

# Membrane processing across the vinification chain

Roberto Ferrarini<sup>1</sup>, Massimiliano Buiani<sup>2</sup> and Enrico Bocca<sup>2</sup>

<sup>1</sup>Science Department, Grapevine and Wine Technologies and Markets (DiSteMeV), University of Verona – Villa Ottolini-Lebrecht, Via della Pieve 70, 37029 San Floriano, Verona, Italy

<sup>2</sup>Vason Group – Località Nassar 37, 37020 Pedemonte, Verona, Italy  
Corresponding author's email: roberto.ferrarini@univr.it

## Introduction

Membrane separation techniques have developed greatly in oenology in the last 20 years. The principal aim of using membranes has been to obtain clarity and, above all, microbiological stability. Material improvement has made it possible to produce much more efficient membranes that carry out processes without detriment to product quality or the environment, as is the case of cross flow filtration.

Development of semi-permeable membranes, together with other separation processes, has allowed use of osmotic processes to reduce sugar concentration and reduce alcoholic content, and to reduce the content of malic acid, acetic acid or undesired molecules such as ethylphenol. Some of these techniques need wine fractionation, a technique not yet adopted in many countries and subject to current discussions at the Organisation Internationale de la Vigne et du Vin (OIV). However, some gaseous membrane techniques (contactor) make it now possible to carry out dealcoholisation and acid reduction in the winery, without having to fractionate the wine. Ion semi-permeable membranes are particularly interesting; these membranes allow electro dialysis to provide tartaric acid stability, pH modification and redox conditioning in wines.

## Membrane techniques

Membranes are applied when some separation is required. Membrane techniques are usually classified on the basis of:

- Selectivity: for particles sizes, chemical affinity, electrical charge, vapour pressure,
- Driving forces: pressure (osmotic, vapour, ..), electrical field, diffusion,
- Material: solid (organic, mineral,...), liquid, gas, porous/non porous
- Flow direction: orthogonal or tangential, and
- Geometry: frame and plate, spiral wound, tubular, hollow and capillary fiber.

There are many membrane processes (Figures 1 and 2). These range from filtration, which separates coarse solids, microorganisms, colloids and dispersed macromolecules (ultrafiltration), to the separation of substances in solution (nanofiltration) or ions (electrodialysis, pH modification) or the passage of electrical charge (redox conditioning).

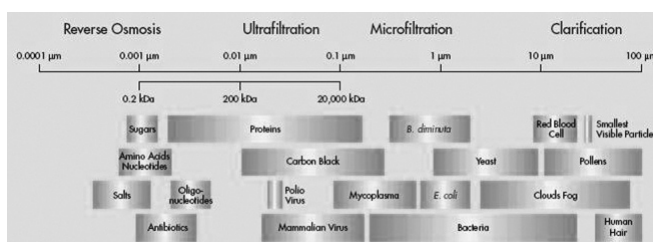


Figure 1. Relationship of types of membrane processes to particle size.

## Osmotic processes

With osmosis, only reverse osmosis (Figure 3, right diagram) is allowed by the European Community and OIV. However, from a qualitative point of view, forward osmosis (Figure 3, left diagram) could also be used, although development of materials and applications have not yet been successful.

## Nanofiltration

This osmotic process separates solutes by their size and molecular weight. Figure 4 shows the rejection curves of two nanofiltration

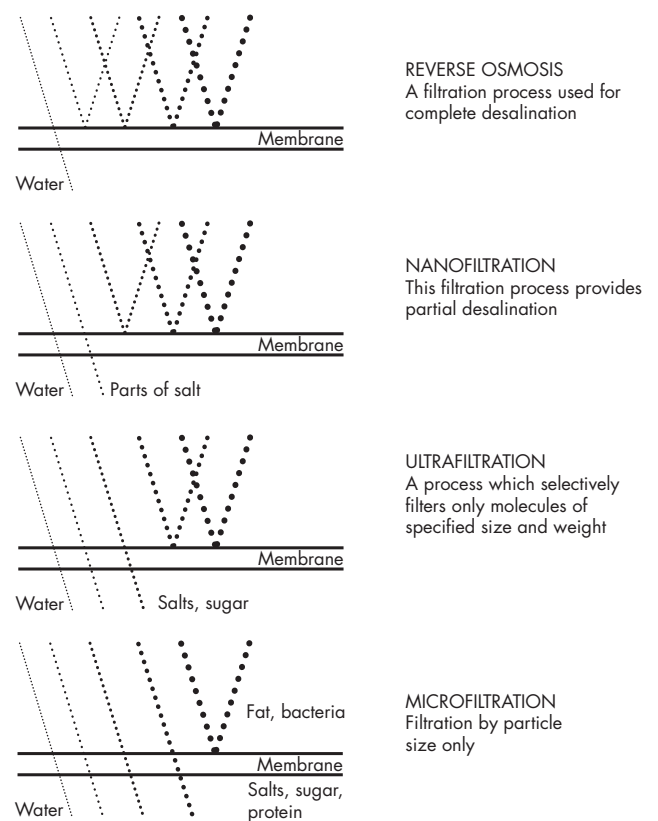


Figure 2. Retention behaviour of different membrane processes.

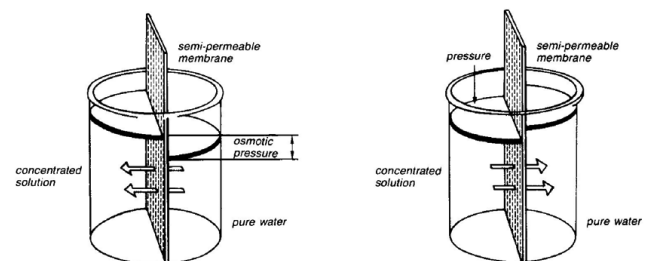


Figure 3. Osmotic processes: (a) in osmosis, water passes through the semi-permeable membrane from the lower salt concentration to the higher salt concentration generating a difference in level leading to a counterbalancing osmotic pressure; (b) in reverse osmosis, water passes through the semi-permeable membrane from the higher salt concentration to the lower salt concentration through the application of an external pressure (this is the principle applied in desalination).

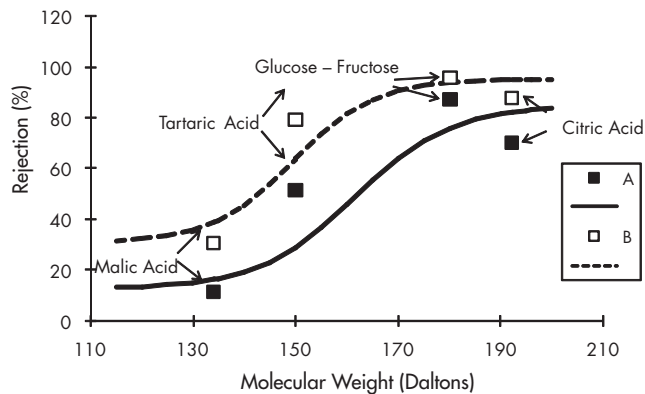
membranes used in some trials of must nanofiltration in 1995. Note that both membranes showed a high rejection of sugars and a low rejection of malic acid. There was a medium to high rejection of tartaric acid, depending on membrane type. Nanofiltration membranes can be used under lower pressure than reverse osmosis, with lower fouling, less expenditure, and a higher permeability.

**Nanofiltration mechanisms**

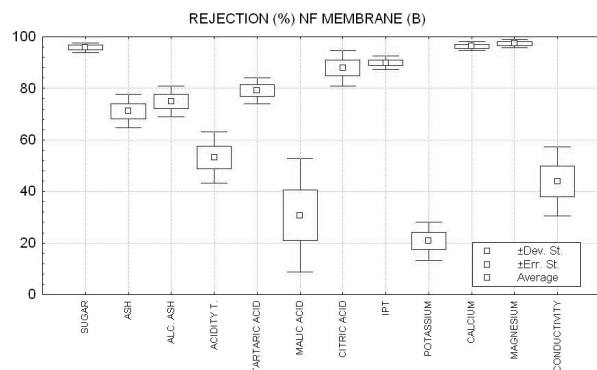
In nanofiltration, the driving forces are the differences in the pressure and osmotic pressure across the membrane. With increasing pressure, the rejection becomes more similar to that of reverse osmosis. Figure 5 shows the rejection of some must components by a specific nanofiltration membrane. The rejection is dependent upon the molecular weight (increasing molecular weight increases the rejection); it is also dependent upon ion valency (increasing valency increases the rejection). Rejection is also affected by pressure (increasing pressure increases rejection) and temperature (increasing temperature increases rejection). Nanofiltration has found good oenological applications in the treatment of must to, amongst others:

- increase sugar content (must self enrichment)
- decrease sugar content (to decrease future wine alcoholic degree)
- decrease malic acid content
- decrease potassium ion content

A study of the effect of nanofiltration was carried out on 20 white grape must samples harvested in 1994. The samples were all of the same grape variety, a productive variety in the Veronese area of Italy. Table 1 shows the range of composition of the musts. Nanofiltration of these musts provided permeates with the composition means and standard deviations shown in Table 2. Interesting in the data is that substrates like malic acid and potassium ion have a rejection that is very low. This allows the design of some oenological processes involving nanofiltration.



**Figure 4.** Rejection curves of two nanofiltration membranes, A and B, for some wine substrates.



**Figure 5.** Nanofiltration selectivity and rejection.

**Sugar management**

Nanofiltration can be used to enrich grape must (Figure 6). It provides a permeate in which there is a partial dehydration, or concentration of must with better results than reverse osmosis. It does not increase the concentration of malic acid or potassium ion ( $K^+$ ) so, generally speaking, it provides a better equilibrium balance in the must and in the resulting wine.

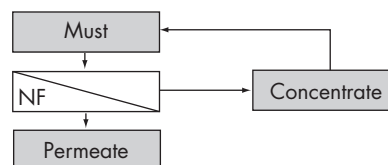
A variation of this technique can be used to reduce the sugar concentration (Figure 7). First, a must that has been clarified is ultrafiltration-treated to provide a concentrate at about 40°Brix. Nanofiltration of this concentrate is followed by return of the permeate to the original must to return to the must a large part of the acids and other extracts.

**Table 1.** Range of composition across 20 white grape must samples used to study the effect of nanofiltration.

Must component	Minimum	Maximum
Sugar (g/l)	160	190
pH	3.10	3.54
Titrateable acidity (g/l)	5.4	9.2
Tartaric acid (g/l)	1.99	4.15
Malic acid (g/l)	2.83	4.82
Citric acid (g/l)	0.15	0.35
Potassium, $K^+$ (mg/l)	765	1012
Calcium, $Ca^{2+}$ (mg/l)	40	103
Magnesium, $Mg^{2+}$ (mg/l)	51	92

**Table 2.** Composition of the permeate from nanofiltration of the must samples of Table 1. The mean and standard deviation are of 20 must samples.

Permeate component	Mean value	Standard deviation
Sugar (g/l)	7.0	3.6
Ash (g/l)	0.9	0.2
Alc. Ash (meq/l)	8.3	3.2
pH	2.9	0.0
Titrateable acidity (g/l)	3.8	1.5
Tartaric acid (g/l)	0.7	0.2
Malic acid (g/l)	2.7	0.9
Citric acid (g/l)	0.0	0.0
Total phenols (mg/l)	17.6	8.9
Proanthocyanidins (mg/l)	0.0	0.0
Catechins (mg/l)	0.2	0.1
Potassium, $K^+$ (mg/l)	818	97
Calcium, $Ca^{2+}$ (mg/l)	3.4	2.2
Magnesium, $Mg^{2+}$ (mg/l)	2.2	1.6
Conductivity ( $\mu S/cm$ )	1113	422



**Figure 6.** Concentration of must without increase of malic acid or potassium ion, using nanofiltration.

Nanofiltration has better performance than reverse osmosis:

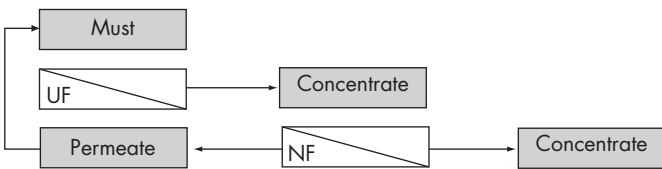
- Lower working pressure and higher membrane permeability.
- Rejection management working on the pressure and the temperature.
- Nanofiltration is also cheaper than reverse osmosis; it has:
- Less power expenditure
- Less plant expenditure
- 

**Reduction of malic acid and potassium ion levels**

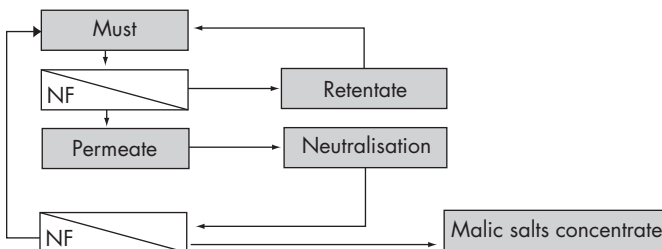
A decrease of must malic acid content can be achieved by the process of Figure 8, involving two stages of nanofiltration. The retentate of the first nanofiltration is remixed with the must. The permeate, which is particularly rich in malic acid, is neutralised to generate organic acids salts. Further nanofiltration of the neutralised permeate removes the salts (mainly malic acid salts), allowing return of the second permeate to the must. Reduction of potassium ion levels can be achieved by cation-exchange of the permeate of must nanofiltration (Figure 9).

**Nanofiltration of wine**

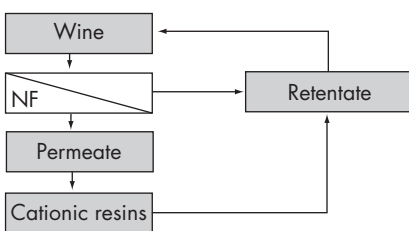
Figure 10 shows the rejection of some wine components with a particular nanofiltration membrane. Compared to must



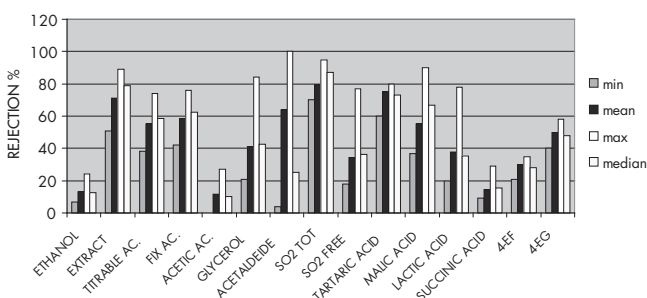
**Figure 7.** Reduction of the sugar concentration of must using nanofiltration.



**Figure 8.** Removal of malic acid using nanofiltration.



**Figure 9.** Removal of potassium ion using nanofiltration.



**Figure 10.** Rejection of wine components in nanofiltration.

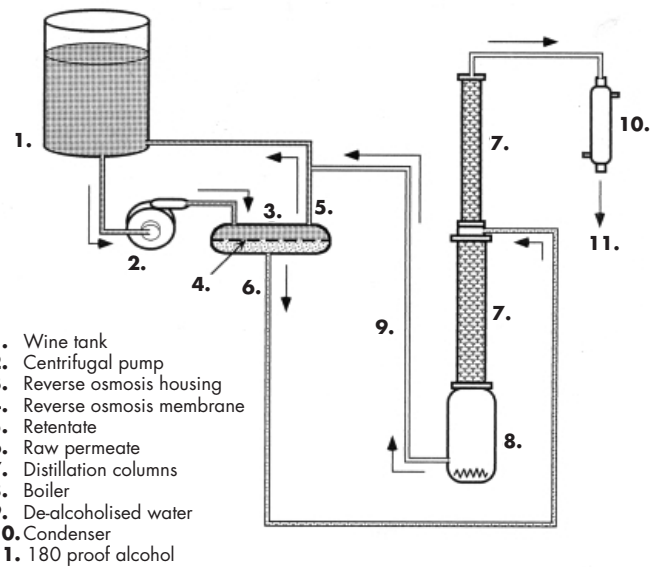
nanofiltration, organic acid rejection is usually increased because the pH in wine is usually higher than in must, leading to more of the organic acids existing in their salt form. It is interesting that there is a low rejection of ethanol, acetic acid and ethylphenol (4-EP in Figure 10).

**Reducing alcohol content**

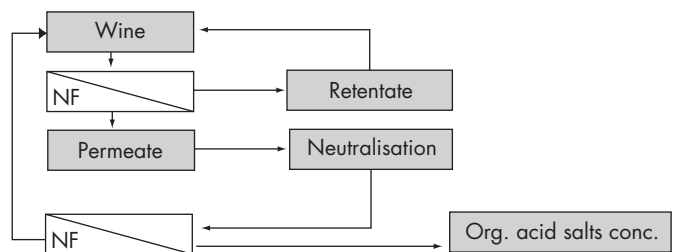
This involves three steps. First, recirculation of the wine over reverse osmosis or nanofiltration membranes to provide an ethanol-rich permeate; then alcohol removal from the permeate with distillation or other processes; finally return of the dealcoholised permeate to the wine (Figure 11).

**Reducing total acidity and/or volatile acidity**

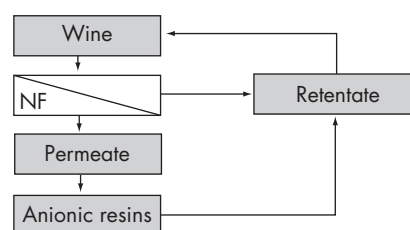
Figure 12 shows wine deacidification involving two stages of nanofiltration. The first stage produces a retentate that is remixed with the wine; the permeate is neutralised and nanofiltration of the neutralised permeate retains organic acids as their salts allowing the return of the permeate to the wine. Figure 13 shows a process to reduce wine volatile acidity by treating the nanofiltration permeate



**Figure 11.** Reduction of wine ethanol concentration through reverse osmosis.



**Figure 12.** Reduction of wine total acidity with nanofiltration (NF).



**Figure 13.** Reduction of wine volatile acidity with nanofiltration (NF).

with anionic resins prior to reintegrating it with the wine and retentate.

**Reducing pH and potassium ion**

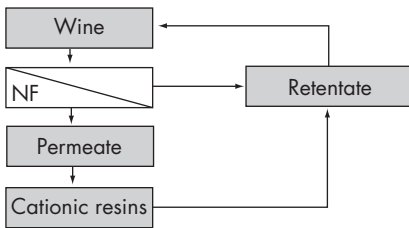
Figure 14 shows a process to reduce pH and potassium ion concentration by treating the permeate of wine nanofiltration with cation-exchange resin then reintegrating it with the wine and retentate.

**Brett off flavour**

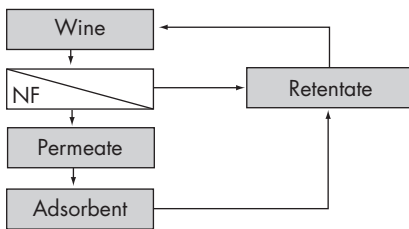
Figure 15 shows a process to reduce ethylphenol content by treating the nanofiltration permeate with adsorbent resins prior to reintegrating it with the wine and retentate.

**Contactor technique**

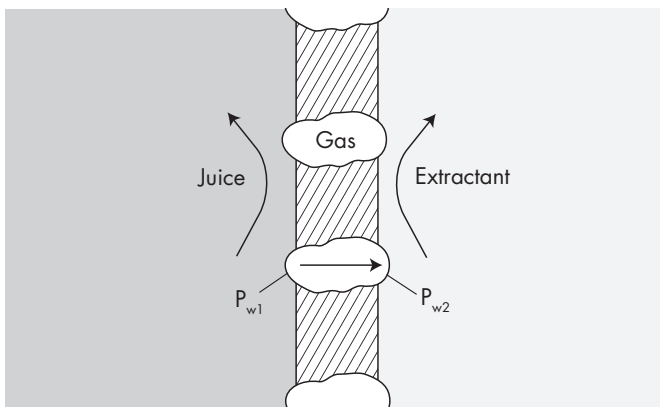
This is a membrane technique in which a gas or liquid is immobilised inside the pores of a hydrophobic membrane that separates two phases. It allows material exchange through the immobilised medium in the membrane pores without dispersal of one phase into the other. Typically, a film of microporous hydrophobic material (about 0.2 micron) supports a gas that acts as a membrane separating two phases. The material exchange through the membrane then happens in the form of gas (vapour) (Figure 16). Although a plate and frame membrane was initially used, it has been replaced by the use of commercially available hollow fibre membranes.



**Figure 14.** Reduction of pH and wine potassium ion concentration with nanofiltration (NF).



**Figure 15.** Reduction of *Brettanomyces* off-flavour with nanofiltration (NF).

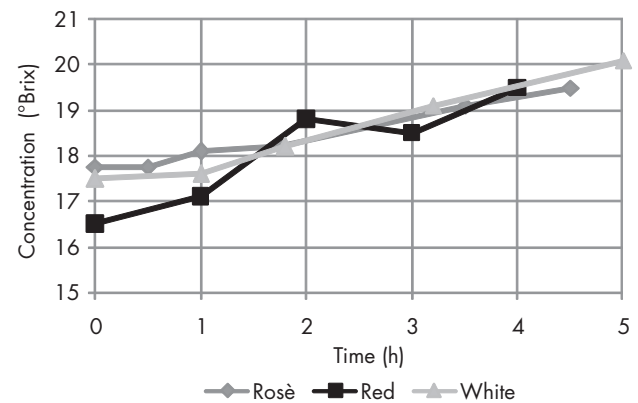
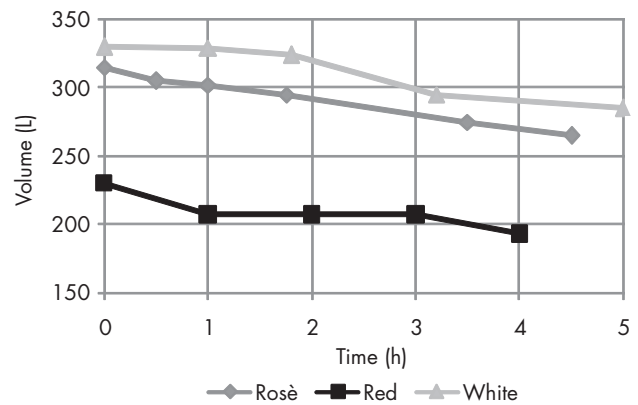


**Figure 16.** Principle of the contactor technique. Juice components diffuse through the gas that is immobilised in a hydrophobic membrane separating the juice from an extractant liquid.

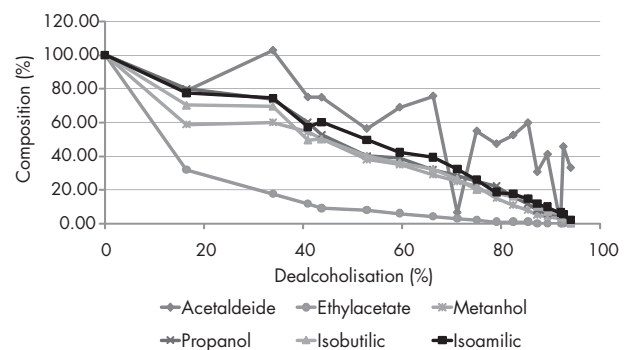
Concentration of sugars can be achieved by removal of a portion of the water of the must by water vapour permeation across the membrane, a process that is driven by a difference in water vapour pressure that arises from the extractant being a solution with high osmotic pressure (70% glycerine; this avoids corrosive phenomena that are typical of other extractants such as sodium chloride) (Figure 17). Afterwards, the diluted glycerine solution must be concentrated through another process, for example hot evaporation. This must treatment gives quality results similar to the use of reverse osmosis.

More interesting and in current use is the application of the membrane contactor technique to wine alcohol reduction, either to partially reduce the alcohol level (by 2–3 %) or to produce wines with lower or no alcohol. In dealcoholisation, the driving force is a difference of vapour pressure created by a difference of concentration using water as extractant. During dealcoholisation, other volatile compounds can be removed (Figure 18).

Using this technique, it is possible to reduce wine volatile acidity by extracting acetic acid through the use of a small extractant quantity which is continually recirculated through an anionic-exchange resin column which absorbs the acetic acid. This allows removal of acetic



**Figure 17.** Change of must sugar concentration with time using the contactor process at 9–15°C with 61–78% glycerol as extractant.



**Figure 18.** Removal of other volatile compounds during dealcoholisation.

acid without substantial change to the amount of other volatile compounds (Figure 19). As this technique processes the extractant outside the wine environment, other undesirable wine compounds can also be specifically eliminated by processing the extractant with methods specific to the compound of interest.

In summary, the 'membrane contactor' technique allows partial dealcoholisation with results similar to other membrane techniques in terms of quality; the technique is currently being evaluated by the OIV. It can also remove some other volatile compounds from the wine, with the advantage that processing of the extractant, for instance with anionic resins for acetic acid removal, is external to the wine.

### Pervaporation (PV)

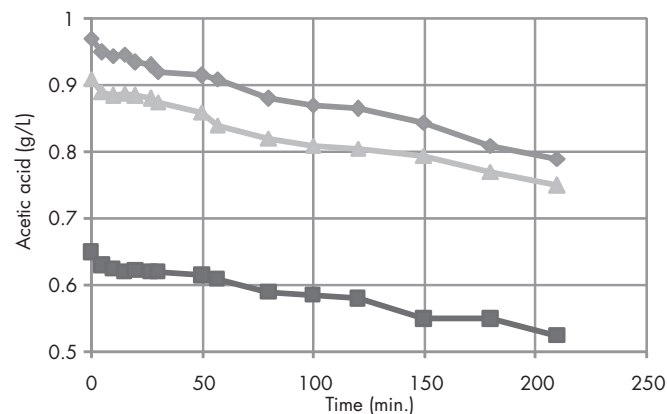
This is a process in which a liquid mixture is separated by a non-porous membrane from a gaseous phase that allows partial evaporation. The process is called pervaporation because the substance crossing the membrane changes its physical state. The mixture is in contact with the membrane as a liquid but the diffusing compound is desorbed on the permeate side as a gas. Evaporation is the driving force. In winemaking, a hydrophilic membrane can be used for must concentration, while a hydrophobic membrane can be used for dealcoholisation. Evaporation can be induced either by application of a vacuum (Vacuum PV) or by heating (Thermo PV).

### Electrodialysis

In this technique, membranes are used that are permeable only to ions. Cationic membranes allow flow of cations; conversely, anionic membranes allow flow of anions. The two membrane types are alternated (Figure 20) creating compartments with wine that alternate with compartments of brine. The driving force for the process is an electric field provided by an anode and cathode placed at the ends of the collection of membranes.

In Italy the process is now widely used for tartaric acid stabilisation. Unlike cold stabilisation, polyphenols and colloids are not involved; other ions including  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are also removed, and more potassium ion is removed than tartaric acid.

It is also possible to perform pH reduction with electrodialysis, using cationic and bipolar membranes, rather than cationic and anionic membranes. The bipolar membranes are impermeable to ions, hence there is removal of cations leading to a decrease of pH and an increase of acidity. The process has been realised by Prof. Michel Moutounet at INRA.



**Figure 19.** Concentration of acetic acid during three wine treatments using the contactor process in which there is removal of acetic acid from the extractant by treatment with anion-exchange resin.

### Electro-treatment for redox conditioning

Wine redox conditioning can occur if an electric current flows through the wine: there is reduction at the cathode and oxidation at the anode. To provide a more homogenous process, the entire tank can be used as an electrode. It can be with either an anodic tank (Figure 21, right diagram) with a (+) charge on the tank, which provides wine oxidation (or oxygen production by water electrolysis), or a cathodic tank (Figure 21, left diagram) with a (-) charge on the tank, which leads to wine reduction (or hydrogen production by water electrolysis). The membrane is used to separate the non-tank electrode from the wine with a reduction or increase, respectively, of wine redox level.

If the metallic tank is used as an anodic electrode (leading to wine oxidation), there will be very strong corrosion making it essential to use an inert metal, for example titanium. Initial results have shown that there is a large fall in wine redox potential with a cathodic (reductive) tank, and some lesser fall in redox potential in the anodic (oxidative) tank. Furthermore, wine stored in a titanium tank has a higher redox potential than wine stored in a stainless tank.

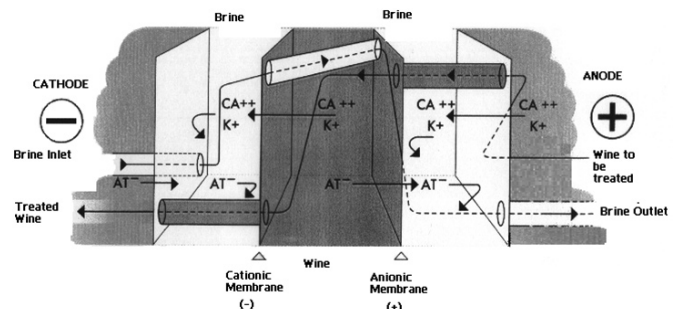
The effects of redox conditioning are evident on red wine colour. Wines with less colour intensity are obtained as the extent of reductive redox conditioning is increased. Organoleptic effects are also very evident.

### Acknowledgements

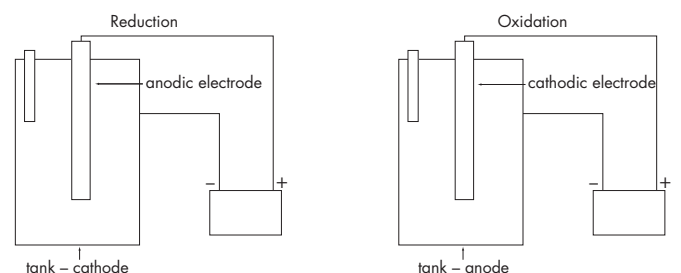
- Vason Group, Italy
- Prof. Carlo Gostoli, Chemical Engineering Department, University of Bologna, Italy.

### References

Amati, A., Ferrarini, R. and Barbieri, P. (1995) Autoarricchimento dei mosti con membrane permeo-selettive. 2° Congresso Italiano di Scienza degli Alimenti 'Ricerche e innovazione nell'industria Alimentare', Cernobbio (CO), 21-22 settembre 1995. Proceedings (II), Chiriotti Editori, 665-686.



**Figure 20.** Use of ion-permeable membranes to create alternating layers of wine and brine, with each layer bounded by a cationic membrane on one side and an anionic membrane on the other. Ion flow is driven by an electric field provided by the cathode and anode.



**Figure 21.** Arrangement of electric charge for redox conditioning; left = cathodic tank, right = anodic tank.

- Bregoli, M., Cervellati, A., Ferrarini, R., Leoni, C., Zani, A., Zardi, G. and Gostoli, C. (2001) Development and modelling of a plate and frame membrane contactor for juice and wine processing. Alvarez J.R. (eds), Proceedings of 'Engineering with membranes', University of Oviedo, Granada, 3–6 giugno 2001, Vol. II, 259–264.
- Celere M. and Gostoli C. (2002) The heat and mass transfer phenomena in osmotic membrane distillation. *Desalination* 147, 133–138.
- Cervellati A., Zardi G. and Gostoli C. (1998) Gas membrane extraction: a new technique for the production of high quality juices. *Fruit Processing* 10, 417–421.
- Ferrarini, R. (1997) Tecniche di autoarricchimento del contenuto zuccherino dei mosti d'uva. XIV° Congresso Nazionale Società Italiana di Alcologia 'L'alcol e i suoi diversi scenari'. Castel S. Pietro Terme (BO), 10–12 ottobre 1996. *Alcologia* 9 (1), 43–54.
- Ferrarini, R., Versari, A. and Galassi, S. (2001) A preliminary comparison between nanofiltration and reverse osmosis membranes for grape juice treatment. *Journal of Food Engineering* (50), 113–116.
- Gostoli C. (1999) Thermal effects in osmotic distillation. *Journal of Membrane Science* 163/1, 75–91.
- Kunz W., Benhabiles A. and Ben-Aim R. (1996) Osmotic evaporation through macroporous hydrophobic membranes: A survey of current research and applications. *Journal of Membrane Science* 121, 25–36.
- Moutounet M., personal communication.
- Pinacci, P., Barbieri, P., Ferrarini, R., Amati, A. (1996) Development of a nanofiltration process for grape must concentration. The 1996 International Congress on Membranes and Membranes Process, Yokohama (Japan), 18–23 August 1996. Proceedings, 868–869.
- Vaillant F., Jeanton E., Dornier M., O'Brien, Reynes M., Decloux M. (2001) Concentration of passion fruit on industrial pilot scale using osmotic evaporation. *Journal of Food Engineering* 47, 195–202.
- Versari, A., Ferrarini, R., Parpinello, G.P., and Galassi, S. (2003) Concentration of grape must by nanofiltration membranes. *Trans IChemE*, September (81, part C), 275–278.
- Versari A., Ferrarini R., Torielli G.B., Parpinello G.P., Gostoli C., and Celotti E. (2004) Treatment of grape juice by osmotic distillation. *Journal of Food Science* 8 (69), 422–427.