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Membrane technologies in wine industry: an overview of applications and recent developments

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Abstract:

Membrane processes are increasingly reported for various applications in wine industry such as microfiltration, electrodialysis and reverse osmosis but also emerging processes as bipolar electrodialysis and membrane contactor. Membrane-based processes are playing critical role in the field of separation/purification, clarification, stabilization, concentration and de-

alcoholization of wine products. They begin to be an integral part of the winemaking process. This review will provide an overview of recent developments, applications and published literature in membrane technologies applied in wine industry.

Keywords: Wine, nanofiltration, reverse osmosis, electrodialysis, membrane contactor, cross-flow microfiltration

1. Introduction

Wine is one of the most consumed alcoholic drinks in the world. It is made using several procedures with objective of marketing limpid and stable product satisfying consumer expectations. Wine stabilization could be divided into physico-chemical and microbiological stabilization. Limpid and stable wine is insured by several procedures of clarification and stabilization including traditional practices as fining and precoat filtration as well as new practices such as membrane technologies.

Over the last 30 years, membrane technologies have become an important tool in the food processing industry. Nowadays, they are commonly used in the processing of several beverages. In wine industries, membrane operations are replacing several conventional processes as shown in figure 1. For example, cross-flow microfiltration replace the traditional filtration techniques as diatomaceous-earth filtration for wines clarification, sugar enrichment becomes to be more insured by reverse osmosis instead of chaptalization or addition of rectified concentrated must as well as electrodialysis is used to tartrate stabilization instead of chilling or cold stabilization. These techniques constitute real alternatives to some traditional enological practices even if some techniques like membrane contactor are still in experimental stages.

One of the most applied membrane process in wine industry is cross-flow microfiltration (CFMF). This technique is developed as an alternative to precoat filtrations. These latters showed quickly their limits in terms of wine quality, wine loss and their implementation especially in cellars dealing with huge volumes of wines. Comparing to the traditional techniques, CFMF can bring the following benefits: i) combination of clarification,

microbiological stabilization and sterile filtration in one single continuous operation; ii) reducing wine loss and energy costs by substitution of several treatments of traditional filtrations in a single operation; iii) elimination the use of diatomaceous earth and sheets, thereby, reducing production costs and wastes and improving hygiene and work safety.; iv) continuous and highly automated processes (elimination of labor costs and saving time) and possibility of data recovery.

Despite all these advantages, the CFMF development in wine filtration has long been hampered by significant fouling of the membrane. The main consequences of this fouling are poor performances, high costs and risk of excessive retention of some wine components which may lead to a loss of some organoleptic characters. Therefore, several studies have been conducted to understand and to control membrane fouling (Peri et al., 1988; Belleville et al., 1992; Czekaj et al., 2000; Vernhet et al., 1999; 2002; 2003; Boissier et al., 2008; Ulbricht et al. 2009; El Rayess et al., 2011; 2012). The application of CFMF in oenology as well as the parameters influencing the membrane fouling or de-fouling (summarized in figure 2) were reviewed by El Rayess et al. (2011) and therefore we will not develop this technique later in the review.

In the recent years, other membrane applications in wine-making processes have been extensively studied. These techniques concern: i) electrodialysis (ED) for tartaric stabilization, acidification and de-acidification of musts and wines; ii) nanofiltration (NF) and reverse osmosis (RO) for must concentration and wine de-alcoholization iii) coupling ultrafiltration (UF)/nanofiltration (NF) for reduction of must sugars; iv) membrane contactor for wine de-alcoholization and management of dissolved gasses.

The objective of this review is to provide an overview on the membrane technologies in wine industry in order to highlight the applications, the advantages, the drawbacks and the developments of these techniques in oenology sector.

2. Electrodialysis for tartaric stabilization and acidification/de-acidification of musts and wines

Electrodialysis (ED) is an electrochemical process similar to ion exchange in which dissolved ions move from one solution to another, employing an electrical potential as driving force (two electrically charged electrodes) (Figure 3). ED differs from a normal ion exchange process by utilizing ion-selective semipermeable membranes to segregate charged ions extracted from a solution (Figure 3). The membranes are composed of polymer chains which are cross-linked and intertwined into a network, and bear either fixed positive or/and fixed negative charges. Three types of ion-exchange membranes are commonly used in electrodialysis: anion-exchange membranes, cation-exchange membranes and bipolar membranes. Anion-exchange membranes are membranes that allow anions to pass through (brine) but do not allow cations to permeate. Cation-exchange membranes are membranes that permeate cations but not anions. In practice, the cationic and anionic membranes are usually arranged alternately with plastic spacers to form thin solution compartments called cells (thickness around 300-700 μm). Bipolar membrane is a cation-exchange membrane laminated together with an anion-exchange membrane, through an intermediate layer (the "junction" layer). They do not allow ions of either charge to permeate all the way through the membrane

2.1. Electrodialysis for tartaric stabilization

The major physical instability in bottled wines remains the precipitation of the tartaric salts (KHT: potassium hydrogenotartrate, CaT: calcium tartrate). These salts are naturally found and supersaturated in musts but their solubility decreases in the presence of ethanol and the low temperatures. This unstable state can lead to the occurrence of KHT crystals in bottles with dramatic consequences on the final aspect of the wine. To overcome the problem of tartaric precipitation in the bottles, the excess of this salt is traditionally removed by cooling the wine to -4°C over several days. Briefly, potassium hydrogenotartrate stabilization is obtained by treating the wine with artificial cold using different technologies: i) slow cold stabilization without KHT crystal seedling, ii) rapid cold stabilization including KHT crystal seedling (Lasanta and Gomez, 2012). The traditional cold stabilization method depends on many factors as wine composition, temperature, KHT initial supersaturation and its time and energy consuming and difficult to control. The limitations of the cold tartaric treatment led to the development of new techniques like electrodialysis.

The principle of electrodialysis for tartrate stabilization is based on the properties of membranes to transfer exclusively either cations or anions. Under the effect of an electric field, anions (mainly TH^{-} and T^{-}) will migrate towards the positive electrode (the anode) while cations (mainly K^{+}) will be attracted by the negative electrode (the cathode). The anions are able to pass through the anion-selective membrane, but are not able to pass by the cation-selective membrane, which blocks their path and traps the anions in the brine stream (Figure 3). Similarly, cations move in the opposite direction through the cation-selective membrane under a negative charge and are trapped by the anion-selective membrane. Wine circulates along one side of the membrane and on the other an electrolyte that removes the ions. The treated wine will constitute

the dilute compartment and the eliminated ions will constitute the concentrate or brine compartment.

The wine is recirculated in the electrodialyser until achieving the reduction level of ions concentration. The deionization rate (DR) or the degree of deionization (DD) is the percentage reduction of electrical conductivity of the wine during the electrodialysis process. This degree of deionization must be determined with accuracy before the wine treatment. It is calculated as follow:

$$DD = \frac{\sigma_{\text{initial}} - \sigma_{\text{final}}}{\sigma_{\text{initial}}} \times 100\% \quad (1)$$

If the predicted DD is underestimated, the wine must be treated again by electrodialysis in a second step which increases the operation time and complexity of the process and adversely affects the reliability of the technology (Soares et al., 2009).

Gonçalves et al. (2003) have measured the influence of electrodialysis operating time on a red and a white wine conductivity. The decrease of conductivity is associated with the removal of potassium and tartaric acid as the cations and anions present in higher concentrations. The values of the degree of deionization are assigned in percentages in figure 4. Soares et al. (2009) reported that white and rose wines deionized by electrodialysis are only stable after a DD of 25% and 30% respectively. Benitez et al. (2003) determined the DD of the three sherry wines (Fino, medium and cream). They found that Fino wine (sugars < 2 g.l⁻¹) was stable after a DD of

26.9%, the medium wine (sugars \acute{e} 40 g.l⁻¹) was stable after a DD of 20.8% and the cream one (sugars \acute{e} 100 g.l⁻¹) was stable even before electrodialysis.

Others analytical methods than DD are used to predict the wine tartaric stability. These methods include the cold or freeze test, the conductivity test, the mini-contact test and the determination of the temperature of saturation. Nowadays, the wine tartaric stability is assessed through the determination of the saturation temperature, T_{sat} . The temperature of saturation of a wine corresponds to the temperature at which the wine becomes saturated in KHT. This point defines two ranges in the temperature δ KHT solubility plot of a given wine: i) the temperature range where the wine is stable (temperatures higher than T_{sat}) and ii) the range where precipitation may occur (temperatures lower than T_{sat}) (Cameira dos Santos et al., 2002). This parameter allows the classification and comparison of wines with regard to their stability, i.e. the lower the T_{sat} , the more stable the wine. The determination of T_{sat} was used to compare the efficiency of cold stabilization and the electrodialysis for wine tartaric stabilization (Cameira dos Santos et al., 2002). The results showed that the treatments of stabilization cause a decrease in the values of the temperature of saturation for all tested wines. Most of the untreated wines are in an unstable conditions if taking as a criterion of tartaric stability a T_{sat} of 12.5°C for white wines and 22°C for red wines. The saturation temperature of treated wines by both techniques showed that wines are stable. Gonçalves et al. (2003) reported that the variation of the saturation temperature with the degree of deionization of a white wine is linearly correlated by the equation:

$$T_{\text{sat}} = 20.3 - 0.44 \times \text{degree of deionization} \quad (2)$$

The chemical and physiological studies of juices and wines under laboratory and industrial conditions after electrodialysis treatment performed in the 80s in a number of European countries showed that no taste or smell changes take place in the product (Romanov and Zelentsov, 2007). This technique was approved by the International Organization of Vine and Wine (oeno 1/93) and authorized it for commercial use for treatment of all types of wines.

The environmental impact of tartaric stabilization by electrodialysis was compared to cold treatment (Bories et al., 2011). It was found that electrodialysis coupled with brine treatment by reverse osmosis generates a very decrease in water consumption (65% of the overall water consumption) and reduction in waste. Concerning waste, the main advantage of tartaric stabilization by electrodialysis in comparison to cold treatment is the elimination of precoat filtration and its residues, the disposal of which is an increasing problem for wineries. Moreover, the loss of wine does not occur in electrodialysis process. Bories et al. (2011) reported that the electrical energy consumption by electrodialysis was reduced to one eighth that of cold treatment. The results presented by Bories et al. (2011) are in disagreement with those presented by Low et al. (2008). This latter study compared the NPV₁₀ (Net Present Value), UOC (Unit Operation Cost) and UPC (Unit Production Cost) of cold stabilization and electrodialysis for tartrate stabilization. It was demonstrated that the lowest NPV₁₀, UOC and UPC are obtained for the cold stabilization, making this technique the most economic processing for tartrate stabilization.

In 2010, the Australian Wine Research Institute (AWRI) published a report comparing the cold treatment and electrodialysis for tartrate stabilization in wines. The summary of the obtained

results is presented in table 1. Electrodialysis offers significant advantage in the power consumption and wine losses. Wastewater volume and labor requirements are higher for electrodialysis than the cold treatment. This report concluded that based on the obtained results, electrodialysis appears to offer viable alternative method to tartrate stabilization in wines.

2.2. Acidification of musts and wines by bipolar electrodialysis

Over the last fifteen years, 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. These high values of pH are not only caused by global warming. In fact, pH values considered very high (≥ 4) are generally not due solely to a lack of organic acid content, but rather an excess of cations, mainly potassium. The excessive presence of the latter in musts is due to cultivation methods of vines as well as to extraction operations that are becoming more efficient and sophisticated. Wine's acidity plays an essential role in the microbiological stability, physico-chemical, color stability and organoleptic quality of wines (Ribéreau-Gayon et al., 2006). It promotes the conservation of wines by limiting the development of microorganisms and reduces the required doses of SO_2 . This situation has led to greater and greater use of tartaric acid to acidify wines. 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 (Usseglio-Tomasset, 1989). According to European Community, only the addition of tartaric acid is allowed to correct the wines pH with maximum doses of 1.5 g.l^{-1} for musts and 2.5 g.l^{-1} for

wines. The addition of tartaric acid is quite difficult to master because part of it then precipitated. As a result, the prediction of pH after the addition of tartaric acid is fairly random.

The method of acidification by bipolar electrodialysis allows physical treatment of the wine with continuous decrease in pH by selective extraction of the potassium at the membrane stack. The bipolar electrodialysis for wine acidification was accepted by the European Commission and the International Organization of Vine and Wine (361-2010 resolution) in 2010.

The bipolar membrane is a composite consisting of three parts: an anion-selective layer, a cation selective layer, and a contact region between the two layers. 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 (H^+ and OH^- ions) in the bipolar membrane under the driving force of an electric field during the treatment (Lutin et al., 2007). 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 in order to acidify the wines (figure 4).

The principle of wine acidification by bipolar membrane electrodialysis is described as following: 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 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 (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 (figure 4). 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.

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 (Moutounet et al., 2005). 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 relatively short (30 hl.h^{-1} with an industrial pilot); 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 sub-contract basis.

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 (Lutin et al., 2007). According to the International Organization of Vine and Wine, when must and wine are acidified, the total increased acidity must not exceed 54 meq.l^{-1} ($\approx 4 \text{ g.l}^{-1}$ expressed as tartaric acid). 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 colour is also more intense (Moutounet *et al.*, 2005). Other analytical criteria (such as must sugars, alcohol content, polyphenols, etc) are not affected by the treatment, which only concerns positively-charged elements (Granès *et al.*, 2009).

2.3. De-acidification of musts and wines by bipolar electrodialysis

Our climate varies from year to year. Every year, wines have a different acidity, which can sometimes produce rather disharmonious wines. Furthermore, some regions with cool climate suffer from insufficient ripeness of grapes leading to wines with high acidity. High acidity and low pH produces unbalanced wines with organoleptic defaults as *õsourõ* taste. Musts with high acidity and low pH (pH ≤ 3.0) may also present some difficulties in fermentation process. One of the strategies to solve these problems is de-acidification of musts and wines. De-acidification is the process of reducing titratable acidity musts or wines. The biological process of de-acidification in wine is the use of *Schizosaccharomyces pombe* yeasts or the lactic acid bacteria. Physico-chemical de-acidification involves either acid precipitation or column ion exchange. The de-acidification agents as calcium carbonate or potassium bicarbonate precipitate some tartaric acid in the form of insoluble salts. De-acidification using an electromembrane process (electrodialysis 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. These practices are defined as physical methods of ionic extraction from the must or wine under the action of an electric field using anionic membranes on the one part and bipolar membranes on the other in order to manage the reduction in the titratable acidity and actual acidity (increase in the pH) of the wine.

The principle of wine de-acidification by bipolar membrane electrodialysis is similar to the acidification one but the anions are affected in this process. 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 (figure 5). The anion forms of organic acids are transferred from the wine compartment to the brine compartment where they are associated with H^+ cations losing their ionic form (figure 5). The wine is impoverished in organic acids reducing the titratable acidity and thus the wine is de-acidified.

3. Membrane processes for controlling alcohol-content in wines

Ethanol is the backbone of wine, yet too little or too much can put a wine off-balance. It plays an important physico-chemical and sensorial role in wine and its content is regulated by law. Despite health benefits of wines, the alcoholic beverages consumption has been reduced due to civil restrictions and also health reasons. There is considerable worldwide interest today, for health reason, to decrease the alcohol content of wines by several processes of wine de-alcoholization or reduction of sugar concentration in must. In contrast, for some particular vintages, enrichment of must with sugars prior to fermentation is one process that is used to overcome reduced levels of ethanol. Taking control of alcohol levels in wines is, therefore, critical to the winemaker's art and surprisingly difficult. Several strategies are used to control the alcohol levels as chaptalization, addition of must concentrate or rectified must concentrate, evaporation, the choice of yeast strain, the date of grape harvesting. Nowadays, the

development of membrane techniques offers several alternatives to the traditional strategies and more accurate results.

3.1. Grape must concentration

When the grape musts have not sufficient potential alcohol content, it is necessary to increase their sugar concentration. Different additive techniques are employed to adjust the level of sugar in the grape must. In the normal chaptalization process, cane sugar is the most common type of sugar added, although some winemakers prefer beet sugar or corn syrup. In many wine regions chaptalization is disallowed and must concentrate (MC) or rectified must concentrate (RMC) may be added. Must enrichment by an additive method leads to an increase of wine volumes and can be a source of economic distortion between the vineyards according to the method used. Additionally, the additive methods could affect the quality of wines. In fact, the must concentrate contains several non-sugar substances (polyphenols and organic acids) often in anomalous amounts and don't respect the quality of must to which they are added. On the other hand, the addition of rectified must concentrate causes a dilution effect (Versari et al., 2003).

To avoid these problems, there is a growing interest in subtractive techniques such as vacuum evaporation, cryoconcentration, pervaporation, nanofiltration and reverse osmosis. The vacuum evaporation is very often associated to the depletion of varietal aromas and to the production of off-flavors. The cryoconcentration consists in concentrating must by partial freezing and elimination of the ice thus formed. The aim is for the ice so formed to be very pure, i.e., only water, without retaining any of the solids in the product. The purpose of removing this ice is to obtain a concentrated liquid product. This technique is an energy consuming process and it is not

well controlled (difficulties in obtaining pure ice crystals and their removal). Therefore, membrane technologies as nanofiltration and reverse osmosis were being used and accepted for must concentration.

The reverse osmosis principle could be explained as following: if a selective membrane separates a sugar solution from pure water, water will pass through the membrane from the pure water side of the membrane into the side less concentrated in water (sugar side) (figure 6). This process is called normal osmosis. If a hydrostatic pressure is applied to the sugar side of the membrane and it is greater than the osmotic pressure (pressure of pure water flow), the flow of water is reversed, and water begins to flow from the sugar solution to the pure water side of the membrane (figure 6). This process called reverse osmosis.

The first tests of must concentration by reverse osmosis with cellulose acetate membranes using reverse osmosis in red wine elaboration have been done in seventies. The conclusions of these tests were that the membranes do enable to concentrate the must, the permeate rate varies in function of must preparation, different components are not concentrated in the same extent because of potassium bitartaric precipitation and the wines that result are not similar to those obtained by chaptalization (Peynaud & Allard, 1970). Mietton-Peuchot et al. (2002) showed that reverse osmosis 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 to cross the membrane. On the other hand, the high pressure and the concentration provoked tartaric acid precipitation at the membrane surface which increased the membrane fouling. Kiss et al. (2004) showed that reverse osmosis (60 bar, 20°C) coupled to

nanofiltration (70 bar, 40°C) may produce must concentrate with high sugar concentration (about 45° Brix \pm 450 g.l⁻¹). They showed that the cost estimations of the membrane process are much cheaper than evaporation. Rektor et al. (2004) used a combination of microfiltration and reverse osmosis for grape must concentration. Microfiltration resulted in the clarification and sterilization of the samples. After microfiltration permeates were concentrated by reverse osmosis. In reverse osmosis, the sugars were concentrated and a very low anthocyanin content was measured in the permeate. The combination of the two processes resulted in a sterile must with a higher sugar content. In 2007, Rektor et al. compared the results obtained with reverse osmosis pilot scale for grape must concentration with those obtained at laboratory scale. They found no significant differences in the permeate fluxes using different flat sheet reverse osmosis membranes with similar salt retentions for the concentration of white and red grape juices at both scales. Gurak et al. (2010) showed that the physical and chemical properties of concentrated grape juice by reverse osmosis increased in proportion to the volumetric concentration factor. They found that the best process conditions to obtain high permeate flux values were 60 bar of applied pressure and a temperature of 40°C.

The reverse osmosis as a process to grape must concentration is well accepted by the International Organization of Vine and Wine with some conditions. The concentration shall not be undertaken to reduce the initial volume of the must by more than 20% nor to increase the initial potential alcohol content of the must by more than 2% v/v. The reverse osmosis technique has its limits also. This process enables an important increase in sugar concentration but also in

all the other components. After reverse osmosis treatment, musts can require an additional operation of ion-exchange or electrodialysis in order to rectify the acidity balance and stability.

Another membrane process tested as an alternative to reverse osmosis is nanofiltration. Nanofiltration is defined as a process intermediate between reverse osmosis and ultrafiltration that rejects molecules which have a size in the order of one nanometer (Eriksson, 1988). This process uses a pressure gradient (up to 40 bar) to transport must or wine through the membrane. Nanofiltration applications in food industry are quite numerous as whey concentration in the dairy sector, dextrose juice concentration in the processing of sugar juice, solutions degumming in the edible oil processing sector (Van der Bruggen, 2008). Because of its versatility in preferential permeation mechanisms, nanofiltration displays a unique capability of sugar/acid aqueous solutions fractionation. Therefore, nanofiltration can provide an alternative to reverse osmosis through the adjustment of the level of acids and salts in musts. The rejection of organic compounds by nanofiltration membranes represents a complex interaction of steric hindrance, electrostatic repulsion, solution effects on the membrane, and solute/membrane properties. When estimating the rejection of a solute by a nanofiltration membrane, properties such as the MWCO, desalting degree, porosity, membrane morphology, charge, and hydrophobicity of the membrane and the MW, molecular size, charge, and hydrophobicity of the solute as well as the feed solution chemistry must be considered (Bellona et al., 2004).

Versari et al. (2003) tested the selectivity of two nanofiltration membranes in order to concentrate grape must. They found that nanofiltration membranes provided rejection coefficients ranging from 77- 97% for sugars, 2-14% for malic acid and 7-18% for potassium

ions. This study concerns only white grape must, so it was wiser to study also the red grape must because nanofiltration performances depend not only on membrane characteristics but also on feed solution composition and operating conditions. Santos et al. (2008) investigated six different membranes for grape must concentration. They found that NF200, NFT50 and NF270 presented higher rejection coefficients of sugars (88%) than organic acids (37%). NF270 membrane (higher hydraulic permeability) presents the higher permeate flux (30 bar of transmembrane pressure) with the most efficient fractionation between sugars and organic acids. In the other hand, no red grape must was tested and the operating conditions were not studied. So, there are possibilities to develop research activities in this sector by studying the feed solution composition effect on the mass transfer through nanofiltration membrane, the operating conditions influence and the methods to limit membrane fouling.

3.2. Reduction of wine alcohol content

Since many years, vine growers implemented a policy of quality which has resulted in making more concentrated wines with more expressive flavors and often richer in alcohol. It is now recognized that the quality of wine is a function of the phenolic compounds maturity in the grape berries. Phenolic maturity is linked to a high concentration of sugars. In the other hand, the higher concentrations of sugars may be also due to an increase in average temperature due to climate evolution (global warming). This increase in sugar concentration leads to wines with higher alcohol content (average 14 % v/v, up to 16 % v/v) with low acidity.

Despite health benefits of wine (especially red wine), the alcoholic beverages consumption has been reduced due to social restrictions (car accident, more acceptable social behavior) and also health reasons. Some studies reported that the partial removal of alcohol from wine does not alter its health beneficial properties, especially its antioxidant and cardiovascular protection effects. In the last years, there is a change of consumer preferences towards light and fruity wines. In addition, in some countries winemakers have to pay taxes when wine alcohol content is over 14.5 % v/v.

Therefore, several approaches have been applied to reduce alcohol content in wines. Where permissible, dilution with water is the simplest means of reducing alcohol concentration (Pickering, 2000; Schmidtke et al., 2012). But, the addition of water leads also to a dilution of wine aromas and flavors. Harvesting unripe grapes results in wine of reduced alcohol content; however, the obtained wine has an inferior quality with unripe aromas and high acidity levels (Pickering, 2000; Schmidtke et al., 2012). The earlier interruption of the fermentation or the use of low-alcohol-producing yeasts results in a wine of low alcohol content (Pickering, 2000; Schmidtke et al., 2012). However, these wines contain residual sugars which allow the development of undesirable microorganisms. It is too difficult to protect these wines and often qualified of unbalanced wines. Traditionally, alcohol has been extracted from wine by fractional distillation (heating up to 78°C). At these temperatures, many wine components are damaged, creating off-flavors. The spin cone column (SCC) distillation is an alternative to traditional distillation where it operates under vacuum at much lower temperatures (Pickering, 2000; Schmidtke et al., 2012). This technique can preserve the wine flavors. This process requires several steps to remove first the wine aromas and afterwards alcohol and finally the aromas are

added back to the de-alcoholized wine. In practice, it is difficult to control the degree of de-alcoholization. So, it is a long and expensive process (Diban et al., 2008).

Membrane processes including nanofiltration, reverse osmosis, pervaporation and membrane contactor can be used to reduce alcohol in wines. These techniques form alternatives to traditional techniques. There are two methods to reduce alcohol content in wine: i) reduction of sugar concentration of musts; ii) de-alcoholization of wine (Mietton-Peuchot, 2010).

3.2.1. Reduction of must sugars

Until 2012, the reduction of sugar content in musts by membrane techniques in Europe was forbidden and just allowed for experimental or with an exemption. In 2012, a specific application on the reduction of sugar content in musts through membrane coupling was adopted (Resolution OIV-OENO 450B-2012). This practice consists in extracting the sugar from a must through membrane coupling combining microfiltration or ultrafiltration with nanofiltration or reverse osmosis.

The first tests were realized in 2004 with a process associating ultrafiltration and nanofiltration. This process is patented by Bucher Vaslin company and is at present marketed under the name of REDUX® (figure 7). It consists of a first stage, ultrafiltration that produces a *œclear mustö* of the same sugar concentration as the initial must. The retentate of the ultrafiltration is reincorporated into the must that is being treated. In a second stage, the *œclear mustö* (permeate of ultrafiltration) 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. The treated must is thus less

concentrated in sugar. Wine made from treated must presents lower alcohol content. The retentate of nanofiltration is a colorless semi-concentrate with sugar concentration of 400 g.l⁻¹. To reduce the alcohol content of 1 to 1.5 %v/v, a volume of 20 to 25% of clarified must should be treated by REDUX[®] process.

The main role of ultrafiltration is to separate the macromolecules (polysaccharides, proteins, anthocyanin and tannin) from the must before nanofiltration stage. The osmotic pressure of the ultrafiltrated must is thus lower. The sugar concentration by nanofiltration may be than greater. The higher sugar concentration leads to a decrease in volume loss.

Nanofiltration is preferred to reverse osmosis because it gives greater flow rates. Nanofiltration membranes presenting higher cut-off threshold allow the transfer of organic acids and potassium into the permeate. This allows the partial reintroduction of acidity with the water recuperated from the must before fermentation. The advantage is to maintain the acid balance of the treated must (which comes from mature grapes with low acidity levels) and thus producing a balanced wine.

During experiments realized by IFV (Institut Français de la vigne et du Vin) and Inter-Rhône in 2005 (Cottureau et al., 2006; Cottureau et al., 2007), chemical analyzes of musts composition revealed that the retention factors of sugars, acids and potassium are almost zero by the first filtration. On the other side, anthocyanins and polyphenols are almost retained (50 up to 80%). Retention of sugars by nanofiltration membranes varies from 70 to 90% while the retention of tartaric acid and potassium averaged respectively 35% and 25%. Variations between nanofiltration experiments for tartaric acid and potassium can be explained by the differences in

pH of tested musts (pH strongly influence the retention of charged molecules in nanofiltration) and sometimes by the tendency of tartaric acid to precipitate in presence of potassium on the top surface of membrane in nanofiltration.

Analytical results of wines from treated musts showed a slight decrease in total acidity comparing with the control wines without a real repercussion on wine tasting. The REDUX[®] process allows the concentration of polyphenols in wines due to volume reduction.

In 2009, there were attempts to simplify the process by eliminating the ultrafiltration step (Cottureau and Noilet, 2011). The must was directly treated by nanofiltration. It was reported that the sugars retention factor in the simplified process is much higher comparing to the REDUX[®] process. This observation was explained by the formation of a dynamic layer by must components (secondary membrane) on the top surface on nanofiltration membrane causing further retention of sugars. The obtained wines by this process correspond to the expected products. Analytical and sensorial profiles are only slightly modified compared to the control at the same harvest time. In 2012, Mihnea et al. showed that the reduction of sugar levels by nanofiltration process had an important impact on the volatile composition of the obtained wines due to some retention phenomena of aromatic and precursor compounds. But, they justified these results by considering the used nanofiltration membrane inadequate to must sugar reduction.

These studies were focused on the chemical composition of musts and wines but they lack data about process performances in term of permeate fluxes and membrane fouling. Further studies on the effects of operating conditions and the choice of membranes materials and characteristics

(pore size, porosity, surface free energy, charge, roughness, hydrophilicity / hydrophobicity, etc.,) must be realized in order to enhance process performances.

Garcia-Martin et al. (2010) studied the sugar reduction by two successive nanofiltration steps. They reported that a dramatic decline in permeate flux appeared during the first filtration due to the presence of larger molecules. It was noticed also that the contribution of the gel layer, the increasing viscosity and the cake formation effects is much more significant in the case of red musts because of the presence of polyphenols. They observed a huge difference in the volatile profile between control and treated wines. In fact, the control wines showed more intense aroma, with higher floral and fruity notes whereas the wines elaborated with filtered musts were less intense in the olfactory phase.

In 2007, IMECA society developed 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.

3.2.2. Wine de-alcoholization

Semi-permeable membranes by which alcohol can be separated from fermented beverages have been studied and available since the 1970s. In the 1980s, several studies were carried out on partial or total removal of alcohol from wines. The reason was principally economic due to the overproduction and lesser quality of wines which were hard to sell. It resulted in new-based

products such as ðlightö and ðalcohol freeö wines. Unfortunately, the commercial success was far from the expected. However, this subject is, at present, once more under study for the reasons stated in paragraph 4.2.

Nowadays, various technologies in which a membrane is used for the selective removal of ethanol from beverages have been developed that rely upon molecular permeation of ethanol from the feed stock with high concentration, to a stripping phase with low concentration. The most widespread technology for the removal of ethanol from wines is reverse osmosis (for technique principle refer to paragraph 4.1 and figure 6) based on the selective separation of water and alcohol from the wine. More commonly, the reverse osmosis permeate is treated using thermal distillation processes in order to separate ethanol and the water content and the water component is redirected back to the feed tank in a closed-loop system (figure 8).

The first patent for the application of reverse osmosis in alcoholic beverages was obtained by the West German brewing company Lowenbrau in 1975 for the de-alcoholization of beer and wine (Schmidtke et al., 2012).

Reverse osmosis operates at ambient temperatures, allows reproducible control over separations, requires no disposable filtration media or other additions, and is easily automated for continuous operation. Specifically, in comparison to other methods of producing low-alcohol wines such as distillation, spinning cone technology or arrested fermentation, the reduced alcohol wines produced by reverse osmosis usually have flavor and aroma profile comparable to the regular wines from which they were obtained (Takacs et al., 2007; Labanda et al. 2009). However, as

water is removed along with ethanol, it must be added back to the concentrated wine to keep the concentrations of wine constituents at the same level and to avoid an increase in osmotic pressure or added to the wine before use of reverse osmosis. This creates legal problems in some countries where the addition of water to the wine is prohibited. This latter problem can be resolved by coupling the reverse osmosis to distillation or to membrane contactor technique which will be developed later in this review. In general, we don't add water to the de-alcoholized wine by reverse osmosis because the concentration factor isn't so significant with a maximum ethanol removal up to 2% v/v.

The wine is pumped at pressures up to 4 MPa (40 bar) through a membrane module and such pressures can result in elevated temperatures at membrane surface. To avoid excessive temperature arising from high pressures, heat exchangers are typically a component of the apparatus with operating temperatures around 20 to 22°C. A membrane is selected with a low NMWCO, typically < 200 Da so that water and ethanol, being small molecules, pass through the membrane into the permeate stream.

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.

In the patent (WO 2004/113489), Gonçalves and De Pinho propose a process of ethanol removal from wine based on the use of nanofiltration membranes coupled to a distillation operation (Figure 8). The nanofiltration membranes provide higher alcohol flow rates together with greater permeation rates than reverse osmosis. Consequently, a lower permeation volume is necessary. Catarino and Mendes (2011) tested several membranes of reverse osmosis and nanofiltration for producing wine with low alcohol content. They found that the reverse osmosis membranes have the lowest ethanol rejection (2.5%) but the lowest permeate fluxes. All tested nanofiltration membranes except one showed high permeate fluxes, low ethanol rejection (é 9%) and high aroma compounds rejection. Another advantage of the use of this type of membranes is that the permeate is richer in ethanol than that obtained with reverse osmosis membranes, resulting in a lower difference of osmotic pressures between the retentate and permeate, and so lower working pressures are needed. Despite a lesser degree of selectivity, the organoleptic repercussion of using nanofiltration for alcohol reduction are very close to results obtained by reverse osmosis. Loss of aroma is compensated by the extraction of lower volumes in nanofiltration. Table 2 gives the results of analyses of wines and intermediate products carried out during partial alcohol removal using nanofiltration in Cabernet Sauvignon wine

In 2011, Bogianchini et al. evaluated the phenolic profile and the antioxidant activity of commercial dealcoholized wines and monitor the stability of their composition over time. They found that the reverse osmosis process didn't affect significantly any phenolic acids regardless to their chemical structure and alcoholic degree but the antioxidant activity decreased in average 40% compared to untreated wine. The antioxidant activity and phenolic compounds of these products were monitored for seven months. No significant changes were observed.

Another process tested for wine de-alcoholization is osmotic distillation. Osmotic distillation is a membrane-contactor technique also known as osmotic evaporation, membrane evaporation, isothermal membrane distillation or gas membrane extraction. Membrane contactors (figure 9) are systems where the microporous hydrophobic membrane acts as barrier between two solutions (feed and stripper agent) permitting the mass transfer of the components without dispersion of one phase within another. Unlike traditional pressure-driven membrane processes, membrane contactors are not selective towards particular components and the separation is based on the principles of phase equilibrium. For wine de-alcoholization, the membrane acts as vapor gap between the wine (feed) and the stripper agent (in general water) (figure 9) and due to its hydrophobicity, it prevents the penetration of solutions into the pores. Therefore, ethanol is selectively removed from wine. The transport mechanism of ethanol in de-alcoholization by osmotic distillation process can be divided into three steps: i) evaporation of ethanol at the membrane pores on the feed side, ii) diffusion of ethanol vapor through the membrane pores, and iii) condensation of ethanol vapor in the stripping solution at the membrane pore exit (Varavuth et al., 2009). Because the vapor pressures of water over the wine and over the strip solution are nearly identical, there is virtually no traffic of water from the strip into the wine.

The main advantage of osmotic distillation lies in its ability to work at low temperature and pressure, thus avoiding mechanical damage and thermal degradation of the components and aroma of wines.

Hogan et al. (1998) were the first to propose the osmotic distillation as a wine de-alcoholization process. They pointed out that osmotic distillation of a high alcohol-content wine at a temperature of 10-20 °C using plain water as stripper agent can rapidly reduce its alcohol content to levels down to 6% with minimal loss of its flavor and aroma components. Nowadays, this alcohol level is not accepted in wine industry because it is allowed to remove maximum 2% v/v of ethanol. To accomplish this task, it is recommended to use a small volume of strip water.

Diban et al. (2008) investigated the feasibility of applying hydrophobic hollow fiber membrane contactors to partially dealcoholize a synthetic wine solution. They showed that the ethanol content can be reduced in the same amount independently of the initial ethanol concentration present in wine in the range studied of 10 to 13% (v/v) of alcohol. They evaluated and modeled ethanol and aroma compounds transfer for feed and stripping sides, showing that the major contribution to the transport resistance was due to the membrane one. They showed that a partial de-alcoholization (reduction of 2% v/v) of Merlot wine gave acceptable aroma losses without a perceptible depletion of the product quality. However, if the residence time of the feed is too high, the aroma compounds losses can reach almost 100% for the most volatile compounds but this observation must be validated with a real wine. In fact, authors didn't protect the model solution from oxidation phenomena. They were stirring the feed tanks throughout the experiments at 25°C without inerting the tanks with CO₂ or N₂. This fact may explain the huge loss of aroma.

Varavuth et al. (2009) compared the performance of the osmotic distillation de-alcoholization process using three different types of stripping agents (pure water, 50% (w/w) glycerol and 40%

(w/w) CaCl_2) by changing the flow rates of feed and stripping solutions and temperature. They concluded that water is the best suitable stripper providing in term of ethanol flux, removal ethanol performance and water flux. They showed also that the ethanol flux and ethanol removal performance were enhanced by increasing feed, stripping solution rates and operating temperatures. The ethanol concentration in the red wine can be reduced to 34% of the initial concentration after 6 hours of operation but it lead to significant aroma components loss especially ethyl acetate and iso-amyl alcohol.

In a recent study, Liguori et al. (2012) showed that the optimal conditions for ethanol removal from model solutions at 10 %v/v were obtained working in laminar conditions for both feed and stripping streams. They observed also a decrease in ethanol flux while increasing the ethanol content of the solutions explained by the saturation phenomena. An increase in temperature accelerates the de-alcoholization process. No significant differences in chemical analyses between crude and de-alcoholized wine were found. The last observation is in agreement with the results obtained by Gambuti et al. (2011) while studying the influence of partial de-alcoholization by membrane contactor on red wines quality.

Membrane contactors can be used lonely for wine de-alcoholization or coupled to other membrane process. For example, the Australian process marketed by Memstar consists of alcohol reduction by a two-stage process of reverse osmosis followed by a membrane module known as a membrane contactor (Liqui-Cel[®]). Wine to be treated is first separated by reverse osmosis into concentrate and permeate streams. The wine concentrate contains all of the precious wine characters. The alcohol rich permeate is passed through the membrane contactor 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 de-alcoholized permeate is then cooled and recombined with the wine, lowering the alcohol of the blend.

The main disadvantage of membrane contactor process is that it uses large quantities of water to extract alcohol. In addition, the alcoholized water must be treated before it can be dismissed.

Aguera et al. (2010) have led a comparative study of different technologies for reduction of wine alcohol content. They found that the REDUX[®] process and the dilution of musts with alcohol free wine give wines similar to control. They found that nanofiltration allows more ethanol transfer in the permeate comparing to reverse osmosis and thus the quantities of permeate needed to de-alcoholize the wines are less than the reverse osmosis. The comparative data of different treatments are presented in table 3. These data show that nanofiltration coupled to distillation is the most performing process in term of de-alcoholization flux and economics where no water is needed for treatment and no wastewater is produced. But the best results in term of wine aromas losses were obtained with the membrane process coupling the reverse osmosis and the membrane contactor where the de-alcoholized wine by this process is similar to the control.

Takács et al. (2007) tested the pervaporation process in order to reduce alcohol content in wines. The pervaporation process consists into separation of liquid mixtures through non-porous membranes by partial evaporation. The procedure called pervaporation because the substance crossing the membrane changes state of phase. The membrane acts as a selective barrier between the two phases, the liquid phase feed and the vapor phase. The authors found that at elevated temperatures (60 ó 70 °C) the permeate flux is higher. However, at higher temperatures the

membrane's separation efficiency and the separation ability decrease. It was noticed a loss of the majority of the wine's organic compounds at higher temperatures making the process unfeasible till now. A compromise must be found between the quality of the product and the economical costs.

Several studies were carried on the effect of partial alcohol reduction by reverse osmosis on the sensory modification of red wines (Meillon et al., 2009; 2010). The Effect of de-alcoholization was variable from one grape variety to another one. The constant effects of alcohol reduction, common to both Merlot and Syrah were the perception decrease of heat sensation, the substitution of heat sensation in attack by astringent (Merlot) or red fruits (Syrah) sensations, the decrease of bitter sensation after attack to the expense of fruity sensations, and the decrease of length in mouth. In case of Merlot, texture and astringency sensations were also affected by alcohol reduction whereas for Syrah, sweet sensation was affected. Wines (from Australian Syrah) with higher alcohol content were perceived as more complex, persistent, strong and with many aromas. They were associated to more complex temporal sensory profiles, with many sensations that blend in-mouth along time. In 2010, Meillon et al. showed that wine professionals didn't appreciate the sensory properties of reduced-alcohol wines (reduction of 1.5% and 3% v/v by reverse osmosis) where less experimented consumers liked the sensory properties of reduced-alcohol wines.

4. Other potential and future applications of membrane processes in wine industry

Several other applications of membrane processes in wine industry other than clarification, tartrate stabilization, must concentration and wine de-alcoholization were cited in the literature.

In 2005, Ugarte et al. tested a two-part integrated process, involving a reverse osmosis membrane process and an adsorptive resin, for the reduction of undesirable volatile compounds from red wine. The process allowed a decrease in the concentrations of 4-ethylphenol and 4-ethylguaiacol (compounds released due to the wine spoilage by *Brettanomyces bruxellensis*). Also, this process partially adsorbed a series of herbaceous aroma and green associated C_6 alcohols, sweaty and rancid-smelling hexanoic, octanoic and decanoic acids. The main disadvantage of this method arises from the use of resins, which require regular regeneration. In 2011, Fudge et al. proposed also a combination of reverse osmosis and solid phase adsorption process as a potential amelioration method for the treatment of smoke-tainted wines. They found that the concentrations of smoke-derived volatile phenols, including markers compounds, guaiacol and 4-methylguaiacol, decreased significantly with treatment. Thus, the removal of volatile phenols improved the sensory attributes of smoke-tainted wines.

A second process is proposed for reducing the volatile acidity in wines which is done by coupling two stages of reverse osmosis (Massot et al., 2008). It is based on the fact that reverse osmosis 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 also subjected to reverse 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.

Ducruet et al. (2010) showed the feasibility of two-stage nanofiltration process for the reduction of acid malic concentrations in the musts. In practice, the racked must undergoes a first nanofiltration. The permeate contains water, malic acid, tartaric acid, and traces of small constituents contained in the must. The nanofiltration permeate is neutralized to a pH of approximately 7 by using potassium hydroxide.



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.

Banvolgyi et al. (2006) used the nanofiltration process to concentrate valuable components in wines. The experiments were carried out at constant pressure, different temperatures (30 ,40 and 50 °C) and different recycle flow rates (400 and 600 l.h⁻¹). They found that the concentrate had a concentration of valuable components two times higher than untreated wine. At high temperature, the retention of components decreased and an aroma loss was observed.

The membrane contactor technique has found another application in the wine industry other than wine de-alcoholization. It was found to be a powerful tool for gas management. In fact, membrane contactors enable implementing liquid-gas separation. It is possible to reduce dissolved gases (CO₂ and O₂) or to add these gases in wines before conditioning in bottles or during ageing of wines. Blank and Vidal (2012) chose to remove the dissolved oxygen by adjusting the level of carbon dioxide to the desired content in one passage. Chiciuc (2010) has studied this technique as an alternative to micro-oxygenation to control the oxygen transfer to the wine. He used membrane contactors in two different ways: loop system (the same tank) and continuous system (from one tank to another).

5. Conclusion

The potential advantages of membrane techniques over conventional techniques in wine processing are undeniable and include improved product, easy scaling up of production and lower energy consumption. However, these techniques are generally limited by problems related to fouling and by the relatively short lifespan of the membranes.

The membranes techniques for reducing alcohol in wine are developed due to the modern trends healthy lifestyle. Even if some techniques are known for mid of 70's like reverse osmosis, others are under developing as osmotic distillation. These techniques didn't achieve their full market potential because there still exists professional and ethic resistance towards wine with low alcohol content even if these techniques have undoubtedly led to improvements in wine quality comparing to traditional techniques as distillation by lowering the process temperatures.

For the future, several promising membrane techniques deserve to be studied and developed as the dynamic filtration for the filtration of must and tanks bottoms as well as the membrane contactor for gases exchange.

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Table 1: Comparison between cold stabilization and electrodialysis for tartrate stabilization

(Forsyth, 2010)

	Cold stabilization	Electrodialysis
Wine stability	Commercially acceptable	Commercially acceptable
Volume of wine processed (L)	29,100	29,100
Power consumption (kWh)	77	1,761 ó 2,968
Water consumption (L)	7,683	3,606
Wastewater (L)	7,683	1,581
Wine losses (L)	136	424
Labour requirements (hrs)	17	9
Time taken to process wine (hrs)	17	384
Sensory results	Not significantly different	

Table 2: Analytical results of wine before and after alcohol removal (Mietton-Peuchot, 2010)

	Wine	Permeate	Concentrate	Wine
	before NF	NF	After NF	After treatment
Alcohol content (%v/v)	12.7	10.9	13.1	10.9
pH	3.64	3.75	3.65	3.62
Total Acidity (g H₂SO₄/L)	3.9	1.5	4.1	3.6
Volatile Acidity (g H₂SO₄/L)	0.2	0.18	0.2	0.19
Tartaric acid (g/L)	1.22	0.5	1.4	1.0
Lactic acid (g/L)	1.4	0.7	1.6	1.0
K⁺ (g/L)	1.0	0.2	1.2	1.2
Anthocyanins (mg/L)	999	nm	1120	914
IPT	56.9	nm	68.9	56

Table 3: Comparison of different processes for a reduction of 2% in alcohol content from a 14% v/v wine (RO = reverse osmosis; NF = nanofiltration; MC = membrane contactor; D = Distillation)(Aguera et al., 2010)

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

Figures legends:

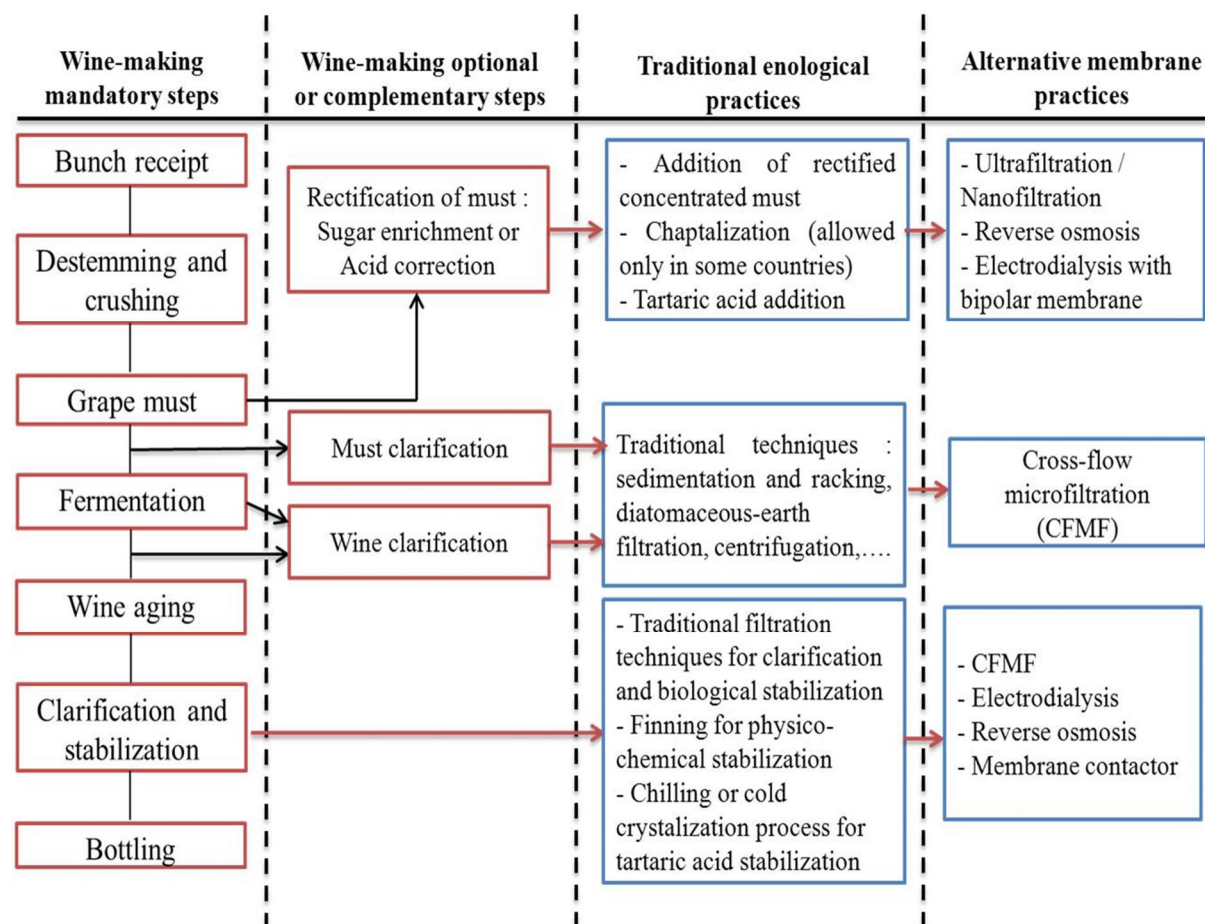


Figure 1: Wine-making process steps with traditional and alternative techniques

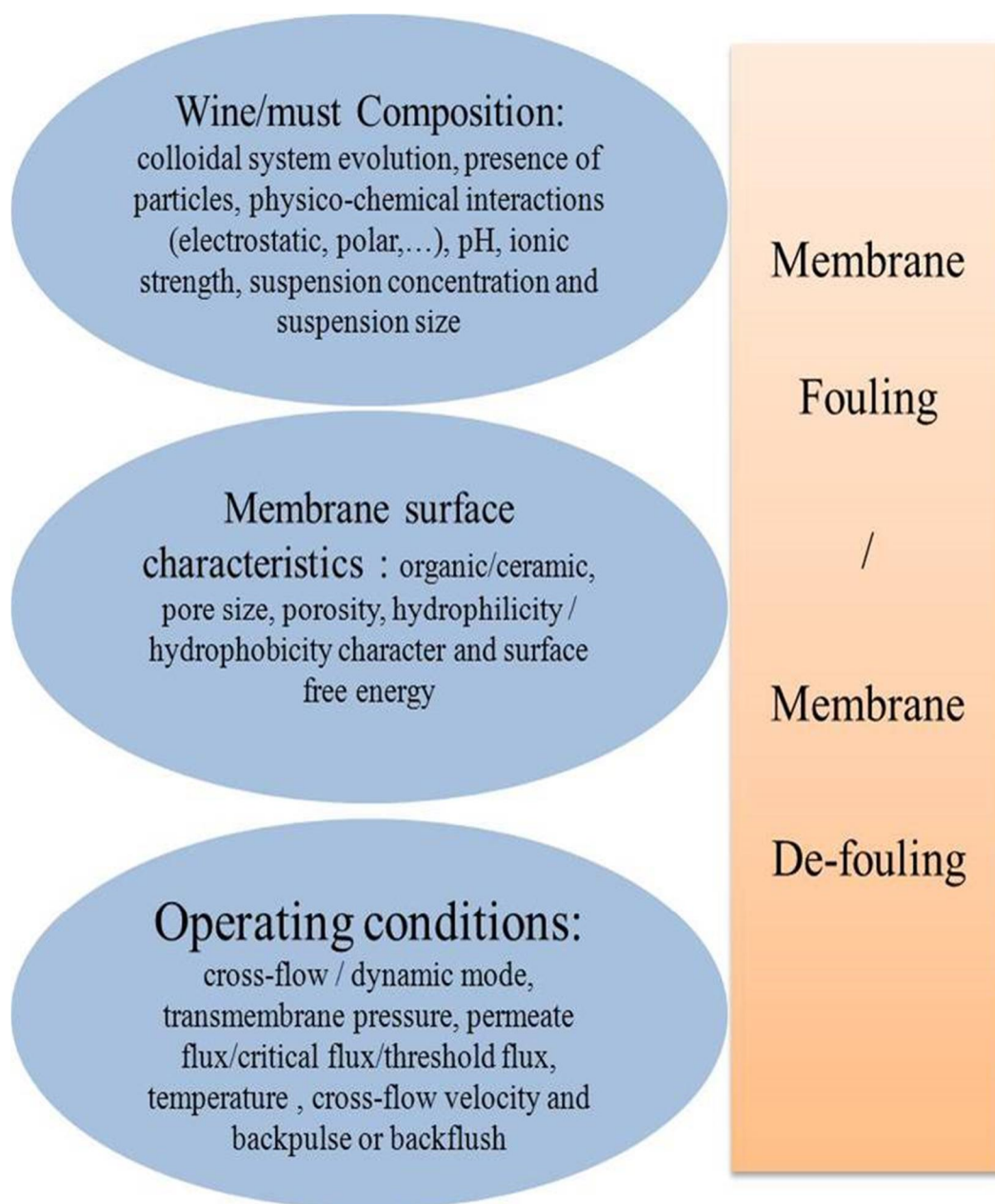


Figure 2: Parameters influencing membrane fouling or de-fouling

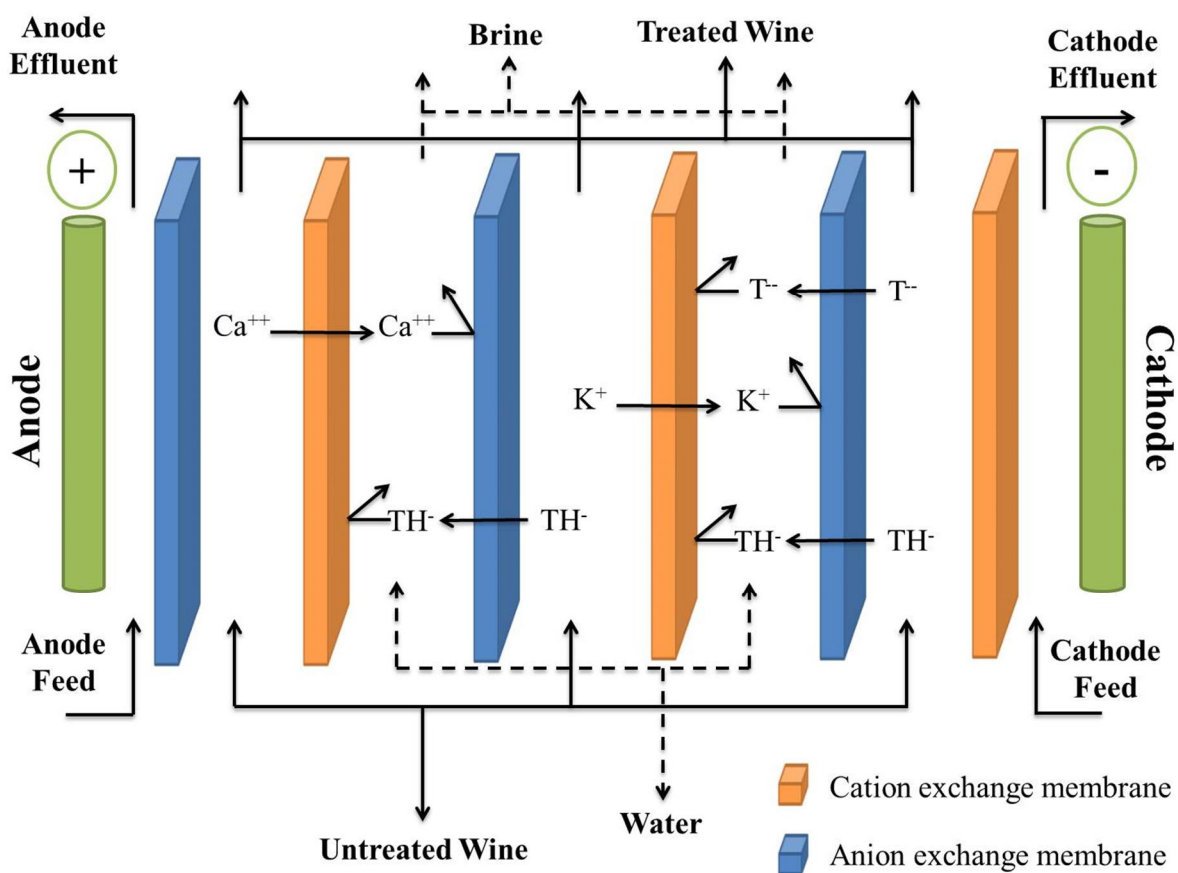


Figure 3: Principle of wine electro dialysis for tartaric stabilization

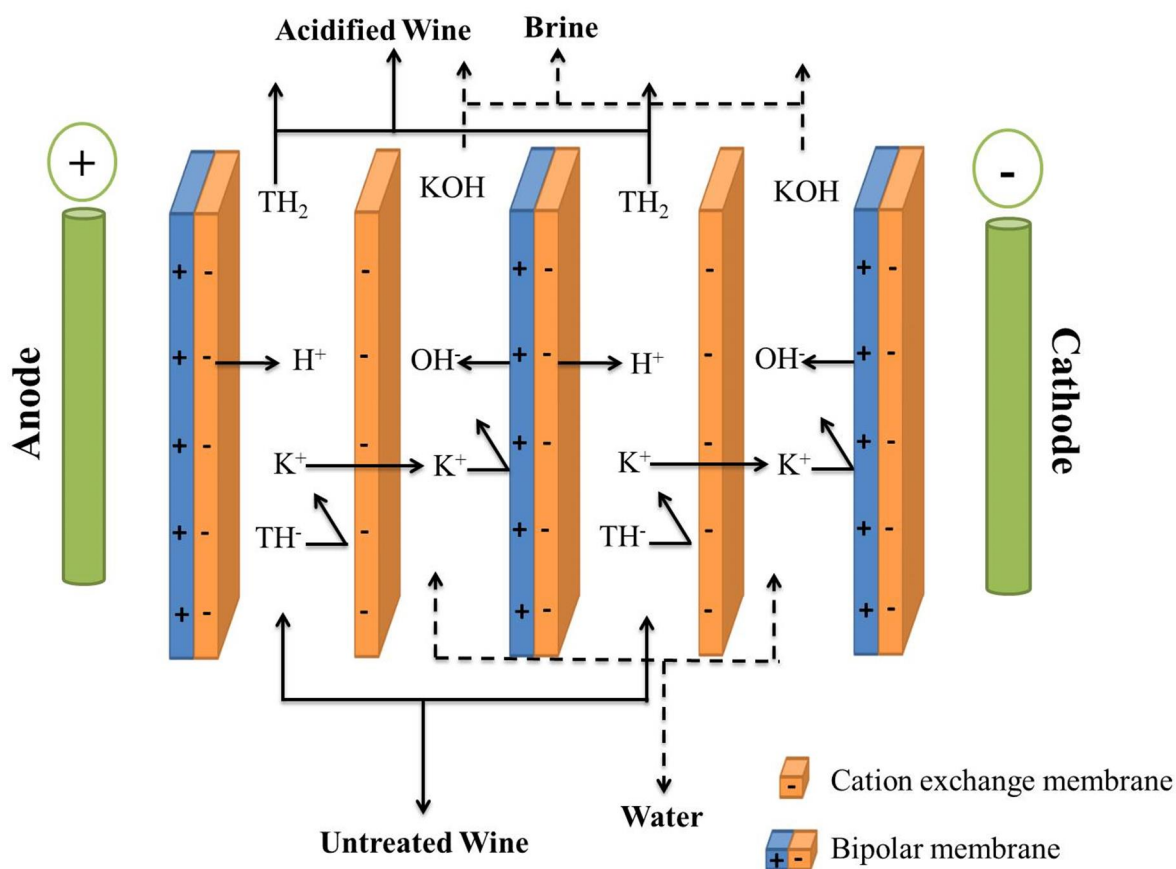


Figure 4: Bipolar membrane electrodialysis for wine acidification

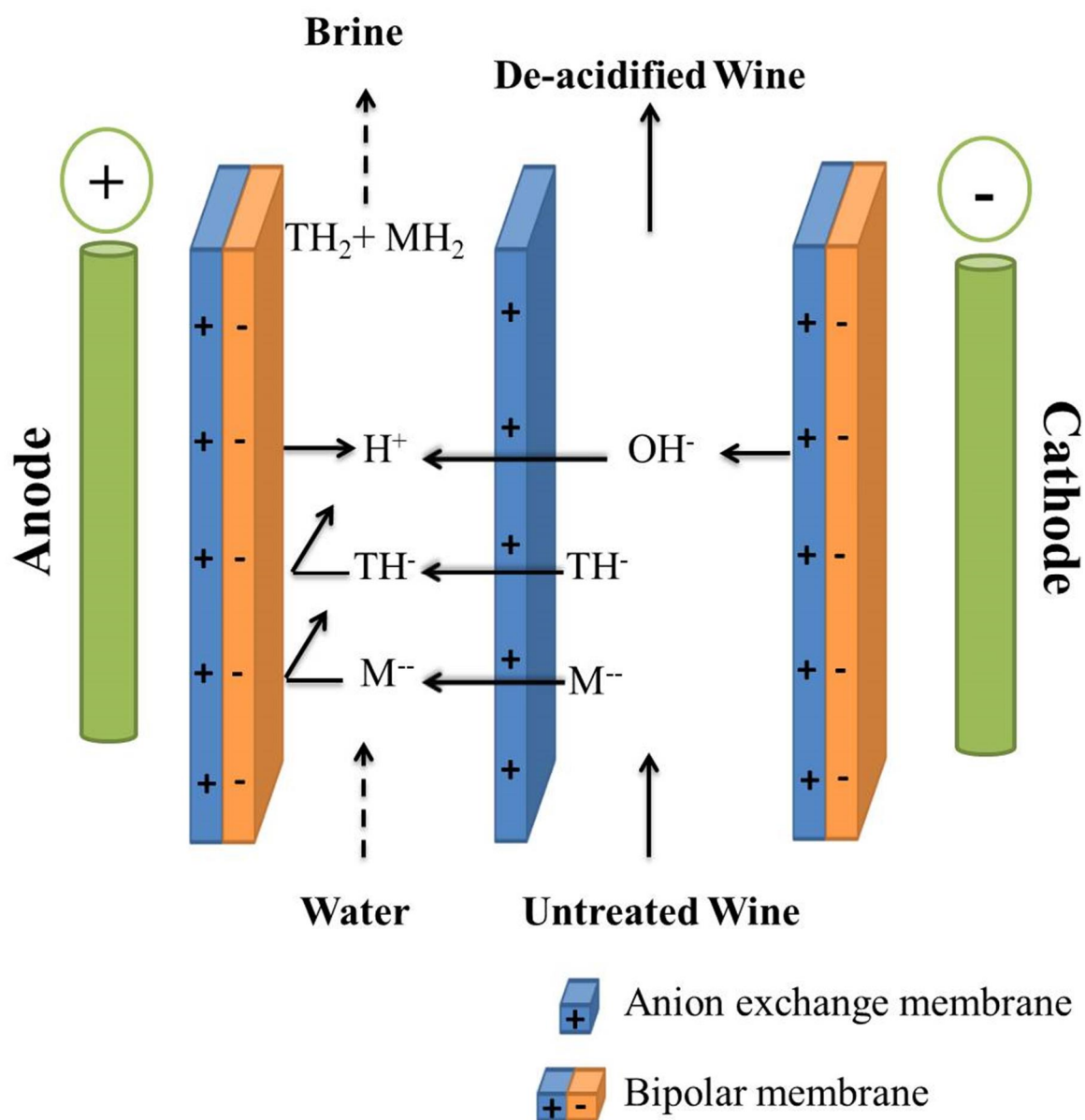


Figure 5: Bipolar membrane electrodialysis for wine de-acidification

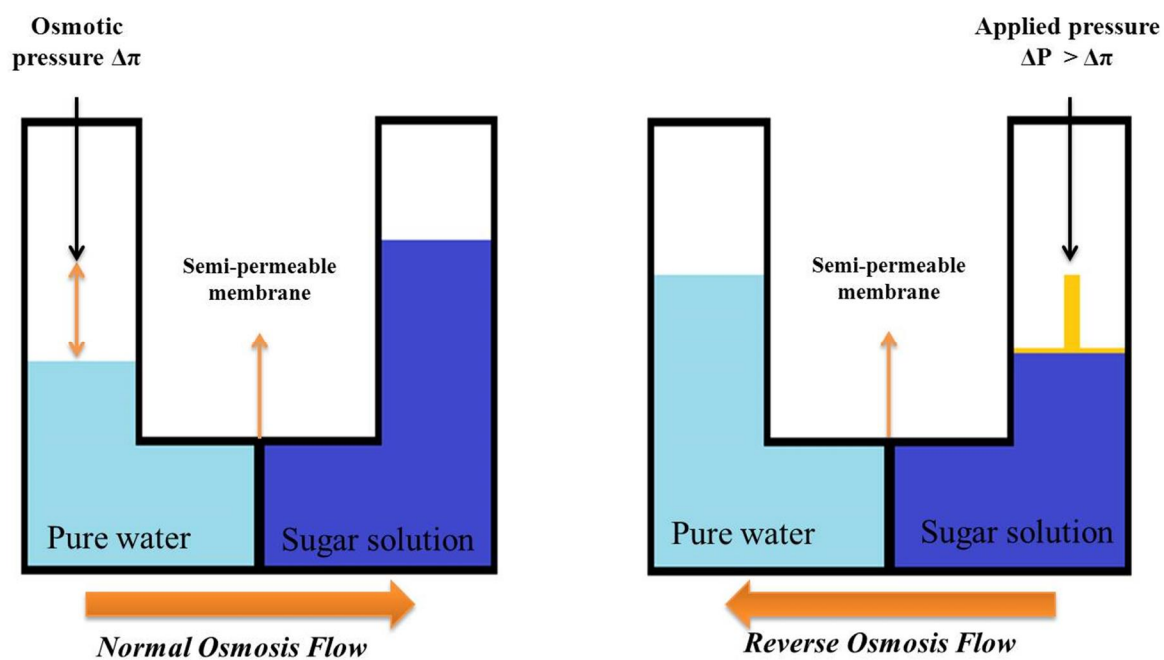


Figure 6: Schematic illustration of normal osmosis and reverse osmosis principle.

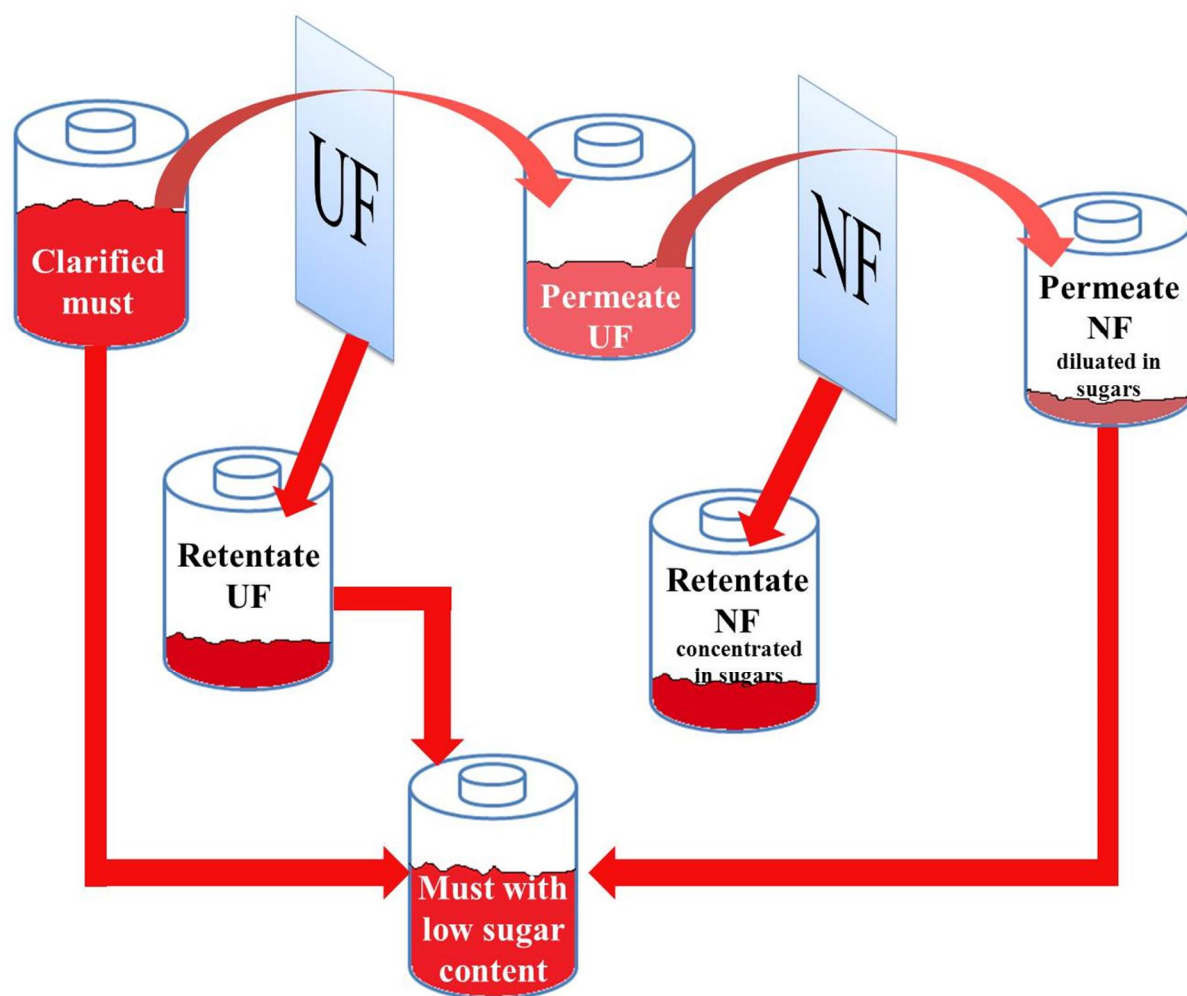


Figure 7 Schematic illustration of the REDUX[®] process (UF = ultrafiltration, NF = nanofiltration)

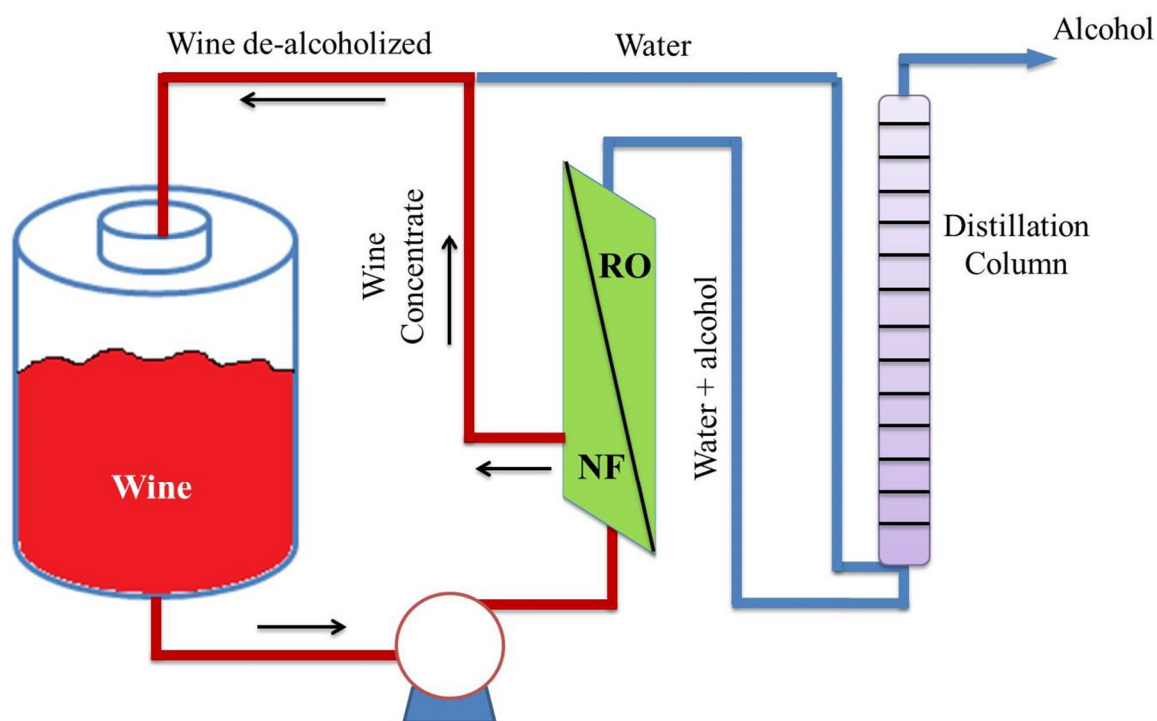


Figure 8: Process of wine de-alcoholization by coupling reverse osmosis or nanofiltration and distillation

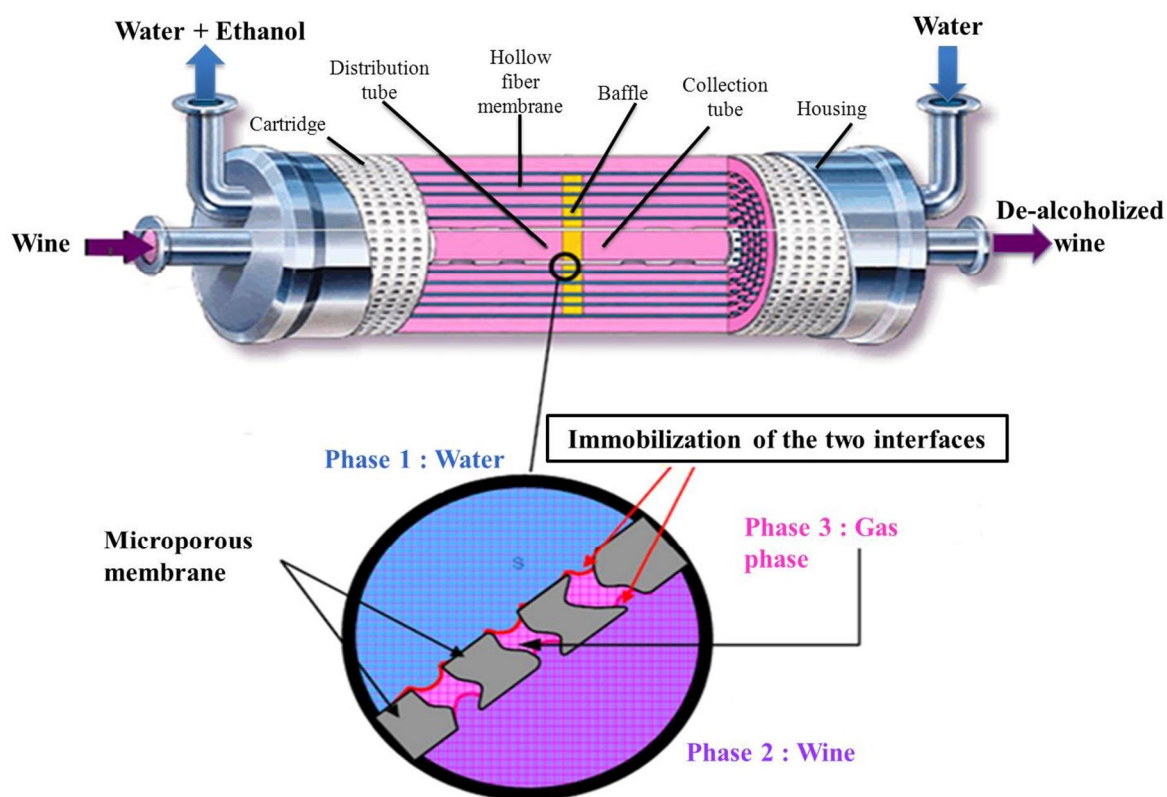


Figure 9: Membrane contactor scheme