Integrated membrane processes in winemaking

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7 Integrated membrane processes in winemaking

Youssef El Rayess and Martine Mietton-Peuchot

7.1 Introduction

Membrane filtration has been applied to wine for a long time. At present, the clarification cartridges are integrated in bottling units. Subsequently, in a crossflow filtration mode, microfiltration membranes were the first to be applied for wine clarification. Today, crossflow microfiltration (CFMF) is largely used in oenology for must, lees and wine filtration at different membrane cut-offs, from 0.2 to 1.2 µm. The development of RO application in must concentration was almost done in parallel with that of microfiltration (MF) in clarification [1].

This chapter is an overview of the application of membrane processes in winemaking. The aim is to present both the application of membrane processes in winemaking and a general philosophy of their development from a process engineering point of view. Several examples illustrate this approach; in particular, applications of nanofiltration (NF) and RO membranes. Reduction of alcohol content is studied with different techniques [NF+ evaporation, NF+ membrane contactor (MC), decrease of sugar content, etc.]. Reduction of sugar content of the musts [ultrafiltration (UF) + NF] could be an alternative process to reduce the alcohol content of the wine and to improve its quality. The volatile acidity or malic acid reduction could also be done by coupling two stages of RO. As the free acids are poorly retained by the membrane, the permeate after the first stage filtration contains free acids, salts, esters and other small molecules. Once the permeate is neutralized with the pH of the targeted acid, it will be retained by the second stage membrane in a salty form. The other components passing through are re-injected in the initial must or wine. The potassium hydroxide is used for neutralization. The proposed processes integrate different steps: two membrane techniques, a membrane process and a chemical reaction or new developments (rotating membranes, bipolar membranes, etc.).

The principal condition for further development of membrane processes in winemaking is a good understanding of membrane techniques, separation techniques and characterization of the membrane itself and the product (must or wine) to be filtered. The second constraint, given the complexity and variability of must and wine composition, is not trivial and needs a considerable effort at both industrial and research levels. For the same reasons, the coupling of the membrane and other physical-chemical treatments appears to be a promising research domain.

7.2 Crossflow microfiltration for must, wine and lees clarification

During red or white winemaking, the filtration process is usually involved in several steps of product elaboration. Filtration in winemaking is used to accomplish two main objectives: clarification and microbial stabilization.

- In clarification, large particles that affect the visual appearance of wine are removed.
- In microbial stabilization, bacteria or yeasts are removed with the aim of reducing the probability of re-fermentation or spoilage.

The limpidity and the microbiological stabilization of wine are two essential parameters that could affect wine organoleptic quality. The compounds removed by filtration can be classified in three groups according to their size: (i) solutes (<1 nm), (ii) colloids (between 1 nm and 1 μm) and (iii) particles (>1 μm) [2]. Depending on the objectives of the filtration and wine characteristics, the winemakers choose the most adapted technique. Wineries can perform filtration according to two main different technologies, by using precoat or membrane filters. In order to obtain the required wine quality, different types of filtration equipments are available: drum filtration, plate-and-frame filtration, cartridges and crossflow filtration [3]. A filtration process must be efficient in terms of retention and produce adequate flow rates without prejudice to the quality of the wine. These criteria can be difficult to reconcile because of the fouling by the filtering solution over time. The fouling modifies the flow rate and the retention characteristics.

CFMF is well implemented in wine cellars. The first trials of CFMF have been conducted in oenology at the beginning of the 1980s with unsatisfactory results in terms of wine quality because the membranes used (UF membranes) were not specific to wine filtration. This technique is an attractive process to the wine industry for one-step clarification and microbiological stabilization compared to traditional techniques. In order to have a limpid wine, the wine makers implement successive solid-liquid separations using traditional technologies such as centrifugation, filtration on plates, diatomaceous earth filtration and the use of exogenic additives. The traditional techniques showed quickly their limits in terms of wine quality, wine loss and its implementation especially in cellars dealing with huge volumes of wines. In addition, the filtration additives have a negative effect on the environment. Their disposal must be done in special waste treatment sites. In addition to a great simplification of the wine processing line, CFMF offers a number of additional advantages, such as elimination of earth use and its associated environmental problems as well as the combination of clarification, stabilization and sterile filtration in one single continuous operation.

For a long time, the development of the CFMF suffered from the significant fouling of the membranes by wine compounds. The consequence of this is a reduction in permeation rates, affecting the economic viability of the process, and a risk of excessive retention of some components, which may affect the product quality. Crude wine after fermentations is a very complex medium with solute molecules as ions, organic acids and sugars (<1 nm), molecules with colloidal behavior as polyphenols, polysaccharides and proteins (between 1 nm and 1 µm) and particles as microorganisms, tartaric crystals and organic precipitates (>1 µm). Several studies have been conducted in order to identify the wine molecules responsible for membrane fouling, the fouling mechanisms and the methods to limit or control membrane fouling. Studies were initiated in the mid –980s and were focused on the identification of the most suitable membrane pore size for wine filtration. Studies [4, 5] showed that 0.2 µm as average pore size presented the best results in term of permeate flux and wine quality. After this, studies were oriented in order to identify the wine compounds responsible for membrane fouling. This was mainly reported as polysaccharides and polyphenols.

Vernhet et al. [6] studied the effect of wine polysaccharides on an organic (PES) membrane fouling. They showed that the effects of polysaccharides on fouling are not similar, owing to the nature of polysaccharides fraction involved in the fouling. It was shown that the pectic polysaccharides of low molecular weight [rhamnogalacturonan type II(RG-II)] have no noticeable effect on the permeation flux, whereas mannoproteins play a crucial role in reducing the fluxes. The researchers noticed that the membrane fouling by a given wine is not directly related to its total polysaccharides content but rather to the composition, structure of these polysaccharides and the balance between different groups of polysaccharides [7]. In 2009, Ulbricht et al. [8] demonstrated that different membrane materials exhibit different levels of polysaccharides adsorption. They showed that larger amounts of polysaccharides were adsorbed on hydrophilic membranes than on hydrophobic membranes. In 2011, El Rayess et al. [9] showed that polysaccharides formed a compact gel layer on the membrane surface which is dependant of transmembrane pressure. Phenolic compounds have a much more important affinity for membranes than the polysaccharides and there are both quantitative and qualitative differences between the different materials tested.

It is worth noticing that polyphenols are amphipathic molecules with hydrophobic aromatic rings and hydrophilic phenolic hydroxyl groups. So their adsorption involves both hydrophobic effects and the formation of hydrogen bonds. The preferential adsorption of phenolic compounds with low polarity suggests the predominance of hydrophobic interactions [2]. It was shown that an increase in polyphenol concentration in wine lead to a decrease of membrane permeability and thus an increase of membrane fouling [10]. Suspended particles yeast, bacteria and cell debris play also a role in membrane fouling. Boissier et al. [11] proved that the increase in the total resistance related to yeast deposition is caused by the compaction of the cake layer on the surface of the membrane. They found also that fouling is governed by fines particles (lactic bacteria and colloidal aggregates) more than yeast. In 2011, El Rayess [12] showed that yeasts may protect the membrane from colloids fouling whether by forming a secondary membrane or by disturbing the pectic gel layer to be uniformly installed on the membrane surface.

To control membrane fouling, it is important to adjust the operating conditions of wine CFMF. Critical flux can be a key parameter of the control of membrane fouling as it is depending at the same time on the hydrodynamics and physico-chemistry (membrane/solutes interactions). El Rayess et al. [9] studied the critical flux for irreversibility (J_{ci}) during wine CFMF. The critical flux for irreversibility (J_{ci}) is defined as the permeate flux above which an irreversible fouling appears on the membrane surface. The method used to determine J_{ci} is the square wave barovelocimetry (SWB) developed by Espinasse et al. [13]; this method also enables the distinction between reversible and irreversible fouling with the determination of reversible (R_{rf}) and irreversible (R_{if}) resistance, respectively. If the permeate flux is the same between these two steps, the fouling associated is considered as totally reversible. If it is not the case, the fouling associated is considered as partly irreversible and the critical flux for irreversibility is determined at the last step where fouling is totally reversible. For all tested macromolecules (tannins, pectins and mannoproteins) and associate concentrations and in the range of tested pressures (200–1000 mbar), it was found impossible to determine a value of the critical flux for irreversibility J_{ci}. This was not the case for filtered wine where J_{ci} was found beyond 1000 mbar ($J_{ci} \geq 1.4 \times 10^{-4}$ m/s).

To improve the efficiency of the filtration process and maintain the state of cleanliness of the membrane filtering surfaces at an acceptable level during the filtration process, most filtration devices are equipped with a reverse filtering system. Backflushing, backwashing and back-pulsing are all methods of operation in which the transmembrane pressure is periodically inverted by the use of a secondary pump, so that permeate flows back into the feed, lifting the fouling layer from the surface of the membrane. The main difference in the methods is mainly the time-frame in which the process operates. Technically, the back-pulsing process is very similar to backflushing or backwashing that is widely used for commercial applications. However, the fundamental difference between a back-pulse and a back-flush is the force and time used to lift accumulated deposits off the membrane. Generally, in back-flushing flow reversal occurs for a few seconds once every several minutes, while back-pulsing occurs at a higher frequency and the pulses are applied for a very short time (<1 s). When a flow reversal system is applied, the residues of particles separated from the wine are eliminated from the membrane surface and the filtrate flow rate is increased. As the restoration of flux lasts only for a relatively short period, the back-flush should be repeated at frequent intervals for maximum effect. The main advantages are: (i) a faster filtration process; (ii) more filtration capacity and overall performance increases of up to 60%; (iii) less filtration stress; (iv) less temperature pick-up; (v) minimum impact on the wine quality.

New developments in CFMF in the wine industry are oriented to filter high charged (suspended solids), viscous and abrasive fluids such as tank bottoms, wine lees, fining agents, retentates from crossflow filters and centrifuged sludges. Therefore, the Bucher Vaslin and Velo group (2011) introduced new membranes to filter very charged fluids from the wine industry. These membranes are made from sintered stainless steel

Figure 7.1: Sintered stainless steel tubular membranes

powder. In fact, the porous stainless steel is used to support the ceramic filtration layer (generally made by titanium oxide TiO_2 or zirconium oxide ZrO_2). These tubular membranes (Figure 7.1) have been used for years, but their introduction into the wine industry is very recent. These membranes (when developed) were supposed to be applied to food filtration in the future as an alternative to the generally used organic and ceramic membranes. This is because the organic ones are easily fouled by food suspensions and need to be frequently cleaned by chemical solutions, which results in a short lifespan; and the ceramic ones are brittle that they are likely to break during service.

Another new development in wine filtration of high charged fluids is the introduction of dynamic filtration. Dynamic or shear-enhanced filtration consists of creating the shear rate at the membrane by a moving part such as a rotating membrane, or a disk rotating near a fixed circular membrane, or by vibrating the membrane either longitudinally or torsionally around a perpendicular axis [14]. This mode of filtration constitutes an alternative to crossflow filtration, which not only increases substantially the permeate flux, but has a favorable effect on membrane selectivity. It also permits to decouple from membrane shear rate, the inlet flow rate into the module, which can be varied independently and does not need to be much larger than the filtration rate. The drawbacks are the complexity and limitations in membrane area for some systems, such as cylindrical rotating membranes or multi-compartment rotating disk systems, which raise the equipment cost. TMCI Padovan introduced the first rotating dynamic crossflow filter (Dynamos®, Figure 7.2A) into the wine industry. This filter is also equipped with a back-pulse system and is covered by an international patent (WO2011/033537) [15]. This system is known in the literature as a multi-shafts systems with rotating ceramic membranes and was developed and commercialized many years ago but without the back-pulse system (Rotostream®, Buss-SMS-Canzler GmbH; MSD, Westfalia-separator). In this system, two stacks of rotating membranes are used. Preferably the two shafts rotate countercurrent to create the maximum shear forces at the membrane surface. This membrane overlapping (Figure 7.2B) can increase the permeate flux considerably (the magnitude depends very strongly on the type of feed and the crossflow conditions).

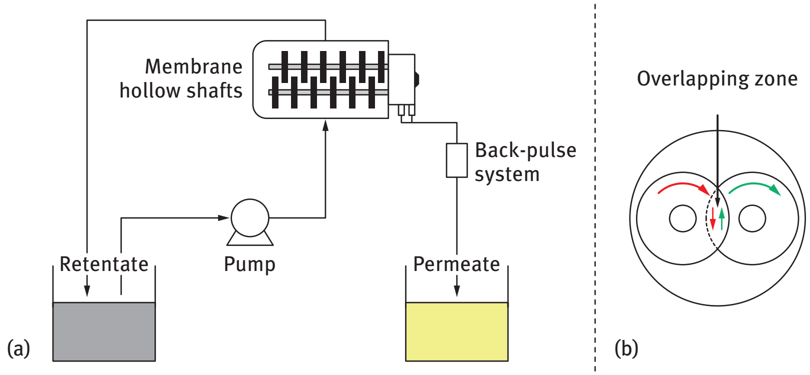

Figure 7.2: (A) Dynamos® system configuration; (B) membrane overlapping

Table 7.1: Analytical results of wine lees after different types of filtration [15]

	Cabernet Lees	Cabernet after rotary drum	Cabernet after tubular crossflow	Cabernet after dynamic filtration
Alcohol (%v/v)	12.44	12.2	12.41	12.4
Total SO_2 (ppm)	82	52	75	70
Anthocyanins (ppm)	713	650	675	691
Total phenolic index	1516	1402	1358	1456
Suspendid solids (%v/v)	30	0.5	0	0
Color intensity	0.766	0.7	0.683	0.735
Turbidity (NTU)	n.d.	50	0.5	0.5
Temperature intake (°C)	0	2	10	1–3

Table 7.1 gives the results of analyses of wine lees after comparison of three different methods of filtration (rotary drum filtration, crossflow filtration and dynamic filtration). The results showed little differences between the three types of filtration with a preference to dynamic filtration.

7.3 Electrodialysis and bipolar electrodialysis

Tartrates are naturally occurring crystals that often form in wines and may be considered undesirable to most customers. The crystals are formed from potassium hydrogenotartrate (KHT), a naturally occurring organic acid, and their solubility in wines decrease with the presence of ethanol. This unstable state can lead to the occurrence of KHT crystals in bottles with dramatic consequences on the final aspect of the wine. Wine stabilization as part of the winemaking process reduces the concentration of KHT in wine. Traditionally, wineries lower the potassium tartrate solubility in wine by chilling the wine to approximately −4°C. There are different types of

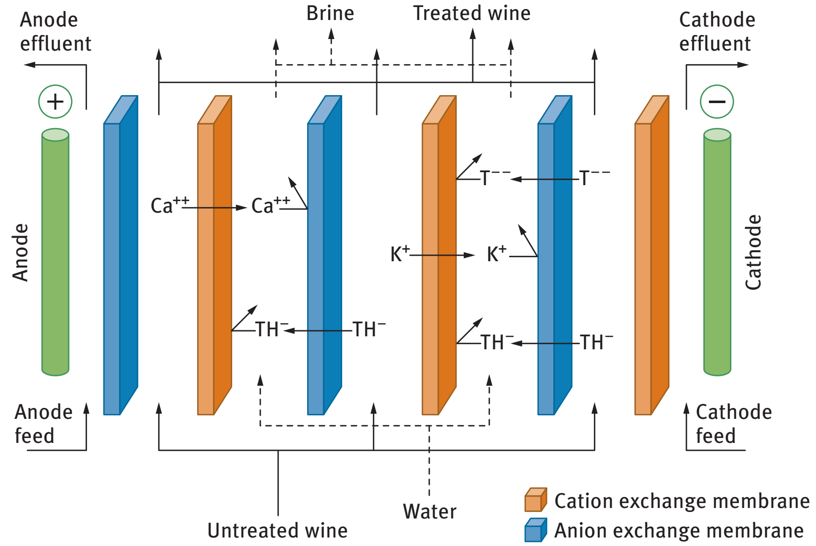

Figure 7.3: Electrodialysis principle for tartrate stabilization in wines

cold stabilization enhancement that may expedite the process, particularly seeding the wine with potassium tartrate crystals [16]. Wines are typically maintained at this temperature for a period of 1.5–3 weeks, depending on how easy it is to crystallize the potassium bitartrate, i.e., how "stable" the wine is. The cold stabilization is time- and energy-consuming and difficult to control. The electrodialysis (ED) process (Figure 7.3), as an alternative to traditional methods, removes the tartaric acids from the wine by passing it through an electric field and collecting ions (potassium K^+ and calcium Ca^{++}) and negatively charged tartaric acids on anionic and cationic membranes. The Eurodia Company and the French National Agronomic Research Institute (INRA) developed ED in the 1990s. The principle of this technology consists of the application of an electric field, because the presence of electrodes on both sides of the cell will lead to ion migration: cations (K^+ and Ca^{++}) will migrate towards the negative electrode (the cathode), whereas anions (TH^- and T^-) will move towards the positive electrode (the anode). The cations in the compartment "untreated wine" will be able to cross the cationic membrane and thus be eliminated from this compartment. However, they will not be able to leave the compartment "water" as they would find an anionic membrane on their way. The anions can be exported from compartment "untreated wine" because they will not be able to cross the next (cationic) membrane.

In principle, all cations and anions can be affected during ED. However, not all ions show the same behavior and their extraction depends on various factors. In theory, the transfer kinetics of ions depends especially on the speed constant (ϖ). This constant is characteristic for every ion in the solution. In practice, this constant depends essentially on the ion mobility and dimension, as well as on the nature of the membrane. Therefore, the choice and development of ED membranes was conducted on the considerations for the regulatory agencies, the technological characteristics of the available membranes and on enological criteria. The electrodialyser for continuous wine tartrate stabilization is composed of a stack of ED membranes of two compartments filled with inert gas, feeding pumps and two tanks allowing the return of the fluids (wine and concentrate) into their respective compartments. The wine return-tank is equipped with level sensors and the two circuits are both provided with a conductimeter. With help of the conductivity probes, an automatic device conducts the circulation sequences and the concentration level of the discharge. The wine is recirculated in the electrodialyser until achieving the reduction level of ions concentration. The deionization rate or the degree of deionization (DD) is the percentage reduction of electrical conductivity of the wine during the ED process. This DD must be determined with accuracy before the wine treatment. It is calculated as follow:

$$DD = \frac{\textit{wine initial conductivity} - \textit{wine final conductivity}}{\textit{wine initial conductivity}} \times 100\% \tag{7.1}$$

If the predicted DD is underestimated, the wine must be treated again by ED in a second step, which increases the operation time and complexity of the process and adversely affects the reliability of the technology [17]. The necessary DD can be determined by applying the conventional cold treatment to a sample of wine as this process is a very time-consuming; the DD is predicted using the minicontact test, which simulates at a bench-scale the cold treatment with seeding.

In 2003, Benitez et al. [18] compared the cold treatment and ED for tartrate stabilization of three sherry wines on an industrial scale with the objective of checking the efficacy of these techniques. The analytical results of the common enological parameters are shown in Table 7.2. The influence of ED treatment on the alcohol content, color intensity, pH and volatile acidity was small or negligible, while the effect on the titratable acidity was small and in direct relationship with the DD. The cold treatment produced a pH decrease of 0.2 units in the Fino wines, while the maximum decrease produced by ED in these wines was only 0.05 units. With regard to potassium, the ED produced an appreciable reduction in its concentration while the effect of cold treatment on potassium reduction depended on the wine type. Cold treatment produced a larger decrease in the tartrate content than ED.

In 2010, the Australian Wine Research Institute (AWRI) published a report comparing the cold treatment and ED for tartrate stabilization in wines [19]. The report showed that ED offers significant advantage in the power consumption and wine losses while wastewater volume and labor requirements are higher for ED than the cold treatment. This report concluded that based on the obtained results, ED appears to offer viable alternative method to tartrate stabilization in wines.

In the past two decades, it has been observed that wines are suffering from higher ethanol levels and pH values that are higher and higher. This phenomenon has

Table 7.2: Analytical results of common enological parameters during electrodialysis and cold treatment [18]

	Fino				Medium				Cream		
	Control	ED		CT	Control	ED		CT	Control	ED	CT
DD (%)		19.6	30.4			20.8	30.1			18.3	
Alcohol content (% vol.)	15.1	15	14.9	15.1	15.3	15.2	15.2	15.3	15.5	15.3	15.5
pH	3.18	3.16	3.13	2.98	3.54	3.5	3.51	3.45	3.43	3.37	3.43
Color Intensity	0.02	0.017	0.036	0.019	0.077	0.08	0.079	0.064	0.104	0.095	0.071
Titratable acidity (g/l)	4.23	4.01	3.9	3.84	4.12	4.11	4.03	4.02	4.09	3.94	3.88
Volatile acidity (g/l)	0.16	0.14	0.13	0.13	0.6	0.62	0.69	0.68	0.65	0.63	0.67
Saturation temperature (°C)	23.9	19.7	16.6	13	24.4	18.8	16.6	19.5	21	16.6	19.1
Minicontact test (µS/cm)	85	61	6	1	67	9	5	9	9	5	8
K (mg/l)	695	535	450	520	1470	825	620	820	705	520	695
Ca (mg/l)	102	72	71	90	97	97	92	120	95	70	120
Tartaric acid (g/l)	2.43	2.33	2.1	1.43	1.55	1.41	1.33	1.13	1.59	1.41	1.35
Malic acid (g/l)	0.177	0.189	0.153	0.161	0.2	0.206	0.192	0.215	0.132	0.148	0.158
Acetic acid (g/l)	0.14	0.136	0.125	0.125	0.59	0.6	0.675	0.653	0.59	0.575	0.58

been attributed to global warming and to enological practices. The lack of acidity in wines leads to the development of undesirable microorganisms and a disequilibrium in the organoleptic qualities of the wines. According to the European Community, only the addition of tartaric acid is allowed to correct the wines pH. An alternative to the addition of tartaric acid, which is difficult to control because tartaric precipitation, the European Commission and the International Organization of Vine and Wine (361–2010 resolution) in 2010 accepted the method of acidification by bipolar ED. The principle of wine acidification by bipolar-membrane ED is similar to ED, but the anion-exchange membrane is replaced by a bipolar-membrane. In its simplest form, a bipolar-membrane is a cation-exchange membrane laminated together with an anion-exchange membrane, through an intermediate layer (the "junction" layer). In the junction layer, water is split into hydroxide (OH–) ions and protons (H+) by a disproportionate reaction. The hydroxide ions and protons produced are separated by migration in the respective membrane layer out of the membrane. When the electric current is applied, the potassium ions (K^+) contained in the wine are attracted towards the cathode, they pass through the cationic membrane and are stopped by the bipolar-membrane. The OH^- ions migrate towards the positive pole (anode) into the brine (concentrate), whereas the H^+ ions migrate towards the negative pole (cathode) and replace the potassium ions that are extracted from the wine in order to conserve the ion equilibrium. This operation causes acidification (lowering the pH) by decreasing the potassium content and thus the salified form of organic acids in the wines. For a lowering of pH values there is a concomitant increase in titratable acidity. Acidification by bipolar ED can correct wine pH with a precision of 0.05 units. The target value of the treatment is determined following tasting with the producer. The maximum treatment value is 0.3 units of pH.

Deacidification using an electromembrane process (ED with bipolar membranes) of musts (resolution OIV-OENO 483-2012) or wines (resolution OIV-OENO 484-2012) is accepted in 2012 by the International Organization of Vine and Wine. The principle of wine deacidification by bipolar-membrane ED is similar to the acidification principle, but the anions are affected in this process because the cation-exchange membranes are replaced by anion-exchange membranes. The application of the electric current drives the anions (TH^- and M^-) towards the anode. They pass through the anionic membrane and are stopped by the bipolar-membrane. The anions are transferred from the wine compartment to the brine compartment where they are associated with H^+ cations losing their ionic form. The wine is impoverished in organic acids, reducing the titratable acidity and thus the wine is de-acidified.

7.4 UF and NF for reduction of must sugars

The process for reduction of must sugars comprises two membrane processes: UF and NF. This process is patented by the Bucher Vaslin company and is at present marketed under the name of REDUX®. In 2012, a specific application on the reduction of sugar content in musts through membrane coupling was adopted (Resolution OIV-OENO 450B-2012). The UF and NF are carried out according to the principle of tangential flow filtration: mass transfer across the membrane is caused by a pressure gradient that may vary from 5 to 80 bar according to the methods. In the REDUX® process, UF is used to separate macromolecules (especially polysaccharides and polyphenols) from musts before sugar concentration by NF. Osmotic pressure of the ultrafiltered must is therefore lowered. The sugar concentration by NF may be greater. The higher sugar concentration leads to a decrease in volume loss (elimination of a semi-concentrated must approximately 400 g/l sugar).

The retentate of UF by macromolecules is reintroduced into the original must. Plus, the permeate of NF is also reincorporated in the original must. The treated wine contains less alcohol but is richer in solids. NF is preferred to RO because it gives greater flow rates. NF membranes presenting higher cut-off thresholds allow the transfer of organic acids and potassium into the permeate.

7.5 RO and NF for sugar must concentration

The climate and the local growing conditions make each year's harvest unique. In some years, especially during poor growing conditions, grape musts do not have sufficient potential alcohol content. So, it is necessary to increase sugar concentration to obtain an increase in alcohol content in order to have a well-balanced wine. Winemakers use chaptalization techniques (adding sugars), must concentrate (MC) or rectified must concentrate (RMC) to compensate for poor growing seasons, or if they are located in areas of the world that experience cooler climates. The additive techniques increase wine volumes and sometimes lead to unbalanced wines. To avoid these problems there is a growing interest in subtractive techniques such as pervaporation, cryoconcentration, RO and NF.

RO is used to eliminate a certain volume of water of grape must by applying hydrostatic pressure (higher than osmotic pressure), leading to an increase in must sugar concentration. RO is considered an adequate technology to concentrate grape musts, with the advantages of:

- lower energy consumption
- minimal heat damage of the quality properties
- maintenance of sensory characteristics and nutritional value of the products
- absence of caramelization reactions
- compact and easy to operate facilities
- higher purity of the permeate compared to other membrane processes.

In 2002, Mietton-Peuchot et al. [1] showed that RO could be an alternative to chaptalization and vacuum evaporation. They showed that low temperature (about 10°C) and high applied pressure (about 75 bar) are conditions that prevent the must components from crossing the membrane. Conversely, the high pressure and the concentration provoked tartaric acid precipitation at the membrane surface, which increased the membrane fouling. Kiss et al. [20] showed that RO (60 bar, 20°C) coupled to high pressure NF (70 bar, 40°C) may produce must concentrate with high sugar concentration (around 45°Brix ≈450 g/l). They showed that the cost estimations of the membrane process are much cheaper than evaporation. In 2011, Santana et al. [21] evaluated the concentration of grape must by RO. The experiments were carried out in two steps. First, three transmembrane pressures (40, 50 and 60 bar) and four temperatures (20, 30, 40 and 50°C) were evaluated without juice concentrations. Under the evaluated conditions, the process conducted at 50°C and 60 bar presented the higher permeate flux and the maintenance of all the physical and chemical parameters of the product. In the second step, the grape juice was concentrated at three temperatures, 20, 30 and 50°C, always at 60 bar of transmembrane pressure. The temperature of 30°C resulted in an adequate value for the permeate flux in addition to maintaining the physical-chemical and nutritional characteristics of the concentrated product when compared to the single-strength juice.

NF is another membrane process tested as an alternative to RO. This process uses a pressure gradient (up to 40 bar) to transport must or wine through the membrane. Versari et al. [22] and Santos et al. [23] tested several NF membranes for must concentration. They found that NF membranes provided rejection coefficients ranging from 80–95% for sugars. In the literature, little has been published about this subject and there are possibilities to develop research activities in this sector.

7.6 RO, NF and MC for wine dealcoholization

Production techniques for manufacturing low or reduced alcoholic strength beverages have been developed over the last 15 to 20 years in order to satisfy a consumer demand for healthier alcoholic products. Decreasing alcohol consumption is a worldwide trend and lower alcohol consumption rates are associated with certain positive health benefits. Several technologies and strategies have been applied for removing alcohol, and among them the membrane processes after alcoholic fermentation.

Overall, RO is probably the most widely used technique at present for reducing the alcohol content in wine. It involves pressure filtration of the wine through a fine porous membrane that is permeable to alcohol and water, but not to most of the wine components. In order to reduce the alcohol content and to limit the volume loss, water from the RO filtrate must be recuperated. The most used process is RO coupled to column distillation (Figure 7.4). In the patent (WO 2004/113489), Gonçalves and De Pinho [24] propose a process of ethanol removal from wine based on the use of NF membranes coupled to a distillation operation. The NF membranes provide higher alcohol flow rates together with greater permeation rates than RO.

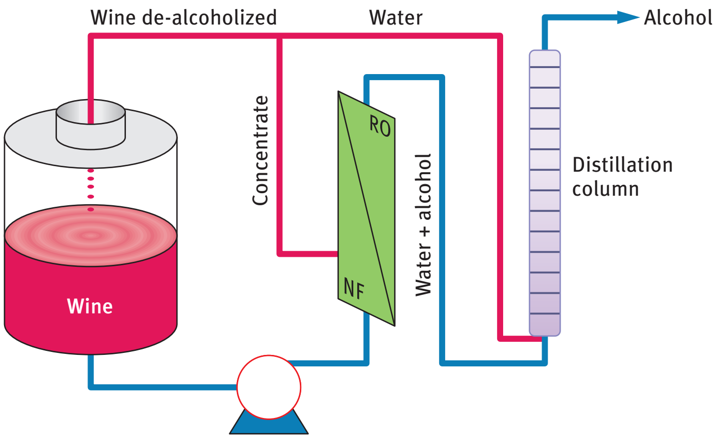

Figure 7.4: Wine de-alcoholisation process using membrane processes coupled to distillation

Another process tested for wine dealcoholization is OD. OD is a MC technique also known as osmotic evaporation, membrane evaporation, isothermal MD or gas membrane extraction. OD is a membrane transport process in which the wine containing one or more volatile components is allowed to contact one surface of a microporous membrane whose pores are not wetted by the wine, while the opposing surface is in contact with a second non-wetting liquid phase (usually water) in which the volatile components are soluble or miscible. The membrane thereby functions as a vapor gap between the two liquid phases, across which any volatile component is free to migrate by either convection or diffusion. The DF for such transport is the difference in vapor pressure of each component over each of the contacting liquid phases.

OD of a high alcohol content wine, at a temperature of 10–20°C and using water as the stripping liquid, can rapidly reduce the alcohol content to levels down to 6%. The mechanism of the process takes advantage of three factors: (i) ethanol is the most volatile component in the wine and the most rapidly diffusing species across the hydrophobic membrane, (ii) the vapor pressure of the flavour/fragrance components is low and, thus, so is their OD flux, and iii) the solubilities of the flavor/fragrance components in alcohol/water solutions are substantially higher (and their vapor pressures correspondingly lower) than they are in water. The main advantage of OD lies in its ability to work at low temperatures and pressures, thus avoiding mechanical damage and thermal degradation of the components and aroma of wines.

Diban et al. [25] investigated the feasibility of applying hydrophobic HF MCs to decrease the alcohol content of a synthetic wine solution. They showed that the ethanol content can be reduced by the same amount independent of the initial ethanol concentration present in wine in the range studied of 10–13% (v/v) of alcohol. They showed that a partial dealcoholization (reduction of 2% vol.) of Merlot wine gave acceptable aroma losses without a perceptible depletion of the product quality. Liguori et al. [26] showed that the optimal conditions for ethanol removal from model solutions at 10% vol. were obtained working in laminar conditions for both feed and stripping streams. They also observed a decrease in ethanol flux, while increasing the ethanol content of the solutions explained by the saturation phenomena. An increase in temperature accelerates the dealcoholization process. No significant differences in chemical analyses between crude and dealcoholised wine were found.

MC can be used on its own for wine dealcoholization or coupled to other membrane process. For example, the Australian process marketed by the company Memstar consists of alcohol reduction by a two-stage process of RO followed by a membrane module known as a MC (Liqui-Cel®). Wine to be treated is first separated by RO into concentrate and permeates streams. The wine concentrate contains all of the wine characters. The alcohol-rich permeate is passed through the MC, on the other side of which is a counter-flow of treated strip water. Alcohol passes through the membrane from the permeate into the water. The dealcoholised permeate is then cooled and recombined with the wine, lowering the alcohol of the final wine.

7.7 Gas control by membrane processes

All through vinification and ageing, as well as during ageing of the bottled wine, oxygen is a major actor in wine transformation. It has a beneficial role in many steps of the wine process (increase of the yeast population, color stabilization, etc.), but oxygen may also be detrimental when present during specific steps (oxidation, growth of microorganisms, etc.) So, micro-oxygenation techniques, allowing mastered oxygen input, are nowadays well known for their stabilizing effect. The basic principle of a micro-oxygenation technique is to continuously deliver to the wine, stored in tanks, oxygen quantities always smaller than the chemical or biological demand, to avoid any accumulation of dissolved oxygen. This oxygen input is done by microbubbling of pure gaseous oxygen into the wine with a small microfiltration membrane and this technique is now accepted practice in wine manufacturing. The major difficulty of micro-oxygenation with hydrophilic microporous membranes is the control of the dimension of the bubbles and of the yield of transfer. All the microporous systems (stainless steel, ceramic, organic membranes) have been characterized by gas-liquid porometry to obtain the pore size distribution. Depending on the media, the pore size distribution varies from 11 µm to 0.3 µm. MC could be used to control the gas transfer in wines (carbon dioxide and oxygen) before bottling. An important developed application of MC is the carbonation of sparkling beverages and the use of MC in oenology belongs to this latter type of application [25]. Indeed, it concerns the control of dissolved gases concentrations (CO_2 and O_2) in the case of wine carbonation/de-oxygenation or wine de-carbonation/de-oxygenation or wine de-oxygenation at the packaging step [27].

7.8 References

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