6
New Applications for Membrane Technologies in Enology

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6.1
Reduction of Alcohol Content

The development of techniques for reducing sugar content in musts and alcohol content in wines is the result of problems that certain vineyards are faced with, of overconcentration of sugars and, therefore, of alcohol in wines. The second reason for decreasing alcohol in the end product is that it corresponds to the wish of certain countries to take measures to restrain alcohol consumption. The problem is partly due, originally, to evolutions in viticultural and wine-making practices. It is now recognized that the quality of wine is a function of the phenolic compounds in the grape berries. Phenolic maturity is directly linked to a high concentration of sugars. This evolution in viticultural practices leads to too high a concentration of sugars that, in turn, can slow down or stop fermentation. A second cause of higher concentrations of sugar may be an increase in average temperatures due to evolutions of the climate.

Knowledge of membrane technologies in the domains of reverse osmosis, nanofiltration, and ultrafiltration has allowed the development of innovative alternatives in the partial reduction of alcohol content in wines [1–4]. Given that traditional methods of alcohol reduction are essentially based on phase changes (evaporation and distillation), there may be associated risks of deterioration of quality [5]. This has lead research teams and companies to introduce membrane technologies in alcohol-reduction processes in order to propose solutions that are more selective and more respectful of the end product.

6.1.1
Reduction of Must Sugars to Obtain a Lower Alcohol Content in Wines

The process is based on a preventive action, reducing the sugar content of musts, thus allowing better control of subsequent alcoholic fermentation. This process is patented by the Bucher Vaslin company and is at present marketed under the name REDUX® [6, 7]. The heart of the system comprises two coupled membrane units that produce a concentrate, which represents the fraction to be eliminated. The
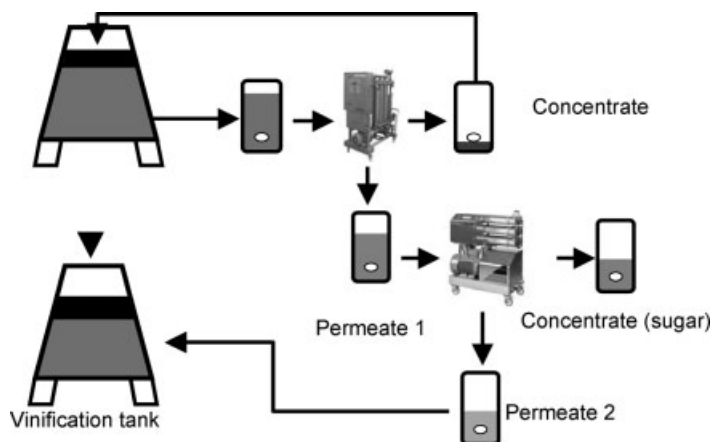
Figure 6.1 Representation of the REDUX® process [7].

sugar-reducing process (Figure 6.1) consists of a first stage, ultrafiltration that produces a "clear must" of the same sugar concentration as the initial must. In a second stage, this "must" is concentrated by nanofiltration and the permeate that is produced, made up essentially of water and acids, is reincorporated into the must that is being treated.

Nanofiltration gives greater flow rates than reverse osmosis. The higher cut-off threshold of the membrane allows the transfer of acids and potassium into the permeate. This allows the partial reintroduction of acidity with the water recuperated from the must before fermentation, the advantage being that mature musts have, in general, low acidity levels and any elimination of this acidity would be detrimental. The acid balance of the treated must will be little affected by the process.

The reduction in the sugar content of the musts, together with the loss of volume inherent in the treatment, leads to a modification of the solids-to-liquid ratio during fermentation on skins, which in turn leads to an increase in phenolic compounds, tannins, anthocyanins, and potassium (Table 6.1). The highest sugar concentration in the concentrate obtainable by nanofiltration is in the region of $400 \, g \, l^{-1}$.

However, differences in alcohol content during fermentation on the skins can modify the quantity and quality of the compounds that are extracted or produced. One notable phenomenon is that a lower alcohol content diminishes the burning sensation given by alcohol, with a corresponding reduction in sugariness and fatness. Nevertheless, this modification of the organoleptic qualities of the wine does not mean that appraisals of wines made from a sugar-reduced must are any less favorable.

The RAW® process, in which the concentration of ultrafiltered must is achieved by evaporation in a vacuum instead of by nanofiltration, results in lower losses in volume, the sugar being eliminated in a more concentrated form. However, the water that is recuperated and then reincorporated into the musts is acid free, which can lead to reduced acidity in the must.

Table 6.1 Analytical results of wines from treated musts [7].

	Merlot	
	Wine without treatment	Wine with Redux® treatment
Alcohol content (%.vol)	15.1	14.2
Total acidity (TA) (gH_2SO_4 L^{-1})	3.4	3.5
Volatile acidity (VA) (gH_2SO_4 L^{-1})	0.57	0.58
pH	3.80	3.85
Potassium (mg L^{-1})	1420	1620
IPT	77.3	81.6
Tannins (g L^{-1})	4.7	5.0
Anthocyanins (mg L^{-1})	654	676
HCl index	31	33
Dialysis index	30	32
Gelatin index	40.8	41.8

6.1.2
Reduction of Alcohol Content in Wine

In the 1980s a large number of studies were carried out on the partial or total removal of alcohol from wines. The reasoning was principally economic, given that wine growers the world over were suffering from chronic overproduction, and lesser-quality wines were hard to sell. This is the background to the attempts that were made to develop new wine-based beverages or grape juices adapted to consumer tastes, and also to create new sales opportunities by producing new wine-based products such as "light" and "alcohol-free" wines. Unfortunately, the commercial success was, at the time, far from that expected. However, this subject is, at present, once more under study for the reasons stated above. The most commonly used alcohol-reduction technique is based on the selective separation of water and alcohol from the wine by reverse osmosis (the aromatic compounds are preserved) together with the separation of alcohol from the reverse osmosis (RO) permeate by distillation (D). Partial alcohol reduction is thus achieved without watering down, this being prohibited by a large number of wine-producing countries. This removal of alcohol is carried out after malo-lactic fermentation for red wines, and at the end of alcoholic fermentation for white wines. This process presents the advantage of being alcohol selective, but treatment capacities are limited: low flow rates through reverse osmosis membranes, combined with low permeation rates, mean that it is necessary to work with large membrane areas and high pressures. This, of course, implies high investment and operating costs.

Nanofiltration (NF), on the contrary, provides substantially higher alcohol flow rates together with greater permeation rates. Working pressures are lower, leading to savings in investment and operating costs. In spite of a lower degree of selectivity in terms of the aromas contained in the wine, the organoleptic repercussions of

Table 6.2 Analysis results of permeate and wine after removal of alcohol [7].

	Wine before NF	Permeate NF	Wine after NF	Wine after treatment
Alcohol content(% vol)	12.7	10.9	13.1	10.9
pH	3.64	3.75	3.65	3.62
Total acidity (g H_2SO_4 L^{-1})	3.9	1.5	4.1	3.6
Volatile acidity(g H_2SO_4 L^{-1})	0.2	0.18	0.2	0.19
Tartaric acid (g L^{-1})	1.22	0.5	1.4	1.0
Lactic acid (g L^{-1})	1.4	0.7	1.6	1.0
K^+ (g L^{-1})	1.0	0.2	1.2	1.2
Anthocyanins (mg L^{-1})	999	nm	1120	914
IPT(Polyphenolic content, OD 280 nm)	56.9	nm	68.9	56

using nanofiltration for alcohol reduction are very close to results obtained by reverse osmosis [6]. Loss of aroma is compensated by the extraction of lower volumes in nanofiltration. Table 6.2 gives the results of analyses of wines and intermediate products carried out during partial alcohol removal in Cabernet Sauvignon wine.

Alcohol removal does not significantly modify the physical or chemical components of wine, only the acidity is slightly affected.

Other membrane processes for alcohol reduction are also available. For example, the Australian process marketed by Memstar consists of alcohol reduction by a two-stage process of nanofiltration followed by a membrane module known as a membrane contactor (Liqui-Cel®). The disadvantage of this process is that it uses large quantities of water to extract alcohol in the membrane contactor (MC). Table 6.3 compares different processes that are applicable to the reduction of alcohol in the end product. The sensorial evaluation has shown that, despite some aroma losses during the partial dealcoholization, the panel could not perceive some differences between initial wine of Merlot grape variety and the dealcoholized one. It can be concluded that this technology is feasible to achieve an alcohol reduction of 2% (v/v), without a perceptible depletion of the product quality [8].

Table 6.3 Comparison of different processes for a reduction of 2% in alcohol content from a 14% wine [9]– RO: reverse osmosis; NF: nanofiltration; D: distillation; MC: membrane contactor.

	RO-D	NF-D	RO-MC	NF-MC
Volume of permeate/volume of wine (%)	25	18	50	30
Volume of water (L) for the treatment/L wine	0	0	0,45	0,3
Coproduct (effluent)	Alcohol (92%)		Water with alcohol (4% RO, 7% NF)	

6.2
Reduction of Malic Acid in Grape Musts or Volatile Acidity in Wines

The volatile acidity or malic-acid reduction could also be done by coupling two stages of reverse osmosis. Since the free acids are poorly retained by the membrane, the permeate after the first stage filtration (permeate 1) contains free acids, salts, esters and other small molecules. Once the permeate 1 is neutralized with pH of the targeted acid, it will be retained by the second stage membrane in a salty form. The other components passing through (permeate 2) are reinjected in the initial wine. Potassium hydroxide is used for neutralization. During the treatment, the decrease of the acid concentration in the must or wine is progressive. For example, the rejection rate of acetic acid in the first reverse osmosis system varies between 40 and 50%. After the neutralization, the rejection rate of potassium acetate in the second reverse osmosis is higher than 90%.

6.2.1
Reduction of Malic Acid in Musts

Different methods can be used to remove acids from grape must or wine: cold stabilizing (partial precipitation of potassium tartrate), by the addition of chemicals such as calcium carbonate, or by malo-lactic fermentation [10, 12]. During malo-lactic fermentation, the transformation of $1 \, \mathrm{g \, l^{-1}}$ of malic acid into lactic acid results in a reduction in acidity corresponding to $0.6 \, \mathrm{g \, l^{-1}}$ of tartaric equivalent. Moreover, the microbiological stability of the wine is enhanced. However, malo-lactic fermentation is not always easy to control and it may provoke significant changes in the aromatic profile of wines, such as an increase in lacteous and buttery characteristics or a decrease in fruitiness [123].

The membrane process for the removal of malic acid is performed in two nanofiltration stages. The racked must is nanofiltered. The permeate contains water, malic acid, tartaric acid, and traces of small constituents contained in the must (Figure 6.2). The nanofiltration permeate is neutralized to a pH of approximately 7 by using potassium hydroxide.

$$C_4H_6O_5{}^{2-} + 2 \, KOH \rightarrow [C_4H_4O_5 \, {}^{2-} + 2 \, K^+] + 2 \, H_2O$$

In the second stage, the neutralized permeate is nanofiltered through the same membrane. The potassium malate is thus retained by the membrane. The permeate is reincorporated into the must. For a continuous process using two membrane units, the permeate flow rates of the two membranes should be identical in order to allow correct control of the pH during neutralization. This can be achieved by adjusting operating pressure.

6.2.2
Reduction of Volatile Acidity

The winemaking process can sometimes produce volatile compounds that impair the quality of the wine. Among these undesirable compounds, the best known is acetic
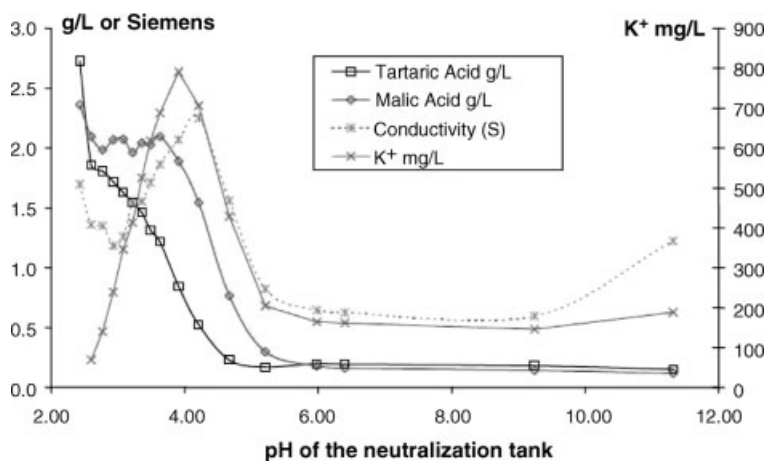
Figure 6.2 Influence of pH on the composition of the second permeate [13].

acid, present in free form or as a salt or ester. Processes have been developed to reduce volatile acidity in wines. They combine a nanofiltration or reverse osmosis stage with ion-exchange resins: following reverse osmosis of a fraction of the wine, the resulting permeate containing acetic acid is subjected to treatment on weak anionic resins and then reincorporated into the initial wine (Vinovation process). The process depends on the ability of a semipermeable membrane to separate from wine a permeate stream containing acetic acid and ethyl acetate, but substantially no flavor or color. Wine from the tank is recirculated via tangential flow against a reverse-osmosis membrane, and a small portion passes through. The retentate contains all the flavor and color, and is returned to the tank. The permeate is a colorless, flavorless liquid containing only water, alcohol, acetic acid and ethyl acetate, and is totally devoid of vinous character. The permeate is passed through a weak-base anion-exchange resin. Ethyl acetate is hydrolysed by the basic conditions within the column. The resin retains acetic acid, while permitting alcohol and water to pass through. The purified permeate is then recombined with the retentate and returned to the tank. The process continues until the desired degree of volatile acidity reduction is achieved. The resulting wine is essentially unchanged in volume and flavor. The main disadvantage of this method arises from the use of resins, which require regular regeneration.

The second process that is proposed is a combination of two membrane processes. It is based on the fact that reverse osmosis and nanofiltration membranes have different retention properties according to pH. Thus, in the case of a weak acid, the membrane will allow compounds with a low pH to pass through and will have a high rate of rejection above its pK. Acetic acid in wine having a pH lower than the membrane pK (4.75), it will not be retained. In a salified form, at a pH higher than that of the pK, it will be retained. The first stage of the process consists of reverse osmosis of the wine, giving a permeate that is relatively rich in acetic acid. This permeate, neutralized by potassium hydroxide, is subjected to osmosis in the second stage of the process. The potassium acetate is retained by the membrane and the acid-reduced

permeate is then reincorporated into the partially concentrated wine, which thus recovers a normal level of volatile acidity. The first reverse osmosis allows 50% of the acetic acid to pass through, whereas more than 99% of malic and tartaric acids are retained (compounds that are more voluminous and pK2 higher than that of wine). The retention rates for acetic acid and potassium from the permeate, for different volatile-acidity neutralization levels, are determined by the use of reverse osmosis and nanofiltration membranes. Both types of membrane retain over 98% of potassium acetate at a pH of 10.

6.3
Acidification of Musts and Wines

Over the last fifteen years or so it has been observed that wines have been appearing that contain higher ethanol levels and pH values that are higher and higher. This phenomenon has been attributed to global warming. Present pH values range from 2.8 to 4.2. This gradual rise in the pH values of wine generates problems in terms of the control of the evolution from both the microbiological point of view and that of color stability. This situation has led to greater and greater use of tartaric acid to acidify wines. Acidification ought to contribute to the balance of the gustative sensations provided by wines, promote correct biological development as well as adequate conservation of the wine, and compensate for a lack of natural acidity caused by local climate conditions or by wine-making practices that result in a lowering of natural acidity. Taking into account the salification balance of the organic acids in wine, the acidifying effect will result from a reduction in the proportion of salified forms and, thus, in mineral cation content. The aim of acidification is to modify pH values and not titratable acidity, which means increasing the proportion of free acids to the detriment of salified forms [14]. Conventional electrodialysis techniques have been successfully used in enology for the tartaric stabilization of wines [15]. The bipolar membrane is a thin polymer wall that is rendered operational by ion-exchange layers. The bipolar membrane has an anion-exchange face and a cation-exchange face, and functions in the same way as separate anionic and cationic membranes. The role of the bipolar membrane is to maintain the acid/base ionic balance of the process, this being achieved by the electrolysis of water molecules in the bipolar membrane under the driving force of an electric field during the treatment. The bipolar membrane must be correctly oriented: the cation-exchange side facing the cathode is permeable only to cations. In this way, a stack of bipolar membranes with cation-exchange membranes will only allow the passage of cations while retaining anions as well as uncharged particles [16]. This operation causes acidification by lowering the pH. The stacking of bipolar membranes in association with cation-exchange membranes means that there are two parallel hydraulic circuits: the compartment called the "diluate", which contains the wine, is acidified, whereas the "concentrate" compartment, containing an ionic solution, becomes more alkaline. The electric current that is applied between the two electrodes splits water molecules into OH^- and H^+ inside the bipolar membrane, which is in contact with the wine. The OH^-

ions migrate towards the positive pole (anode) into the brine, whereas the H^+ ions migrate towards the negative pole (cathode) and make up for the potassium ions that are extracted from the wine. 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 H^+ ions passing through the bipolar membrane then replace the K^+ ions in the wine in order to conserve the ion equilibrium.

Acidification by bipolar electrodialysis 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. Following acidification, malo-lactic fermentation takes place in the different wines, leading to slight variations in the pH values obtained. From the organoleptic point of view, products treated by electrodialysis are perceived as being "fresh" and not so "heavy in the mouth". The phenomenon of harshness in the mouth, which is the main disadvantage of the addition of tartaric acid, is not remarked upon, and color is also more intense [15].

Lowering the pH of wines essentially means a reduction in the concentration of potassium. The anion content remains unchanged, as is shown by the analyses of the organic acids and the determination of volatile acidity levels. For a lowering of pH values there is a concomitant increase in titratable acidity. Other analytical criteria (such as must sugars, alcohol content, residual sugars in wine, etc.) are not affected by the treatment, which only concerns positively charged elements.

The product is treated in a continuous process controlled via on-line readings of pH values. The process can be fully automated and requires only one treatment cycle, with no need for recycling [15]. Real-time supervision allows decisions to be taken at the right moment as a function of reasoned technological or commercial objectives. The treatment is carried out at normal temperature and atmospheric pressure with no mixing or stirring, through a series of membranes until the desired pH is obtained. Treatment time is short; the membrane modules are relatively small and efficient: this new technology is, therefore suitable for installation in mobile units so that it can be made widely available on a subcontract basis. The low-pollutant waste products can be easily used, for example for cleaning, and need not penalize the process.

6.4
Other Potential Applications

The reduction of bad tastes seems to be one of the fields being at present explored. Chilean researchers [17] have been working on the reduction of 4-ethylphenol and 4-ethylguaiacol in red wines by nanofiltration and adsorption. The permeate from the membrane is put into contact with a hydrophobic adsorbant resin, XAD-16HP. This is circulated in the wine until the desired concentrations are obtained. The process also allows the elimination of herbaceous aromas. The results of the study show that the resin is not sufficiently selective. The isolation of bad tastes in nanofiltration

permeate is possible, but it is necessary to find a way to eliminate theses bad tastes by a specific treatment (adsorption, fining, etc.).

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