12		3		83
RDV filtration, 30m^2, 2 kL/h	80%	80%	1.5	2.3	130		3		718
Crystalliser, 20 kL/h	100%	100%	2	3.15	110	3	3	660	1040
Centrifugal Feed pump, 45 kL/h	60%	60%	1.5	2.3	14	1	4	13	77
Centrifuge SC150, 20 kL/h	60%	60%	1.5	2.3	500	1	4	450	2760
Bentonite fining tanks	60%	60%	2	3.15	98	3	3	353	556
Refrigeration system, 25 % capacity increase		100%	2	3.15	85		1		268
Direct Cost Sub-totals								1480	6760
Design & project management			0.1					150	680
Contractors' fees			0.1					150	680
In-direct cost Sub-total								1780	8120
Contingency			0.1					180	810
Capital cost (10^3 of AUD)								**1960**	**8930**

Table A-XI. Summary of capital cost of Option 5- nanofiltration with centrifugation.

	Derate		**Lang factor**		**Unit Cost**	**No. of Equipment**		**Cost (10^3 of AUD)**	
Equipment	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**	**(10^3 of AUD)**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Feed centrifugal pump, 45 kL/h	60%	60%	1.5	2.3	14	2	3	25	58
Centrifuge SC150, 20 kL/h	60%	60%	1.5	2.3	500	2	3	900	2070
Insulated jacketed tank, 278 kL	60%	60%	2	3.15	98		3		556
DE filter feed pump, cent., 45 kL/h	70%	70%	1.5	2.3	14		3		68
DE filtration, 35 kL/h, 80 micron	70%	70%	1.5	2.3	129		3		623
Lees pump, positive displacement, 3 kL/h	70%	70%	1.5	2.3	12		3		58
RDV filtration, 30m^2, 2 kL/h	80%	80%	1.5	2.3	130		3		718
NF plant, 20 kL/h [feed pump included]	80%	80%	1.5	2.3	490	3	3	1764	2705
Retentate tank, 139 kL	80%	80%	2	3.15	65	3	3	312	491
Permeate tank, 139 kL	80%	80%	2	3.15	65	3	3	312	491
Feed pump, centrifugal, 45 kL/h	60%	60%	1.5	2.3	14	1	4	13	77
Centrifuge SC150, 20 kL/h	60%	60%	1.5	2.3	500	1	4	450	2760
Bentonite fining tanks	60%	60%	2	3.15	98	3	3	353	556
Direct Cost Sub-totals								4130	11230
Design & project management			0.1					410	1120
Contractors' fees			0.1					410	1120
In-direct cost Sub-total								4950	13470
Contingency			0.1					500	1350
Capital cost (10^3 of AUD)								**5450**	**14820**

Table A-XII. Summary of capital cost of Option 6- electrodialysis.

	Derate		**Lang factor**		**Unit Cost**	**No. of Equipment**		**Cost (10^3 of AUD)**	
Equipment	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**	**(10^3 of AUD)**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Feed centrifugal pump, 45 kL/h	60%	60%	1.5	2.3	14	1	4	12.6	77.28
Centrifuge SC150, 20 kL/h	60%	60%	1.5	2.3	500	1	4	450	2760
DE filter feed pump, centrifugal, 45 kL/h	70%	70%	1.5	2.3	14		3		68
DE filtration, 35 kL/h, 80 micron	70%	70%	1.5	2.3	129		3		623
Lees pump, positive displacement, 3 kL/h	70%	70%	1.5	2.3	12		3		58
RDV filtration, 30m^2, 2 kL/h	80%	80%	1.5	2.3	130		3		718
Electrodialysis system, 20 kL/h	100%	100%	1.5	2.3	1550	3	3	6975	10695
Bentonite fining tanks	60%	60%	2	3.15	98	3	3	352.8	555.66
Insulated jacketed tank, 278 kL	60%	60%	2	3.15	98		3		555.66
Direct Cost Sub-totals			0.1					7790	16110
Design & project management			0.1					780	1610
Contractors' fees								780	1610
In-direct cost Sub-total			0.1					9350	19330
Contingency								940	1930
Capital cost (10^3 of AUD)								**10290**	**21260**

A.3 Estimation of Maintenance Cost

Where specific information was not available, standard heuristics were assumed for estimation of annual maintenance costs: 5% value for mechanical and electrical equipment; and 2% for civil, structural and process equipment. Usage of the equipment for the particular process is taken into account in maintenance cost as well.

Table A-XIII. Summary of maintenance cost of Option 1 – cold stabilisation.

		Actual maintenance %		**Cost (10^3 of AUD)**	
Equipment	**Maintenance %**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Transfer centrifugal pump, 45 kL/h	5.0%	3.5%	3.0%	1.32	1.74
Heat exchanger [energy recovery]	2.0%	2.0%	2.0%	1.73	2.72
Ultracooler	2.0%	2.0%	2.0%	4.80	7.56
Insulated jacketed tank, 278 kL	2.0%	2.0%	2.0%	14.11	22.23
DE filter feed pump, centrifugal, 45 kL/h	5.0%	3.5%	3.0%	1.54	2.03
DE filtration, 35 kL/h, 80 micron	2.0%	2.0%	2.0%	8.13	12.46
Lees pump, positive displacement, 3 kL/h	5.0%	3.5%	3.0%	1.32	1.74
RDV filtration, 30m^2, 2 kL/h	5.0%	3.5%	3.0%	16.38	21.53
Centrifuge feed pump, 45 kL/h	5.0%	3.5%	3.0%	1.32	2.32
Centrifuge SC150, 20 kL/h [inc. hydrocyclone]	5.0%	3.5%	3.0%	47.25	82.80
Bentonite fining tanks	2.0%	2.0%	2.0%	0.00	11.11
Refrigeration system, 30 % capacity increase	5.0%	3.5%	3.0%	6.65	8.98
Total maintenance (10^3 AUD/yr)				**100.00**	**180.00**
($/batch)				**257.73**	**463.92**

Table A-XIV. Summary of maintenance cost of Option 2 – cold stabilisation with seeding.

		Actual maintenance %		Cost (10^3 of AUD)	
Equipment	**Maintenance %**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Transfer centrifugal pump, 45 kL/h	5.0%	3.5%	3.0%	1.32	1.74
Heat exchanger [energy recovery]	2.0%	2.0%	2.0%	1.73	2.72
Ultracooler	2.0%	2.0%	2.0%	4.80	7.56
Insulated jacketed tank, 278 kL	2.0%	2.0%	2.0%	14.11	22.23
DE filter feed pump, centrifugal, 45 kL/h	5.0%	3.5%	3.0%	1.54	2.03
DE filtration, 35 kL/h, 80 micron	2.0%	2.0%	2.0%	8.13	12.46
Lees pump, positive displacement, 3 kL/h	5.0%	3.5%	3.0%	1.32	1.74
RDV filtration, 30m^2, 2 kL/h	5.0%	3.5%	3.0%	16.38	21.53
Mixing tank, 5 kL+ Agitator	5.0%	3.5%	3.0%	4.20	5.67
Dosing pump, pos disp, 1 kL/h	5.0%	3.5%	3.0%	0.79	1.04
Centrifuge feed pump, 45 kL/h	5.0%	3.5%	3.0%	1.76	2.32
Centrifuge SC150, 20 kL/h	5.0%	3.5%	3.0%	63.00	82.80
Bentonite fining tanks	2.0%	2.0%	2.0%	7.06	11.11
Refrigeration system, 25 % capacity increase	5.0%	3.5%	3.0%	6.65	8.03
Total maintenance (10^3 AUD/yr)				**130.00**	**180.00**
($/batch)				**335.05**	**463.92**

Table A-XV. Summary of maintenance cost of Option 3 – cold stabilisation by Westafalia process.

Equipment	Maintenance %	Actual maintenance % Retrofit	Actual maintenance % Greenfield	Cost (10^3 of AUD) Retrofit	Cost (10^3 of AUD) Greenfield
Transfer centrifugal pump, 45 kL/h	5.0%	3.5%	3.0%	1.32	1.74
Heat exchanger [energy recovery]	2.0%	2.0%	2.0%	1.73	2.72
Ultracooler	2.0%	2.0%	2.0%	4.80	7.56
Insulated jacketed tank, 278 kL	2.0%	2.0%	2.0%	14.11	22.23
DE filter feed pump, centrifugal, 45 kL/h	5.0%	3.5%	3.0%	1.54	2.03
DE filtration, 35 kL/h, 80 micron	2.0%	2.0%	2.0%	8.13	12.46
Lees pump, positive displacement, 3 kL/h	5.0%	3.5%	3.0%	1.32	1.74
RDV filtration, 30m^2, 2 kL/h	5.0%	3.5%	3.0%	16.38	21.53
Tartrate tank, 10 kL+ Agitator	5.0%	3.5%	3.0%	6.30	8.51
Dosing pump, pos disp, 1 kL/h	5.0%	3.5%	3.0%	0.79	1.04
Centrifuge feed pump, 45 kL/h	5.0%	3.5%	3.0%	1.76	2.32
Hydrocyclone	2.0%	2.0%	2.0%	2.40	3.78
Centrifuge SC150, 20 kL/h	5.0%	3.5%	3.0%	63.00	82.80
Bentonite fining tanks	2.0%	2.0%	2.0%	7.06	11.11
Refrigeration system, 25 % capacity increase	5.0%	3.5%	3.0%	6.65	8.03
Total maintenance (10^3 AUD/yr)				**140.00**	**180.00**
($/batch)				**360.82**	**463.92**

Table A-XVI. Summary of maintenance cost of Option 4 – cold stabilisation by fluidisation.

		Actual maintenance %		Cost (10^3 of AUD)	
Equipment	**Maintenance %**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Feed centrifugal pump, 45 kL/h	5.0%	3.5%	3.0%	1.32	1.74
Heat exchanger [energy recovery]	2.0%	2.0%	2.0%	1.73	2.72
Ultracooler	2.0%	2.0%	2.0%	4.80	7.56
DE filter feed pump, centrifugal, 45 kL/h	5.0%	3.5%	3.0%	14.11	2.03
DE filtration, 35 kL/h, 80 micron	2.0%	2.0%	2.0%	1.54	12.46
Lees pump, positive displacement, 3 kL/h	5.0%	3.5%	3.0%	8.13	1.74
RDV filtration, 30m^2, 2 kL/h	5.0%	3.5%	3.0%	1.32	21.53
Crystalliser, 20 kL/h	2.0%	2.0%	2.0%	13.20	20.79
Centrifugal Feed pump, 45 kL/h	5.0%	3.5%	3.0%	63.00	82.80
Centrifuge SC150, 20 kL/h	2.0%	2.0%	2.0%	14.11	11.11
Bentonite fining tanks	2.0%	2.0%	2.0%	7.06	11.11
Refrigeration system, 25 % capacity increase	5.0%	3.5%	3.0%	6.65	8.03
Total maintenance (10^3 AUD/yr)				**140.00**	**190.00**
($/batch)				**360.82**	**489.69**

Table A-XVII. Summary of maintenance cost of Option 5 – nanofiltration (combined with centrifugation).

		Actual maintenance %		Cost (10^3 of AUD)	
Equipment	**Maintenance %**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Feed centrifugal pump, 45 kL/h	5.0%	3.5%	3.0%	2.21	1.74
Centrifuge SC150, 20 kL/h	5.0%	3.5%	3.0%	78.75	62.10
Insulated jacketed tank, 278 kL	2.0%	2.0%	2.0%	0.00	11.11
DE filter feed pump, centrifugal, 45 kL/h	5.0%	3.5%	3.0%	1.54	2.03
DE filtration, 35 kL/h, 80 micron	2.0%	2.0%	2.0%	8.13	12.46
Lees pump, positive displacement, 3 kL/h	5.0%	3.5%	3.0%	1.32	1.74
RDV filtration, 30m^2, 2 kL/h	5.0%	3.5%	3.0%	16.38	21.53
NF plant, 20 kL/h [feed pump included]	5.0%	3.5%	3.0%	61.74	81.14
Retentate tank, 139 kL	2.0%	2.0%	2.0%	6.24	9.83
Permeate tank, 139 kL	5.0%	3.5%	3.0%	0.44	2.32
Feed pump, cent., 45 kL/h	5.0%	3.5%	3.0%	15.75	82.80
Centrifuge SC150, 20 kL/h	2.0%	2.0%	2.0%	7.06	11.11
Bentonite fining tanks	2.0%	2.0%	2.0%	14.11	11.11
Total maintenance (10^3 AUD/yr)				**210.00**	**310.00**
($/batch)				**541.24**	**798.97**

Table A-XVIII. Summary of maintenance cost of Option 5 – electrodialysis.

		Actual maintenance %		Cost (10^3 of AUD)	
Equipment	**Maintenance %**	**Retrofit**	**Greenfield**	**Retrofit**	**Greenfield**
Feed centrifugal pump, 45 kL/h	5.0%	3.5%	3.0%	1.76	2.32
Centrifuge SC150, 20 kL/h	5.0%	3.5%	3.0%	63.00	82.80
DE filter feed pump, centrifugal, 45 kL/h	5.0%	3.5%	3.0%	1.54	2.03
DE filtration, 35 kL/h, 80 micron	2.0%	2.0%	2.0%	8.13	12.46
Lees pump, positive displacement, 3 kL/h	5.0%	3.5%	3.0%	1.32	1.74
RDV filtration, 30m^2, 2 kL/h	5.0%	3.5%	3.0%	16.38	21.53
Electrodialysis system, 20 kL/h	5.0%	3.5%	3.0%	244.13	320.85
Bentonite fining tanks	2.0%	2.0%	2.0%	7.06	11.11
Insulated jacketed tank, 278 kL	2.0%	2.0%	2.0%	14.11	11.11
Total maintenance (10^3 AUD/yr)				**360.00**	**470.00**
($/batch)				**927.84**	**1211.34**

APPENDIX B SURVEY FORM OF MCDA STUDY

Survey Form

Name: ____

Position: ____

Contact Details: ____

I. Assessment of Alternatives

Tartrate stabilisation technologies to be assessed include:
A1 – Cold stabilization;
A2 – Cold stabilisation with seeding;
A3 – Cold stabilisation by Westfalia process;
A4 – Cold stabilisation by fluidisation;
A5 – Nanofiltration (combined with centrifugation); and
A6 – Electrodialysis.

Refer to previous section for simple descriptions of the unit operations and their advantages and disadvantages.

Please perform **two** tasks for each nominated criteria:

1. ***SCORE* – *You are required to score between 1 (least preferred) and 10 (most preferred) rating the performance of the Alternatives for each of the criteria presented in following sections.*** The criteria represent various technical, operating and cost parameters have been calculated for each Alternative. These calculations are based on current performance of cold stabilisation, or performance subsequent to retro-fit of another process technology, at Berri Estates Winery, for processing 106.5 ML of wine per annum in individual lots of 275 kL.
   Write your scores in the appropriate location in the table provided.

2. ***SENSITIVITY –You are also asked to indicate your sensitivity to differences in performance between Alternatives for each performance criteria. Two questions will always be asked for each criterion – please tick (√) the applicable box.***

CRITERION G_1 : ESTIMATED PROCESSING TIME PER 275 kL LOT

SCORE

			Alternatives					
	Criteria	**Units**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
g_1	**Processing time**	hrs	188	52	56	41	48	44
	Score	(1-10)						

Note: Estimated total processing time per 275 kL lot including wine transfers, stabilisation, filtration (if applicable) and cleaning.

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in processing time (hours) *would not* concern you?

(a) 1		(b) 5		(c) 10		(d) 15		(e) other __________	

ii. what maximum difference in processing time (hours) would make you choose an alternative over the other?

(a) 1		(b) 5		(c) 10		(d) 15		(e) other __________	

CRITERION G_2 : ENERGY CONSUMPTION

SCORE

			Alternative					
	Criteria	**Units**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
g_2	**Energy consumption**	kWh/kL	10.19	10.26	10.16	10.01	6.13	7.32
	Score	(1-10)						

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in energy consumption (kwh/kL) *would not* concern you?

(a) 0		(b) 0.5		(c) 1		(d) 5		(e) other __________	

ii. what maximum difference in energy consumption (kwh/kL) make you choose an alternative over the other?

(a) 0.1		(b) 0.5		(c) 1		(d) 5		(e) other __________	

CRITERION G_3 : LABOUR REQUIREMENT

SCORE

	Criteria	Units	Alternative					
			A1	A2	A3	A4	A5	A6
g_3	**Labour requirement**	hrs/275 kL lot	24	30	34	36	34	27
	Score	**(1-10)**						

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in labour required (hours) *would not* concern you?

(a) 1		(b) 5		(c) 10		(d) 15		(e) other __________	

ii. what maximum difference in labour required (hours) would make you choose an alternative over the other?

(a) 1		(b) 5		(c) 10		(d) 15		(e) other __________	

CRITERION G_4: WINE LOSS

SCORE

	Criteria	Units	Alternative					
			A1	A2	A3	A4	A5	A6
g_4	**Wine loss**	%	0.40	0.76	0.56	0.75	0.72	0.70
	Score	**(1-10)**						

SENSITIVITY

Assuming that any two methods give comparable wine quality,

iii. what maximum difference in wine loss (%) *would not* concern you?

(a) 0.05		(b) 0.1		(c) 0.5		(d) 1		(e) other __________	

iv. what maximum difference in wine loss (%) would make you choose an alternative over the other?

(a) 0.05		(b) 0.1		(c) 0.5		(d) 1		(e) other __________	

CRITERION G_5: TOTAL UNIT OPERATING COST

SCORE

			Alternative					
	Criteria	**Units**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
g_5	**Operating costs**	AU¢/L wine	4.7	7.7	5.5	6.3	5.9	7.1
	Score	**(1-10)**						

Note: *The operating cost estimates include energy and water consumption, costs of chemical, maintenance, consumables and labour, as well as estimated wine loss and degraded per run.*

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in operating costs (Au¢/L) *would not* affect you?

(a) 0.1		(b) 0.5		(c) 1		(d) 1.5		(e) other _________	

ii. what maximum difference in operating costs (Au¢/L) would make you choose an alternative over the other?

(a) 0.1		(b) 0.5		(c) 1		(d) 1.5		(e) other _________	

CRITERION G_6: CAPITAL COSTS

SCORE

			Alternative					
	Criteria	**Units**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
g_6	**Capital costs**	*$AUD ,millions*	0	1.28	1.50	1.96	5.45	10.29
	Score	**(1-10)**						

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what difference in capital costs (millions of AUD) *would not* concern you?

(a) 0.1		(b) 0.5		(c) 1.0		(d) 1.5		(e) other _________	

ii. what difference in capital costs (millions of AUD) would you have a marked preference for a cheaper alternative?

(a) 0.1		(b) 0.5		(c) 1.0		(d) 1.5		(e) other _________	

CRITERION G$_7$: TARTRATE RECOVERY (FROM WINE)

SCORE

			Alternative					
	Criteria	Units	A1	A2	A3	A4	A5	A6
g$_7$	**Cost savings**							
	Nett tartrate recovery	*$AUD/275 kL lot*	59	470	470	470	235	0
	Score	**(1-10)**						

Note: Based on selling tartrate deposits at $AUD 1.50/kg to Australian Tartaric Production.

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in tartrate recovery ($AUD/275 kL) *would not* concern you?

(a) 5		(b) 10		(c) 50		(d) 100		(e) other ________	

ii. what maximum difference in tartrate ($AUD/275 kL) would make you choose an alternative over the other?

(a) 5		(b) 10		(c) 50		(d) 100		(e) other ________	

CRITERION G8 : VOLUME OF LIQUID WASTE

SCORE

			Alternative					
	Criteria	Units	A1	A2	A3	A4	A5	A6
g$_8$	**Liquid waste**	L/kL of wine	46.2	75.3	73.2	91.1	85.8	215.9
	Score	**(1-10)**						

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in liquid wastes generated (L/kL of wine) *would not* affect you?

(a) 1		(b) 5		(c) 10		(d) 15		(e) other ________	

ii. what maximum difference in liquid wastes generated (L/kL of wine) would make you choose an alternative over the other?

(a) 1		(b) 5		(c) 10		(d) 15		(e) other ________	

CRITERION G_9 : SOLID WASTE PRODUCED

SCORE

			Alternative					
	Criteria	**Units**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
g_9	**Solid wastes**	kg/ kL of wine	2.42	2.42	2.42	2.42	2.42	2.42
	Score	**(1-10)**						

Notes: *Generally, diatomaceous earth (DE) used in filtration is the dominant solid waste, requiring landfill disposal.*

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in solid wastes generated (kg/kL of wine) *would not* affect you?

(a) 0.5		(b) 1.0		(c) 1.5		(d) 2.0		(e) other ________	

ii. what maximum difference in solid wastes generated (kg/kL of wine) would make you choose an alternative over the other?

(a) 0.5		(b) 1.0		(c) 1.5		(d) 2.0		(e) other ________	

CRITERION G_{10} : LIQUID EFFLUENT QUALITY

SCORE

			Alternative					
	Criteria	**Units**	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**
g_{10}	**Effluent quality**							
	COD Load	*kg/kL $_{wine}$*	1.08	1.82	1.35	1.78	1.70	2.01
	Score	**(1-10)**						

Notes: *On-site treatment involves by screening, pH correction, anaerobic sump, sequencing aerobic batch reactor with disposal to woodlot.*

SENSITIVITY

Assuming that any two methods give comparable wine quality,

i. what maximum difference in COD load (kg/kL$_{wine}$) *would not* affect you?

(a) 0.1		(b) 0.5		(c) 1.0		(d) 1.5		(e) other ________	

ii. what maximum difference in COD load (kg/kL$_{wine}$) will make you choose an alternative over the other?

(a) 0.1		(b) 0.5		(c) 1.0		(d) 1.5		(e) other ________	

Assessment of criteria

In this section, you are required to evaluate the relative importance or priority of the criteria. This involves using the table below to ***perform a pair-wise comparison between the criteria*** as follows. For each criterion in the base criteria column, work across the each row comparing the base criterion with the comparison criterion listed for that column. For example, in the first row of the table, the base criterion is g_1. In this row, move across and compare g_1 with each of the comparison criterion listed above, i.e. compare g_1 versus g_2, then g_1 versus g_3, and so on.

For each pair-wise comparison, ***assign a value of 1, 0 or –1***:
1 indicates you value or prioritize the comparison criteria above the base criteria for decision-making; **0** indicates you regard each criterion as equal; and
-1 indicated the base criterion is more important to you than the comparison criterion.

	Comparison Criteria	Processing time	Energy consumption	Labour requirement	Wine loss	Operating costs	Capital costs	Cost savings	Liquid waste volume	Solid waste	Liquid effluent quality
Base Criteria	**Item**	**g_1**	**g_2**	**g_3**	**g_4**	**g_5**	**g_6**	**g_7**	**g_8**	**g_9**	**g_{10}**
Processing time	**g_1**	**0**									
Energy consumption	**g_2**		**0**								
Labour requirement	**g_3**			**0**							
Wine loss	**g_4**				**0**						
Operating costs	**g_5**					**0**					
Capital costs	**g_6**						**0**				
Cost savings	**g_7**							**0**			
Liquid waste volume	**g_8**								**0**		
Solid waste	**g_9**									**0**	
Liquid effluent quality	**g_{10}**										**0**

APPENDIX C DESIGN DRAWINGS OF STIRRED CELL

This appendix presents the drawings with dimensions of different parts of stirred cell (i.e. cylinder, top and bottom plate, and stirrer post) used in the nanofiltration laboratory studies as described in Chapter 5.

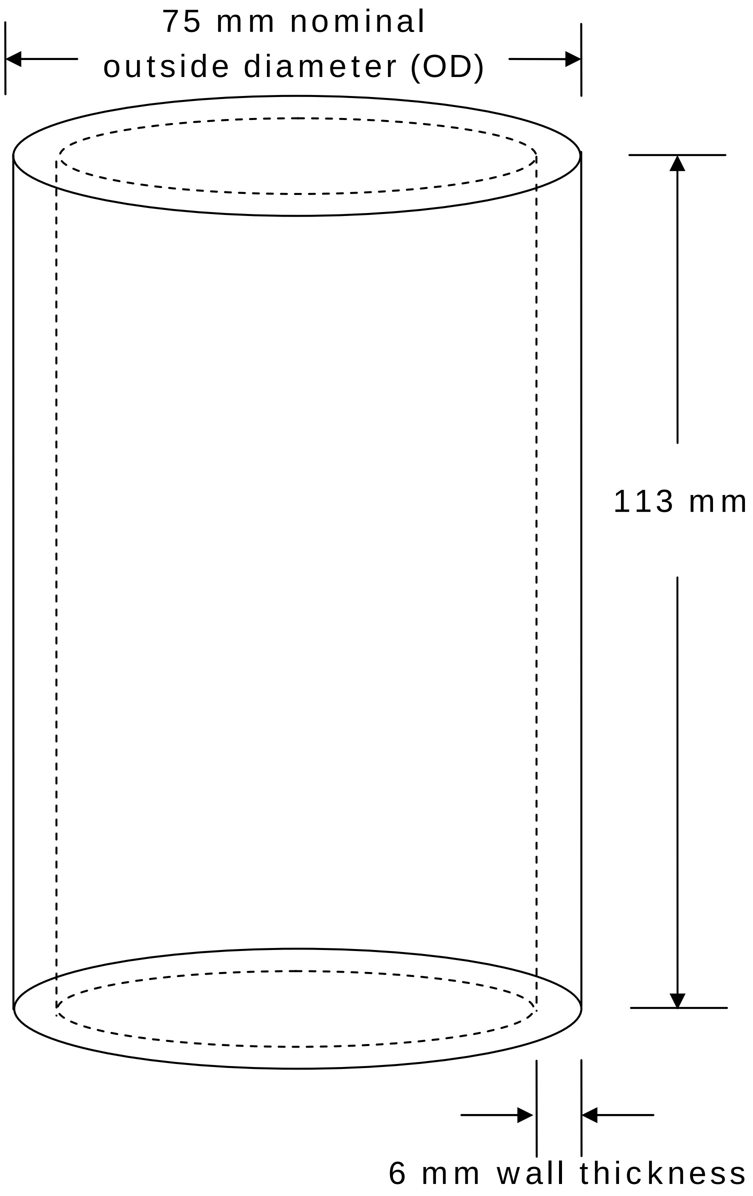


Figure C-1. Dimension of borosilicate glass cylinder.

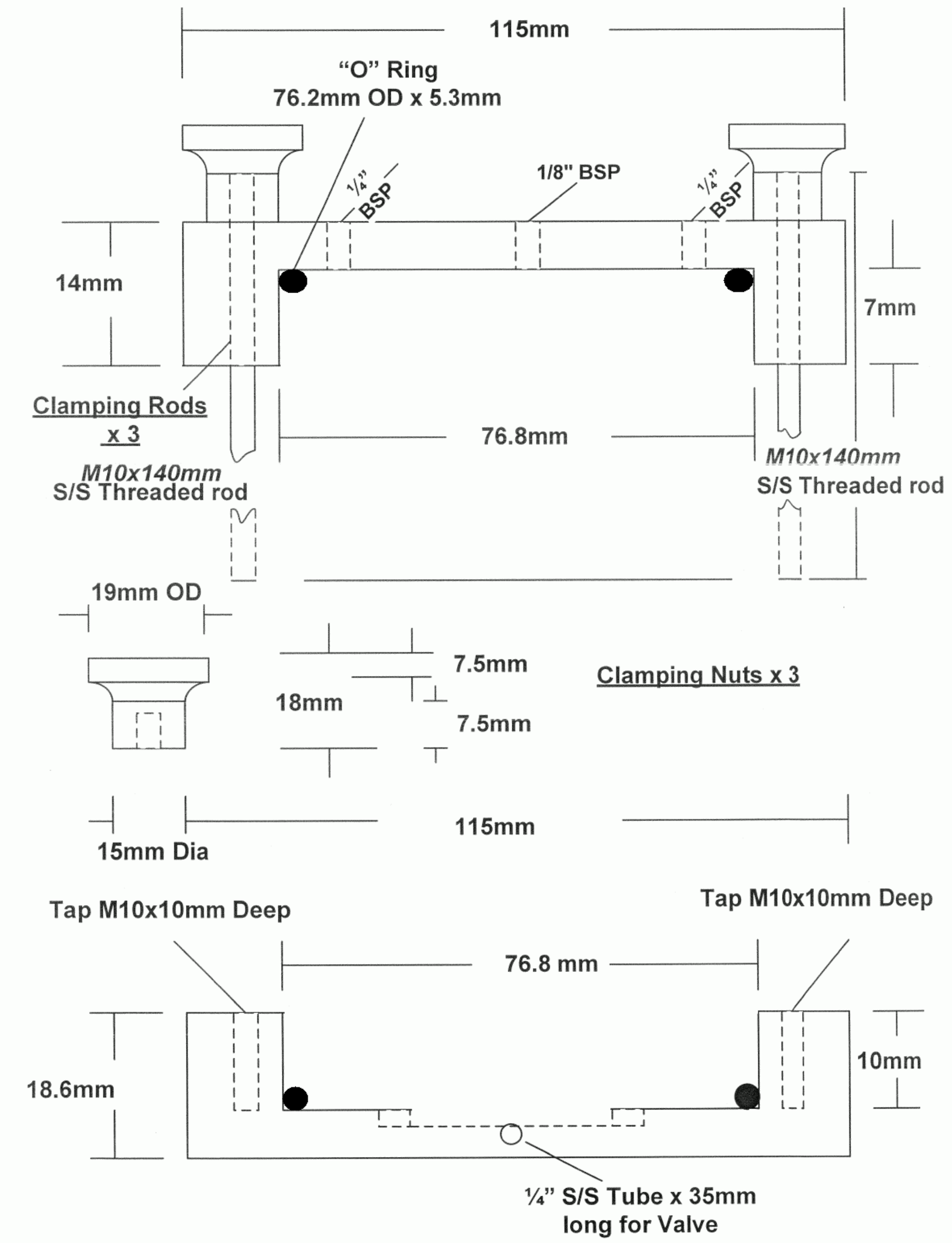


Figure C-2. Dimension of top and bottom plates.

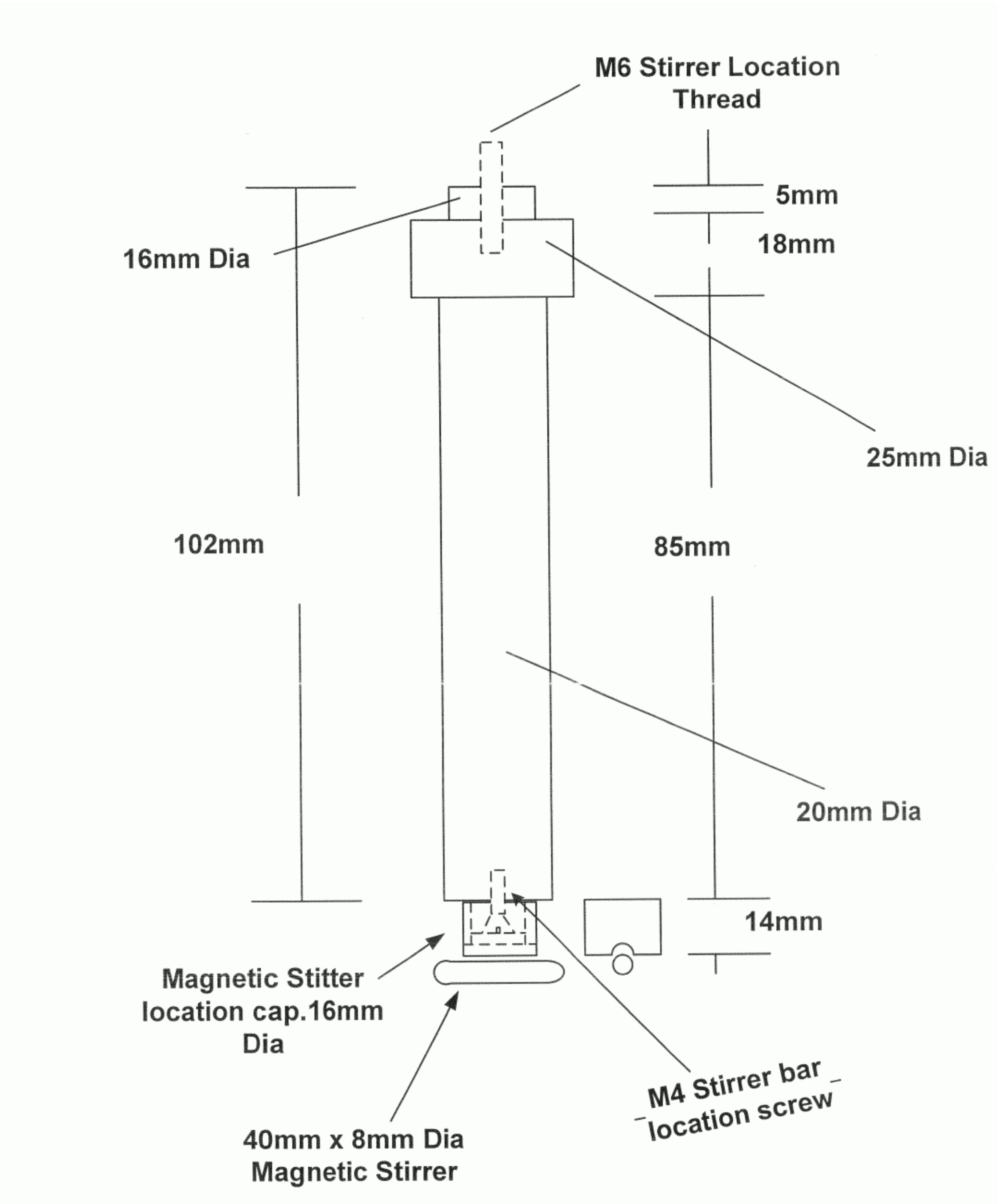
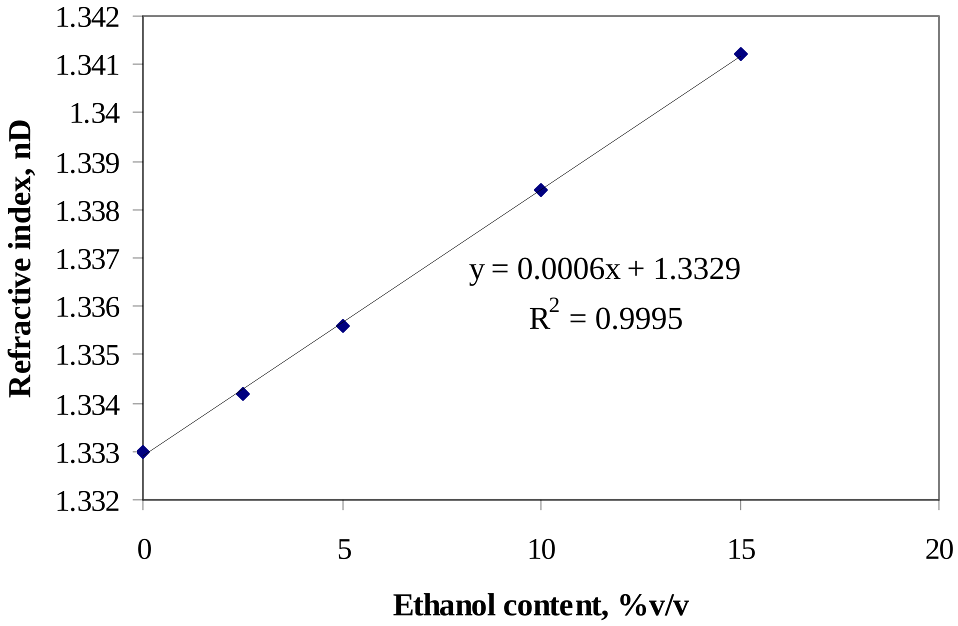
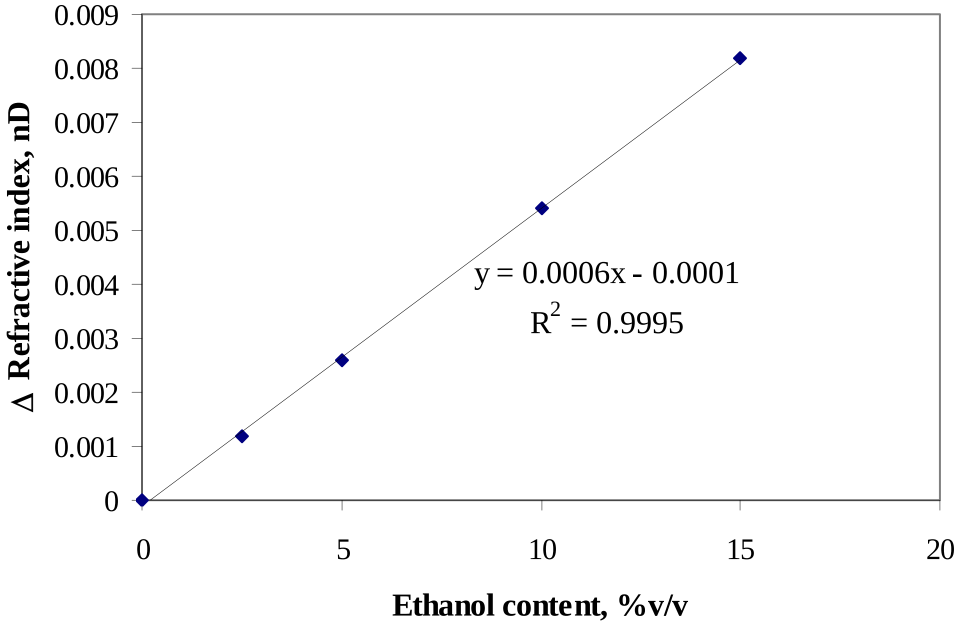


Figure C-3. Dimension of stirrer post.

APPENDIX D REFRACTIVE INDEX (R.I) – ETHANOL CALIBRATION CURVE



(a)



(b)

Figure D-1. Calibration curve for: (a) R.I reading corresponding to ethanol content; and (b) changes in R.I reading with respect to ethanol content

APPENDIX E DETERMINATION OF DEGREE OF SUPERSATURATION OF WINE

Steps involved in estimation of degree of supersaturation of potassium bitartrate (KHT) in wine are described as follows:

1. Determine concentrations product value for the initial feed wine, CP_0 using the following equation:

$$CP_0 = \left[K^+\right]_0 (mol/L) \times \left[H_2T\right]_0 (mol/L) \times \left(\%HT^-\right) \tag{E.1}$$

   where value for % HT^- (partial dissociated tartaric acid) is given by Berg and Keefer (1958) at measured pH and alcohol.

2. Determine the solubility product, K_{SP} by referring to Berg and Keefer (1958).

3. Estimate the concentration of potassium and tartaric acid of retentate (wine concentrated by nanofiltration), $[K^+]_c$ and $[H_2T]_c$, respectively, as follows:

$$\left[K^+\right]_c = \frac{\left[K^+\right]_0 \times \%rejection}{\left(1 - \%recovery\right)} \quad mol/L \tag{E.2}$$

$$\left[H_2T\right]_c = \frac{\left[H_2T\right]_0 \times \%rejection}{\left(1 - \%recovery\right)} \quad mol/L \tag{E.3}$$

4. Determine CP value of retentate (CP_c) where

$$CP_c = \left[K^+\right]_c (mol/L) \times \left[H_2T\right]_c (mol/L) \times \left(\%HT^-\right) \tag{E.4}$$

5. Determine degree of supersaturation of retentate, S where

$$S = \frac{CP_c}{K_{SP}} \tag{E.5}$$

6. If KHT crystal seeds are added to the retentate, determine concentration of potassium and tartaric acid ions of retentate taking into account of amount of KHT added:

$$\left[K^+\right]_{seed} = \left[K^+\right]_c + \left[K^+\right]_{KHT\ added} \quad mol/L \tag{E.6}$$

$$\left[H_2T\right]_{seed} = \left[H_2T\right]_c + \left[H_2T\right]_{KHT\ added} \quad mol/L \tag{E.7}$$

7. Determine CP value of the retentate with added KHT:

$$CP_{seed} = \left[K^+\right]_{seed}\left(mol/L\right)\times\left[H_2T\right]_{seed}\left(mol/L\right)\times\left(\%HT^-\right) \tag{E.8}$$

8. Estimate degree of supersaturation of retentate with added KHT:

$$S = \frac{CP_{seed}}{K_{SP}} \tag{E.9}$$

APPENDIX F TEMPERATURE CORRECTION FACTOR FOR ESTIMATING MEMBRANE PERFORMANCE

Performance of nanofiltration (NF) membrane is affected by temperature of feed solution. Hence, temperature correction factor (Table F-I) is used to determine the permeate flux of NF system used during trials.

Table F-I. Temperature correction factor used to estimate membrane performance (extracted from Applied Membrane Inc., 2007).

NOTE: This table is included on page 217 of the print copy of the thesis held in the University of Adelaide Library. Also freely available at:

http://www.watertreatmentguide.com/temperature_correction.htm

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