5
Membrane Processes in Must and Wine Industries

Maria Norberta De Pinho

In wine industries the conventional processes of filtration for clarification and cold treatment for tartaric stabilization are giving place to an increasing use of alternative membrane processes namely micro/ultrafiltration (MF/UF) for clarification and electrodialysis (ED) for tartaric stabilization. This wide use of membrane processes is carried out, most of the times, having in mind a single operation of application. For example, the clarification by MF or UF is optimized in terms of productivity and of preservation of the organoleptic properties like flavors and aromas. However, the removal of macromolecules like polysaccharides and polyphenols not only has a crucial importance on the organoleptic properties but also plays an important role on the wine tartaric stability and therefore in the subsequent operation of Electrodialysis (ED). For that reason, the integration of these operations will be the object of analysis. Nanofiltration (NF) is assessed as a fractionation technique for the simultaneous concentration and rectification of grape musts.

5.1
Introduction

Membrane operations are nowadays an essential part of the wine-making process. As shown in Figure 5.1 after must fermentation the clarification operation is associated with tangential microfiltration (MF)/ultrafiltration (UF) and the tartaric stabilization operation is associated to electrodialysis (ED).

Wine clarification, traditionally carried out by diatomaceous-earth filtration, is being replaced by tangential microfiltration (MF) and ultrafiltration (UF). Besides their advantages on the continuous and automatic mode of operation they brought enormous environmental benefits on the elimination of solid wastes of diatomaceous-earth filtration media and microorganisms. In wine tartaric stabilization the complex conventional sequence of wine cooling, tartrate crystal seeding, dynamic crystallization and diatomaceous-earth filtration is being replaced by electrodialysis (ED) [1–3]. In parallel with the operating advantages of being an easy and controllable process there are benefits of energy savings and of no generation of large amounts of diatomaceous-earth solid wastes that constitutes an important asset from the environmental point of view.

Membrane Technology, Volume 3: Membranes for Food Applications.
Edited by Klaus-Viktor Peinemann, Suzana Pereira Nunes, and Lidietta Giorno

ISBN: 978-3-527-31482-9

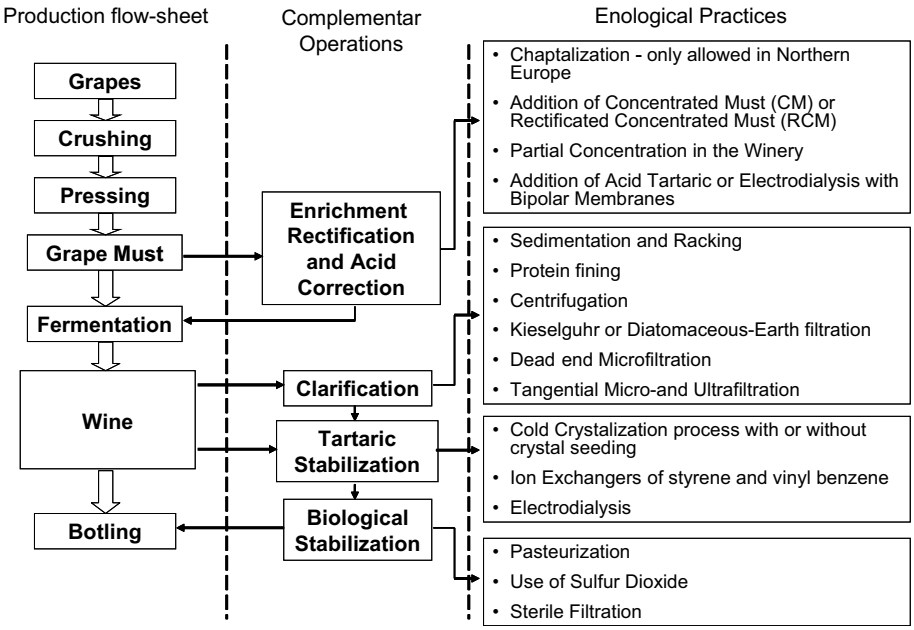

Figure 5.1 Grape must and wine production.

One of the facts behind the restricted application of MF/UF to wine clarification has to do with the lack of knowledge on the possible removal of polysaccharides or other macromolecules that may be of major relevance to the wine quality. At the same time, these macromolecules play an important role on the tartaric stability. Moreover, the colloids removed by clarification may act as natural inhibitors of potassium hydrogen tartrate precipitation.

The integration of MF/UF with ED becomes therefore of crucial importance and will be the object of concern in the analysis that follows [4, 5].

As shown in Figure 5.1, the grape must, prior to the fermentation, may be subjected to enrichment and acid correction by addition of rectified concentrated must and tartaric acid, respectively. The substitution of these operations by membrane operations like nanofiltration and reverse osmosis is the object of research [6–8] and again one should view these operations further integrated with those of wine processing and namely with electrodialysis for tartaric stabilization.

5.2 Wine Clarification by Microfiltration and Ultrafiltration

Feuillat [9] claims that wine turbidity is caused by suspended material like yeast residues and macromolecular compounds with colloidal behavior. The clarification operation, performed to remove these compounds, is assessed both in terms of

productivity and polysaccharide removal. Serrano *et al.* [10] compared traditional filtration with tangential MF and concluded that tangential microfiltration led to wines with lower polysaccharide content. The membrane fouling, besides having direct consequences on MF and UF productivity, brings additional problems related to the removal of macromolecules essential to wine quality. Belleville *et al.* [11, 12] identified some polysaccharide as major responsible for the fouling of MF mineral membranes. Cameira-dos-Santos [13] and Vernhet *et al.* [14, 15] have proved that polysaccharides and polyphenols also play an important role in the fouling of MF organic membranes.

In the prespective of optimizing productivity and minimizing polysaccharide removal, tangential microfiltration and ultrafiltration are analysed in Figures 5.2 and 5.3 as a function of the operating parameters of transmembrane pressure and concentration factors. The membranes used are: a MF membrane with 1 μm pore size and a UF membrane with the molecular weight cut-off (MWCO) of 100 kDa. Both membranes are made of a fluorpolymer and are supplied by Alfa Laval – Denmark (former DSS-Denmark).

Figure 5.2 displays the productivity or the permeate fluxes decline in microfiltration of a white wine, "Vinho Verde" (Portugal) [4, 16], versus the concentration factor. An increase of the transmembrane pressure from 0.6 to 1.0 bar means a significant gain in the permeate fluxes.

Figure 5.3 displays the productivity or the permeate fluxes decline in ultrafiltration of a white wine, "Vinho Verde" (Portugal) [4, 16], versus the concentration factor. The permeate fluxes are practically independent of the transmembrane pressure and no gain in productivity is obtained for transmembrane pressures higher than 1.0 bar.

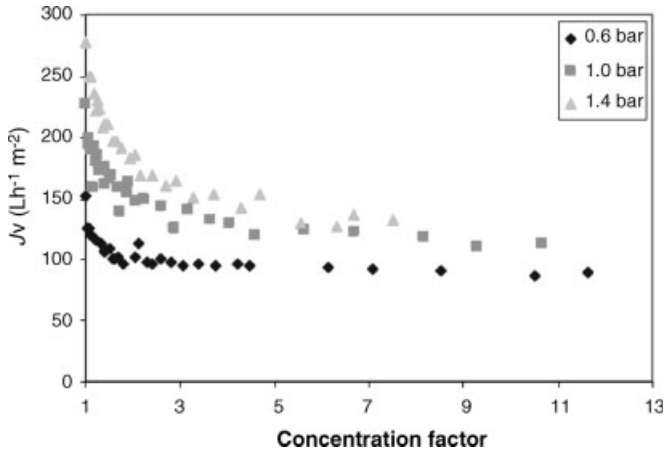

Figure 5.2 Variation of white wine microfiltration permeate fluxes, J_v ($L\,h^{-1}\,m^{-2}$), with the concentration factor. Transmembrane pressures ranging from 0.6×10^5 to 1.4×10^5 Pa. MF membrane – FSM1.0PP – with 1.0 μm pore size. Experiments run in a plate and frame DDS Lab-Unit, type 20, with 0.036 m^2 of membrane surface area.

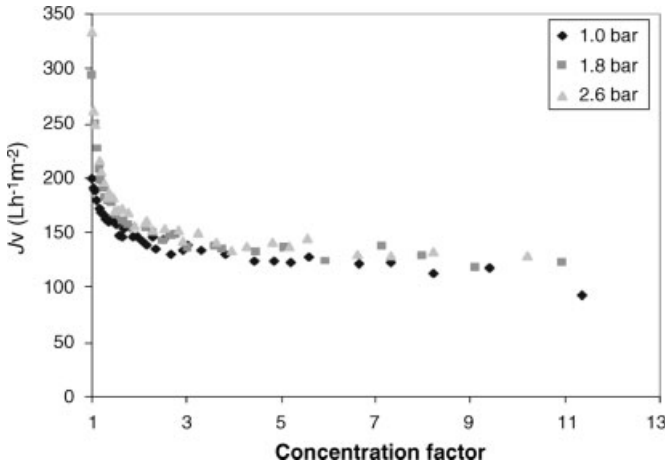

Figure 5.3 Variation of white-wine ultrafiltration permeate fluxes, J_v ($L\,h^{-1}\,m^{-2}$), with the concentration factor. Transmembrane pressures ranging from 1.0×10^5 Pa to 2.6×10^5 Pa. UF membrane – FS40PP – with MWCO of 100 kDa. Experiments run in a plate and frame DDS Lab-Unit, type 20, with 0.036 m^2 of membrane surface area.

Figure 5.4 displays the productivity or the permeate fluxes decline in microfiltration of a red wine, "Vinho Verde" (Portugal) [4, 16], versus the concentration factor. The permeate fluxes are practically independent of the transmembrane pressure.

Figure 5.5 displays the productivity or the permeate fluxes decline in ultrafiltration of a red wine, "Vinho Verde" (Portugal) [4, 16], versus the concentration factor. The

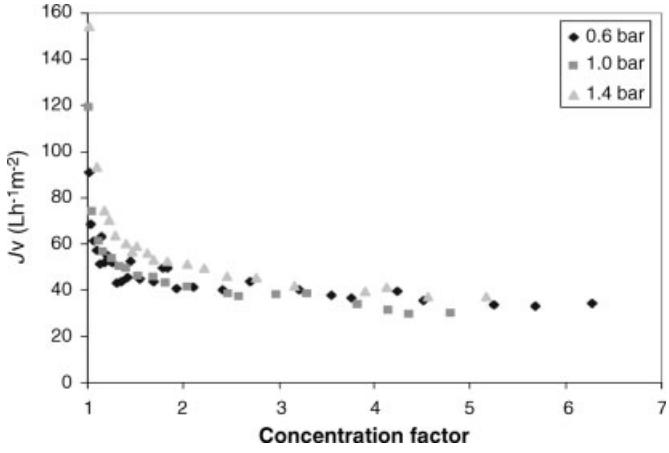

Figure 5.4 Variation of red-wine microfiltration permeate fluxes, J_v ($L\,h^{-1}\,m^{-2}$), with the concentration factor. Transmembrane pressures ranging from 0.6×10^5 to 1.4×10^5 Pa. MF membrane – FSM1.0PP – with 1.0 μm pore size. Experiments run in a plate and frame DDS Lab-Unit, type 20, with 0.036 m^2 of membrane surface area.

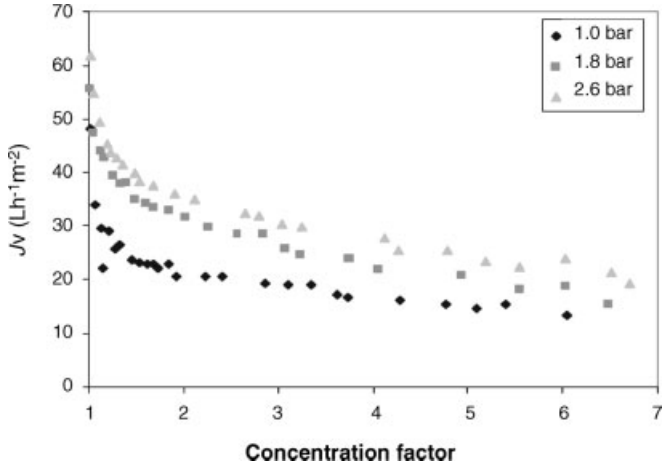

Figure 5.5 Variation of red-wine ultrafiltration permeate fluxes, J_v ($L\,h^{-1}\,m^{-2}$), with the concentration factor. Transmembrane pressures ranging from 1.0×10^5 to 2.6×10^5 Pa. UF membrane – FS40PP – with MWCO of 100 kDa. Experiments run in a plate and frame DDS Lab-Unit, type 20, with 0.036 m^2 of membrane surface area.

permeate fluxes are dependent on the transmembrane pressure and its increase leads to a significant productivity gain.

The permeate fluxes of MF and UF of a red wine are much lower than those of MF and UF of a white wine. At the transmembrane pressure of 1.0 bar, the MF and the UF of a white wine yields final permeate fluxes of 118 and 129 $L\,h^{-1}\,m^{-2}$, respectively. At the same transmembrane pressure of 1.0 bar, the MF and the UF of a red wine yields final permeate fluxes of 34 and 18 $L\,h^{-1}\,m^{-2}$, respectively.

For white and red wine, the removal of polysaccharides and polyphenols in the operations of MF and UF is shown in Tables 5.1 and 5.2, respectively.

The wine clarification by microfiltration is associated with a small removal of polysaccharides and polyphenols for the case of white wine and to a slightly higher removal for the case of red wine.

Table 5.1 Clarification by microfiltration.

Wine	ΔP (bar)	Percentage of removal	
		Polysaccharides (%)	Polyphenols (%)
White	0.6	11.4	2.1
	1.0	7.6	0.9
	1.4	7.7	2.6
Red	0.6	24.6	9.6
	1.0	22.8	12.6
	1.4	23.1	10.2

Table 5.2 Clarification by ultrafiltration.

Wine	ΔP (bar)	Percentage of removal	
		Polysaccharides (%)	Polyphenols (%)
White	1.0	16.4	0.0
	1.8	16.4	0.8
	2.6	18.7	4.0
Red	1.0	82.9	31.5
	1.8	83.9	43.4
	2.6	94.5	54.1

The clarification of white wine by ultrafiltration also leads as in the case of MF to a low removal rate of polysaccharides and negligible removal of polyphenols. In contrast, for the case of red wine there is a significant removal of polysaccharides and polyphenols.

Upon the degree of fouling, the regeneration of MF and UF membranes is made through the circulation of water or solutions of detergent at different temperatures and circulation times. A cleaning sequence is composed of the following steps:

1) circulation of water at the temperature of 20 °C and for 30 min;
2) circulation of water at the temperature of 50 °C and for 30 min;
3) circulation of water at the temperature of 50 °C and for 60 min;
4) circulation of Ultrasil11 solution at the temperature of 50 °C and for 30 min;
5) circulation of Ultrasil11 solution at the temperature of 50 °C and for 60 min;
6) circulation of Ultrasil11 solution at the temperature of 50 °C and for 3 h.

The different cleaning sequences yield the results shown in Tables 5.3 and 5.4 for microfiltration and ultrafiltration, respectively. They show along the different steps the percentage of permeate fluxes recovery.

Table 5.3 Sequence of membrane regeneration operations after clarification by microfiltration.

Clarification		Cleaning procedure		
Wine	ΔP (bar)	First step: water 20 °C, 30 min	Second step: water 50 °C, 30 min	Third step: Ultrasil11 0.5%, 50 °C, 30 min
White	0.6	83%	93%	—
	1.0	82%	104%	—
	1.4	80%	94%	—
Red	0.6	81%	73%	97%
	1.0	48%	75%	97%
	1.4	31%	57%	98%

Table 5.4 Sequence of membrane regeneration operations after clarification by ultrafiltration.

Clarification		Cleaning procedure			
Wine	**ΔP (bar)**	**First step: water 20 °C, 30 min**	**Second step: water 50 °C, 60 min**	**Third step: Ultrasil11 1%, 50 °C, 60 min**	**Fourth step: Ultrasil11 1%, 50 °C, 3 h**
White	1.0	93%	—	—	—
	1.8	95%	—	—	—
	2.6	92%	—	—	—
Red	1.0	27%	38%	75%	95%
	1.8	18%	—	65%	91%
	2.6	15%	—	44%	66%

The easier process of regeneration is relative to ultrafiltration of white wine and consists just on a single step of circulation of water at the temperature of 20 °C and for 30 min. The microfiltration of white wine requires a further step of circulation of water at the temperature of 50 °C for 30 min.

For red wine the regeneration process is more difficult and in the case of MF it requires an additional step of cleaning through circulation of a solution with 0.5% of Ultrasil11 at the temperature of 50 °C for 30 min. The UF of red wine leads to severe membrane fouling and to the need for circulating 1% Ultrasil11 solutions for longer times of 3 h. Moreover, if the UF operating pressures are as high as 2.6 bar, the membrane fouling is irreversible and the permeate fluxes are only recovered to 66%.

5.3
Wine Tartaric Stabilization by Electrodialysis [4, 5]

Potassium hydrogen tartrate (KHT) is a natural constituent of grapes. Alcoholic fermentation during winemaking leads to a decrease in the KHT salt solubility due to the presence of ethanol. As a consequence, at normal storage temperatures an untreated wine is supersaturated in KHT and undesirable precipitation can occur in the bottles. To overcome this problem, the cold tartaric stabilization method is traditionally used. As shown in Figure 5.6 this consists of a complex sequence of wine cooling, tartrate crystal seeding, dynamic crystallization and diatomaceous-earth

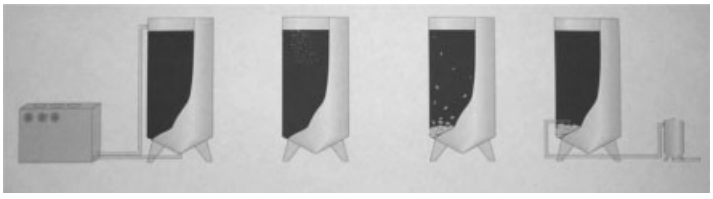

Figure 5.6 Cold tartaric stabilization process.

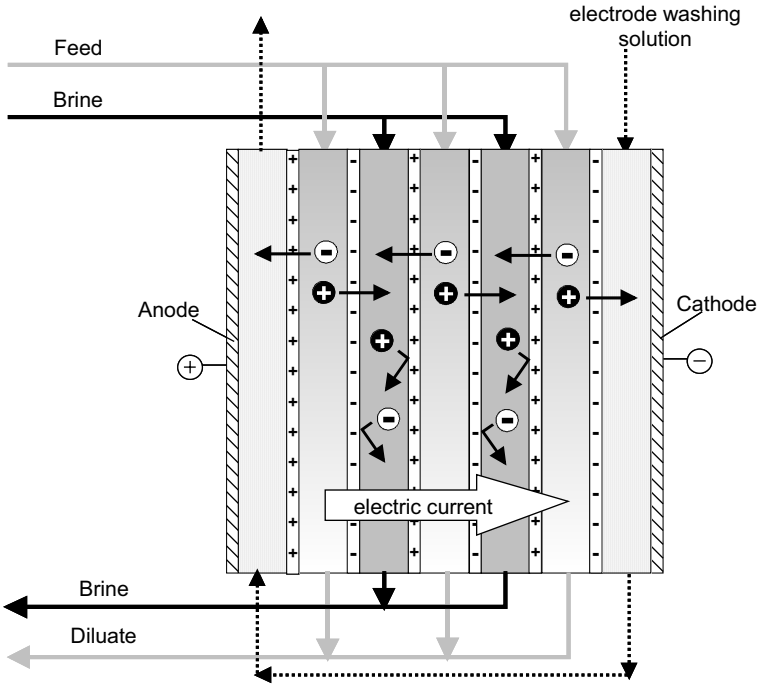

Figure 5.7 Schematic representation of electrodialysis.

filtration. Besides not allowing a precise control of the final KHT concentration this method may lead to unwanted precipitation of polysaccharides and polyphenols together with KHT crystals. These limitations are overcome in the treatment by electrodialysis (ED), which is a method based on ion electrical migration in a single-stage operation, as shown in Figure 5.7.

In ED the wine circulates in rectangular channels confined by cation- and anion-selective membranes and by the action of an external electric field normal to the membranes, the ions are forced to migrate to the electrodes, giving rise to a wine stream depleted in ions [17]. This is schematically shown in Figure 5.7 where the wine circulates in the diluate compartments that alternate with the brine compartments.

An important feature of ED is the fact that during wine circulation there is a reduced surface area of contact with the membrane walls of the diluate compartment. This is in contrast with the cold tartaric stabilization process that involves a filtration step where the wine percolates through porous media of extensive surface areas and leads very often to adsorption of organic molecules of great relevance for the organoleptic properties of the wines. Also, the ED dense polymeric membranes are not prone to adsorption phenomena. The nonalteration of the organoleptic properties of the wines constitutes therefore a strong asset of ED. Another asset is the flexibility in reaching any degree of KHT removal through the variation of the ED operating time.

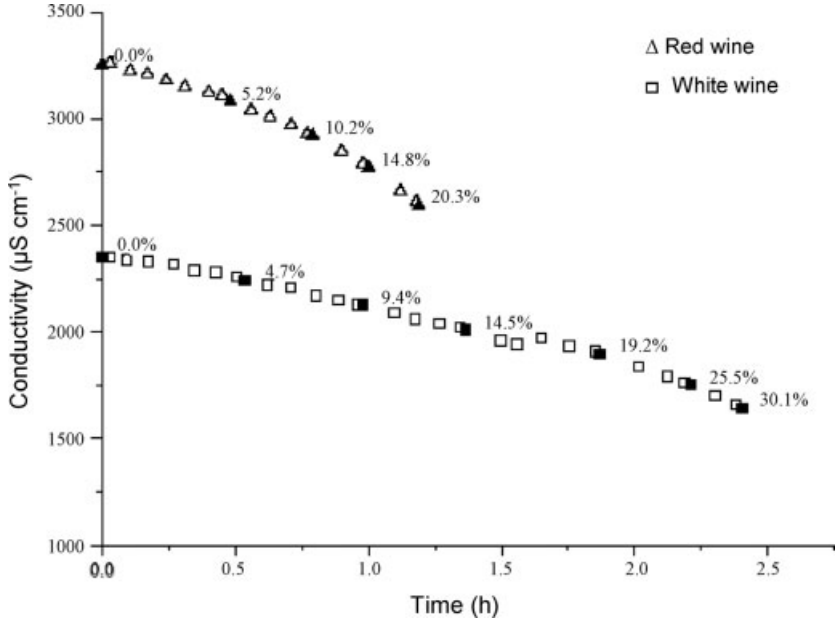

Figure 5.8 Influence of electrodialysis operating time on the wine conductivity.

Figure 5.8 displays the variation of the wine conductivity with ED operating time. The decrease of conductivity is associated with the removal of potassium and tartaric acid as the cations and anions present in higher concentrations. The deionization degree (DEID) is defined as: DEID = ((initial conductivity–final conductivity)/initial conductivity). In Figure 5.8, the DEID values are assigned in percentages at the points of sample collecting, full squares and full triangles, for white and red wine, respectively.

At the various degrees of KHT removal, the wine tartaric stability is assessed through the determination of the saturation temperature, T_{sat} [5].

Figure 5.9 displays for a white wine the variation of the saturation temperature as a function of the degree of ED deionization. The experimental results are correlated by the equation:

$$T_{sat} = 20.3 - 0.44 \times \text{deionization percentage} \quad (5.1)$$

5.4 Influence of MF/UF Polysaccharide Removal on Wine Tartaric Stability

After wine clarification by microfiltration with a membrane of 1 μm pore size and ultrafiltration with a membrane of 100-kDa MWCO, the permeate and concentrate streams were subjected to a polysaccharide precipitation process [4, 16]. The results

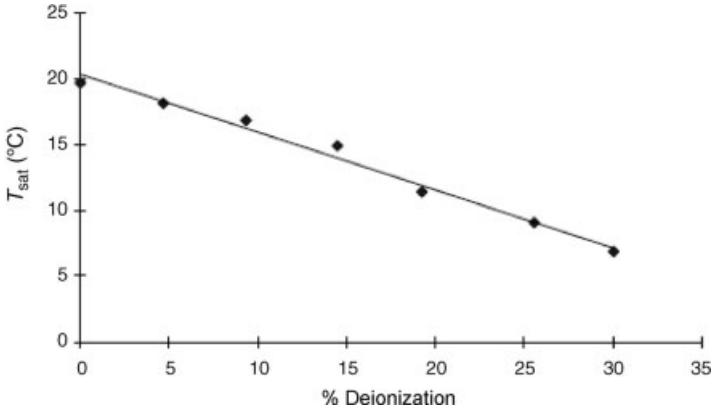

Figure 5.9 Variation of the saturation temperature with the degree of ED deionization.

obtained together with the corresponding values for raw wine are presented in Table 5.5.

The 10% polysaccharide removal during MF with a membrane of 1 μm pore size is relatively low when compared with 50.3% obtained by Serrano *et al.* [10] with a 0.4-μm organic membrane. A 16% polysaccharide removal is obtained with the UF membrane of 100 kDa. Escudier *et al.* [18] reported a value of 92% with a 20 kDa membrane and that led to a very unstable wine.

The role of the polysaccharides on wine stability is assessed through the measurement of the crystallization induction times of potassium hydrogen tartrate on a model solution of ethanol, potassium hydrogen tartrate and tartaric acid in the same concentration as in raw wine and three model solutions prepared from the model solution and adding raw wine polysaccharides, UF permeate polysaccharides and UF concentrate polysaccharides.

The crystallization induction times are determined by monitoring the conductivity of a solution while lowering the temperature to a pre-set value, in order to induce salt precipitation. After an initial decay, the conductivity stabilizes in a plateau and then decreases again when precipitation starts. The time interval between this instant and the instant when temperature reaches the pre-set value is the induction time.

The results are displayed in Table 5.6.

Table 5.5 Variation of polysaccharides content in raw wine and wine clarified by MF and UF.

	Polysaccharides (mg l^{-1})	
	MF	**UF**
Raw wine	334	334
Permeate	300	281
Concentrate	665	800

Table 5.6 Influence of polysaccharides of UF streams on KHT crystallization induction time.

	Polysaccharides ($mg\,L^{-1}$)	Induction time (h)
Model solution	0	14.3
Model solution with raw wine polysaccharides	30.2	20.3
Model solution with UF permeate polysaccharides	30.0	22.0
Model solution with UF concentrate polysaccharides	30.8	35.6

The induction times obtained with UF permeate polysaccharides are slightly higher than those obtained with raw wine polysaccharides. The UF concentrate polysaccharides led to higher induction times and therefore showed a higher inhibition effect.

5.5 Nanofiltration of Grape Must for Sugar/Organic Acids Fractionation

Grape must quality is of major importance in the definition of the wine character. Enrichment of must prior to fermentation is one process that is used to overcome reduced levels of sugars in a particular vintage. As shown in Figure 5.1 this is traditionally done by adding sucrose from beet and cane sugar or grape musts – concentrated must (CM) and rectified concentrated must (RCM). The vacuum evaporation (VE) is used to produce CM and is very often associated to the depletion of varietal aromas and to the production of off-flavors [19, 20]. More recently, reverse osmosis (RO) is being used for must concentration [6, 21]. However, if must rectification is considered, an additional operation of ion exchange is required and that brings severe ecological problems due to the need for resin regeneration and its disposal [22]. Rosa Santos *et al.* [8] propose nanofiltration for the simultaneous concentration and rectification of grape must. This is investigated through the capability of NF to fractionate sugars from the organic acids in a grape must from

Table 5.7 Composition of the grape must model solutions and the EDM grape must.

	Grape must model solutions				
	RD_1		RD_2		EDM
	RD_1T	RD_1M	RD_2T	RD_2M	
Tartaric acid ($g\,L^{-1}$)	2.0	—	2.6	—	2.0
Malic acid ($g\,L^{-1}$)	—	2.5	—	3.3	5.0
Total sugar ($g\,L^{-1}$)	150	150	200	200	107
pH	2.64	2.41	2.52	2.33	3.19
Conductivity ($\mu S\,cm^{-1}$)	892	700	913	685	2200

the region of "Vinho Verde" production (Entre Douro e Minho (EDM), Portugal) and four model solutions of grape must. The composition of the grape must designated by EDM and of the four model solutions is shown in Table 5.7. The grape must model solutions were prepared as described by Rosa Santos *et al.* [8] and designated by RD_1T, RD_1M, RD_2T and RD_2M.

The nanofiltration is performed with a NF 270 membrane supplied from FilmTec (Minneapolis, MN) and yields the results displayed in Figure 5.10.

For the model solutions, the gap between the rejection coefficients to the sugars –glucose and fructose – and to the acids – tartaric and malic acids – is very pronounced. The sugars being rejected more than 88% and the acids less than 37% means that the major part of the sugars are retained in the NF concentrate stream and the organic acids permeate preferentially to the permeate stream. This demonstrates the NF capability for sugars/organic acids fractionation in grape musts. This fractionation is enhanced with the increase of the total sugar content from 150 g L^{-1} in the RD1T and RD1M to 200 g L^{-1} in the RD2T and RD2M.

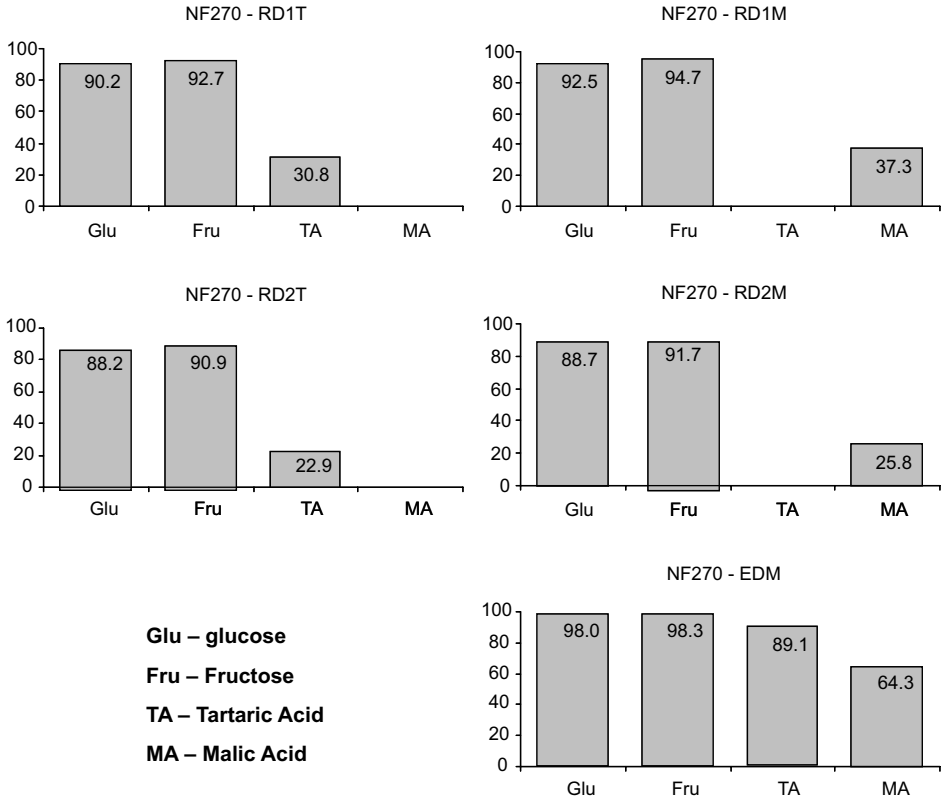

Figure 5.10 NF Rejection coefficients to glucose, fructose, tartaric acid and malic acid in grape musts. Membrane NF270.

For the EDM grape must, the gap between the rejection coefficients to the sugars and to the acids is less pronounced. Among the acids, there is a preferential permeation of malic acid.

Acknowledgments

Thanks go to Dr Rui Viegas for helpful discussions and to the financial support of the Foundation for Science and Technology (FCT) through POCI/AGR/58450/2004 and REEQ/764/EQU/2005.

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