Membrane technologies assisting plant-based and agro-food by-products processing: A comprehensive review

Roberto Castro-Muñoz, Grzegorz Boczkaj, Emilia Gontarek, Alfredo Cassano,
Vlastimil Fíla

PII: S0924-2244(19)30592-8

DOI: https://doi.org/10.1016/j.tifs.2019.12.003

Reference: TIFS 2674

To appear in: *Trends in Food Science & Technology*

Received Date: 19 July 2019

Revised Date: 21 November 2019

Accepted Date: 5 December 2019

Please cite this article as: Castro-Muñoz, R., Boczkaj, G., Gontarek, E., Cassano, A., Fíla, V., Membrane technologies assisting plant-based and agro-food by-products processing: A comprehensive review, *Trends in Food Science & Technology* (2020), doi: https://doi.org/10.1016/j.tifs.2019.12.003.

Membrane technologies assisting plant-based and agro-food by-products processing: a comprehensive review

Authors: Roberto Castro-Muñoz[1*], Grzegorz Boczkaj[2], Emilia Gontarek[2], Alfredo Cassano[3], Vlastimil Fíla[4]

(1) Tecnologico de Monterrey, Campus Toluca. Avenida Eduardo Monroy Cárdenas 2000 San Antonio Buenavista, 50110 Toluca de Lerdo, Mexico.

E-mail: food.biotechnology88@gmail.com; castromr@tec.mx

(2) Gdansk University of Technology, Faculty of Chemistry, Department of Process Engineering and Chemical Technology
11/12 Narutowicza St., 80-233 Gdansk, Poland

(3) Institute on Membrane Technology, ITM-CNR, c/o University of Calabria
Via P. Bucci 17/C, 87030 Rende (CS), Italy

(4) University of Chemistry and Technology Prague
Technická 5, 166 28 Prague 6, Czech Republic.

Abstract

Background: Nowadays, membrane-based technologies (e.g. microfiltration, ultrafiltration, nanofiltration, membrane distillation, and pervaporation) have demonstrated to meet the requirements to be involved in different food and bioproduct processes.

Scope and approach: Several applications have been developed, including either separation, recovery or concentration of bioactive molecules from agro-food products and by-products, treatment of natural extracts, recovery of aromas from natural and processed products, production of non-alcoholic beverages, as the most popular ones. Therefore, the goal of this review is to give a comprehensive outlook of the latest developments focused on the separation, fractionation and concentration of several bioactive compounds contained in their original sources, as well as the food processes-assisted by membrane technologies.

Key findings and conclusions: Throughout this review, ongoing literature has been analyzed, discussing the relevant insights according to the type of membrane-based separation process, properties of molecules, membrane features and key factors influencing the separation performance of those technologies. Specific applications have been analysed and discussed, highlighting typical advantages and drawbacks over conventional technologies.

Keywords: *Agro-food products, high-added value compounds, microfiltration, ultrafiltration, nanofiltration, membrane distillation, pervaporation.*

Nomenclature

MF: Microfiltration

UF: Ultrafiltration

NF: Nanofiltration

MWCO: Molecular weight cut-off

MD: Membrane distillation

PV: Pervaporation

1. Introduction

The usage of membrane-based technologies has been nowadays considered for multiple approaches within the industrial processing of food products and by-products. Since couple of decades, different membrane-based techniques have been actively used for the separation, recovery and concentration of biologically active compounds (e.g. phenolic compounds, anthocyanins, carotenoids, antioxidants, polysaccharides) from agro-food products and their derivatives (e.g. wastewaters), clarification and concentration of natural extracts, recovery of aromas from natural and processed products, and production of non-alcoholic beverages (Castro-Muñoz et al., 2016; Figoli et al., 2006a). Recently, particular attention has been pointed out to recovery of high added-value compounds from agro-food by-products and the development of new products with a market value (Cassano et al., 2018; Santamaría et al., 2000). Thanks to their intrinsic properties, specific membrane-based techniques (e.g. MF, UF and NF) are currently considered as an emerging alternative to enhance the current valorization protocols, within sustainable strategies for biorefinery, providing remarkable advances in terms of environmental sustainability (Castro-Muñoz et al. 2018a;

Galanakis, 2013). On the other hand, emerging membrane processes, including MD and PV, are also involved in the strategies for the reclamation of bioactive molecules from food systems (Figoli et al., 2010; Galiano et al., 2019). Membrane technologies supply featured advantages over traditional separation processes (e.g. precipitation, coagulation, flocculation, evaporation, solvent extraction, adsorption, gravity sedimentation, centrifugation, among others)(Le & Nunes, 2016), such as simple operating conditions in terms of pressure and temperature, thus preserving the biologically active properties of bio-molecules contained in natural and processed products, non-use of chemical (e.g. solvents) or biological agents, and, consequently, minimal risk of contamination. Moreover, membrane processes are recognized as highly selective techniques towards target solutes, with simple implementation, feasible scale-up, reduced number of operation steps and high energy savings (Van Der Bruggen et al., 2003).

In the light of the continuous and growing demand of both users and manufacturers for minimally-processed foods free of contaminants and health-promoting foods, the extraction of natural antioxidants using membrane-based technologies has been widely explored in the recent years (Cassano et al., 2019; Galanakis, 2015a). Therefore, the goal of this review is to provide a comprehensive outlook about the ongoing research works focused at enhancing the separation-extraction, fractionation and concentration of several bioactive molecules, as well as the food processing technologies-assisted by membrane technologies. By exploring the literature data acquired mainly at laboratory scale experiments, the performance of these processes is influenced by factors and parameters, which should be carefully considered, evaluated and optimized case-by-case for a real scenario and feasible scale-up. Thereby, those aspects are fully addressed and discussed in detail according to the up-to-date literature insights.

2. Microfiltration, Ultrafiltration and Nanofiltration

Microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) are membrane processes based on the use of a perm-selective porous barrier, so-called “membrane”, through which fluids and solutes are selectively transported when a transmembrane pressure (Δp) is applied. The membrane enables the partial fractionation of the feed bulk into two streams: a permeate stream, which contains the solvent (usually water) passing across the membrane accompanied by all those molecules presenting lower molecular weight than the membrane’s molecular weight cut-off (MWCO), and a retentate stream which contains all compounds partially or totally rejected by the membrane (**Figure 1**). The separation is based mainly on molecular size and to a lesser extent on shape and charge (Galanakis, 2015b).

Figure 1. General depiction of a pressure-driven membrane process.

MF membranes are typically characterized by nominal pore sizes of the order of 0.1 -10 μm. This process is commonly used to concentrate, purify or separate macromolecules, colloids and suspended solids from solutions (i.e. wine, juice and beer clarification in the food industry).

UF membranes have pore sizes in the range of 1-100 nm and are capable of retaining species in the molecular weight range of 300-1,000,000 Da (i.e. biomolecules, polymers and colloidal particles as well as emulsions and micelles).

NF is mainly used to separate ions and molecules in the molecular weight range of 200-2,000 Da (pore sizes of NF membranes are in the range 0.5-2 nm) (Wei et al., 2018; Winter, Barbeau, & Bérubé, 2017). NF membranes have relatively high charge and are characterized by lower rejection of monovalent ions in comparison to that of multivalent ions.

Since MF, UF and NF membranes differ in the size of molecules they separate, the operating pressure involved is considerably different between the related processes. MF typically requires pressures between 110 and 300 kPa; operating pressures of UF are in the range of 150-500 kPa; a range from 500 to 1500 kPa is common for NF.

All these processes can be operated either in dead-end or in cross-flow configurations. In the dead-end filtration the feed is pumped perpendicularly onto the membrane surface; the retained particles tend to form a cake layer on the membrane surface whose thickness increases with the filtration time. Therefore, dead-end operation has to be run batch-wise to relieve the retained particles. In the cross-flow configuration the feed is pumped tangentially across the membrane surface so limiting the build-up of retained compounds on the membrane surface. As such the cross-flow operation allows for continuous process and it is a standard operation for most filtration processes in the food industry.

The performance of a membrane process is mainly evaluated by two parameters: the degree of separation (related to the retention during concentration) and productivity. The membrane productivity is characterized by the *permeate flux* (J, L m^{-2} h^{-1}) which indicates the rate of mass transport per unit membrane area and time:

$$J = \frac{Q_p}{A} \qquad (1)$$

where Q_p (L h^{-1}) is the volumetric flow rate of permeate and A (m^2) is the area of the membrane.

The membrane selectivity is generally expressed in terms of rejection or retention factor (R):

$$R = \left(1 - \frac{c_p}{c_r}\right) \qquad (2)$$

where c_p and c_r are the solute concentration in the permeate and retentate, respectively. Rejection values range between 0 and 1 (or 0 and 100% if expressed as percentage)(Castro-Muñoz, 2019b).

The volume concentration ratio (*VCR*) is defined as the ratio between the initial feed volume (V_f) and the volume of resulting retentate (V_r) according to the following equation (Sánchez, Carmona, Prodanov, & Alonso, 2008):

$$VCR = \frac{V_f}{V_r} \qquad (3)$$

The yield (*Y*) of a component, that is the fraction of a such component recovered in the final retentate with respect the initial feed, is expressed as:

$$Y = \frac{c_r V_r}{C_f V_f} \qquad (4)$$

It is a function of VCR according to the following equation:

$$Y = VCR^{(R-1)} \qquad (5)$$

Some specifications and characteristics of MF, UF and NF operations are detailed in **Table 1**.

The valorization of agro-food by-products is nowadays one of the primary challenges for scientists (Castro-Muñoz, 2018; Mirabella et al., 2014). In such a way, the interest in implementing the integral strategy “5-Stages Universal Recovery Process” has impressively raised in last years (Galanakis, 2015b). In particular, UF and NF are non-destructive techniques which can be applied in several steps of the above downstream processing; these processes are largely recognized for their ability to recover bioactive molecules from agro-food manufacturing wastes, also through their coupling in hybrid systems (Cassano et al., 2018; Dhillon et al., 2013).

Table 1. Main characteristics of MF, UF and NF processes. Adapted from (Castro-Muñoz et al., 2018).

Table 2 reports the most recent literature data obtained at laboratory scale, in which different bioactive molecules have been successfully separated and thus recovered from agro-food wastes, including agricultural residues (fruit seeds, orange press liquor, grape marc, fermented grape pomace, etc.) and wastewaters (from corn, olive, artichoke, citrus and winemaking industry), and some other by-products (e.g. winery effluents, red wine lees) representing a rich source of phenolic compounds (Cassano et al., 2016a; Cassano et al., 2018). Interestingly, natural products have been also employed as potential sources of bioactive compounds (Castro-Muñoz & Fíla, 2018). Basically, these membrane operations provide high recovery efficiency being highly selective towards targeted derivative polyphenols, including catechol, tyrosol, hydroxytyrosol, and phenolic acids (e.g. caffeic and p-cumaric).

Table 2. Bioactive molecules recovered from agro-food wastes using membrane technologies.

2.1. Key parameters influencing the separation performance of pressure-driven membrane-based technologies

Typically, the separation performance of pressure-driven membrane operations (like MF, UF and NF) in terms of permeation rate and solute rejection, depends on multiple factors, such as (Astudillo-Castro, 2015; Fane & Fell, 1987):

- *Physico-chemical properties of the feed stream*: this parameter strongly contributes to membrane fouling phenomena. In principle, the fouling is the main drawback of these processes since it produces a long term permeate flux decline caused by the accumulation of specific compounds on the membrane surface (Fane & Fell, 1987). It may occur due to the formation of a concentration polarization layer on the membrane surface, cake layer formation and/or partial or complete blockage of the membrane pores. Fouling results by particular types of interactions between the membrane and solutes contained in the bulk feed stream. Therefore, the physicochemical composition and the properties of individual feed molecules (i.e. nature, morphology, hydrophobic interactions, charge, zeta potential, etc.) have a meaningful effect on these interactions. For instance, phenolic-based molecules have shown adsorption properties on polyethersulfone (PES) membranes due to weak polar interactions (Susanto et al., 2009; Cartalade & Vernhet, 2006). Also, polyphenols can interact with some other solutes (i.e. proteins, polysaccharides) to form up large particles which may have a negative effect during filtration.

- *Operating parameters:* Operating parameters including feed flowrate (cross-flow velocity), transmembrane pressure (TMP), temperature and feed concentration, have a key effect on membrane fouling, and thus affect both membrane selectivity and productivity. In general, an increase of the feed temperature produces a decrease in the fluid viscosity, as well as an increase of the diffusion coefficient of molecules: the effect of these two factors is to enhance mass transfer and to increase the permeation rate (Ramli & Bolong, 2016). For small pressures the permeation flux increases linearly with the applied pressures. As the pressure is increased flux shows a deviation from a linear flux-pressure behaviour and it becomes independent of pressure: at this limiting TMP or higher pressures, the permeate flux does not depend on the pressure anymore; the existence of a limiting flux can be attributed to concentration polarization and fouling phenomena (Astudillo-Castro, 2015). On the other hand, the retention of some molecules (e.g. phenolic-based solutes) tends to increase by raising the TMP (Díaz-Reinoso et al., 2009). This is due to the thin layer formation close to the membrane surface, which acts as an extra barrier and thus promote the retention of solutes (Bacchin et al., 2002).

The cross-flow velocity affects the shear stress at the membrane surface and, consequently, the rate of removal of deposited particles responsible of flux decay: herein, an increase of cross-flow velocity has a large effect on flux. Finally, according to the film theory model the permeate flux decreases exponentially with increasing the feed concentration.

- *Membrane properties:* The intrinsic features of the membrane, such as surface topography, hydrophobicity/hydrophilicity, pore size and charge have an important influence on solute-membrane interactions, and consequently on membrane fouling. Hydrophobic polymeric membranes are the most used in this type of processes. In fact, many manufacturers (e.g. GE Osmonics, Nadir, Nitto-Denko, Lenntech, Toray) are using highly hydrophobic polymeric materials (i.e. polyamide, sulfonated polyether-sulfone, polypiperazineamide, polysulfone) for manufacturing of membranes.

Crucially, pore size is the primary feature that differentiates MF, UF and NF membranes (see **Table 1**). The membrane’s ability to retain specific molecules is generally described by manufacturers in terms of molecular weight cut-off (MWCO) which is defined as the molecular weight of a solute 90% retained by a given membrane. However, molecules with the same molecular weight but different shapes and conformation (i.e. linear and spherical molecules) can be characterized by different permeabilities. In this sense, the MWCO is not a reliable tool to predict the separation capability of a membrane. Another important aspect is the asymmetric characteristic, which is that the membrane pores do not always possess a fair MWCO range across all membrane (Galanakis, 2015a). The asymmetric structure is generally related to the membrane preparation technique.

The asymmetric porous membranes can be obtained by means of wet phase inversion, one of the most common membrane preparation methods for NF and UF membranes (Blanco et al., 2006; Russo et al., 2019). Commercially, NF and UF membranes are normally prepared to possess an additional skin layer (i.e. dense selective barrier) to provide higher retention rates. This skin layer can be realised by manipulating preparation conditions (e.g. exposure time, humidity, polymer concentration) or ii) coating a top layer on the membrane' surfaces.

The surface roughness also influences the separation performance of NF and UF membranes. For instance, membrane fouling is promoted by rougher surfaces (Evans et al., 2008). The presence of protuberances on the surface of polyamide membranes may be responsible for fouling initiated by fouled matter capture. Interestingly, membranes based on cellulose acetate display smoother surfaces which are less susceptible to fouling.

Most of the membranes exhibit a net negative charge under common operating conditions; therefore, electrostatic forces take place between the membrane surface and some of the compounds present in the treated solution. The membrane surface charge is depending on type of membrane (i.e. functional groups present on its surface) as well as the pH and ionic strength of the bulk feed. This surface charge becomes relevant in case of charged molecules (e.g. proteins) present in the feed solution (Kanani, 2015). Finally, hydrophobic and Coulombic intermolecular interactions between the molecules and membrane surface (e.g. polyphenols- polyphenols, polyphenols-membrane) contribute to the molecule retention (Crespo & Brazinha, 2010).

NF membranes and tight UF membranes (in the range 1-3 kDa) have been recognized for their capability to recover low molecular weight molecules (e.g. carotenoids, peptides, anthocyanins, low molecular weight phenols and sugars) from several types of agro-food products and by-products (see **Table 2**). For instance, Díaz-Reinoso et al. (2017) proposed a combination of UF and NF membranes with adsorption-desorption processes in order to recover and concentrate phenolic antioxidant compounds from white wine vinasses, as depicted in the flow diagram depicted in **Figure 2.** The final dried product contained 45% of phenolics (expressed as gallic acid equivalent, GAE) and presented a radical scavenging capacity equivalent to almost 2 g of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid). The proposed process allowed to reduce also the pollution load of the final effluent: indeed, COD and total solids were reduced of about 85% and 92%, respectively, with respect the treated effluent.

Figure 2. Layout scheme and overall mass balance of the developed process for the recovery and concentration of polyphenols from white wine vinasses (GAE, gallic acid equivalents; Trolox, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) (Díaz-Reinoso et al., 2017).

3. Membrane distillation

Membrane distillation (MD) is a thermally driven membrane process, in which hydrophobic microporous membranes are commonly used for separating non-volatile solutes. The temperature difference between separated solutions results in a vapour pressure difference, followed by the transport of vapour molecules from the higher vapour pressure stream to the lower vapour pressure stream (**Figure 3)**. For example, in seawater desalination, this technology operates at atmospheric pressures and temperatures below 100°C (Belessiotis, Kalogirou, & Delyannis, 2016), which represents an attractive alternative to classic processes according to several advantages, such as lower operating temperatures and pressures when compared to conventional distillation and pressure-driven membrane processes (e.g. reverse osmosis), mild processing conditions for heat-sensitive food ingredients and reduction of energy consumption when using industrial waste energy or solar energy (Blanco Gálvez et al., 2009; Qtaishat & Banat, 2013). Moreover, a theoretical rejection of about 100% for non-volatile compounds makes this technique one of the most effective processes for desalination.

Typical membranes for MD applications are realized in flat-sheet or tubular configuration with hydrophobic polymers including polypropylene (PP), polyvinyldifluoride (PVDF) and polytetrafluoethylene (PTFE). Typical pore sizes of MD membranes range between 0.2 and 1.0 μm. The transmembrane flux through a MD membrane is related to the membrane pore size and other characteristic parameters by the following equation (Fawzy, Varela-Corredor, & Bandini, 2019):

$$N \propto \frac{r^{\alpha}\varepsilon}{\delta_m \tau} \qquad (6)$$

where *N* is the molar flux, r the mean pore size of the membrane pores, α a factor whose value is 1 for Knudsen diffusion and 2 for viscous fluxes, respectively, δ_m the membrane thickness, ε the membrane porosity and τ the membrane tortuosity (Lawson & Lloyd, 1997). According to equation (6) the thinner the membrane and the greater the porosity of the membrane, the greater the flux rate. On the contrary, thicker membranes assure better heat efficiency limiting the heat loss by conduction through the membrane matrix.

When dealing with the use of MD in food and bioproducts processing, most ongoing developments are focused on the concentration of fruit juices (see **Table 3**).

Figure 3. General drawing of a membrane distillation process.

At large scale, the concentration of fruit juices in the food industry is performed by multi-stage vacuum evaporation. This process results in a loss of fresh juice flavors, color degradation and the appearance of a ‘‘cooked’’ taste due to thermal effects. Since MD can be carried out at the atmospheric pressure and at a temperature much lower than the boiling point of the solution, it has received a great attention as technique for fruit juice concentration.

To date, many studies evaluating the performance of MD for juices concentration have been developed, including those performed on apple juice (Gunko et al., 2006), sugarcane (Nene et al., 2002) and orange juice (Deshmukh et al., 2011). In these studies MD has been carried out according to the direct contact membrane distillation (DCMD) configuration in which the permeate side of the membrane consists of a condensing fluid in direct contact with the membrane (cold distillate) separated by the hot feed. Gunko et al. (2006) observed an important temperature dependence on the capacity of the DCMD process. Their results showed that at the same temperature difference between feed and permeate, higher fluxes are achieved while increasing the temperature of the feed.

Even though DCMD seems to be the most common configuration for the separation of water (as a volatile component), there are some reports evaluating the potential of vacuum membrane distillation (VMD) configuration as concentration process. In VMD, there is a vacuum pressure applied on the permeate side of the MD membrane while condensation takes place outside the membrane module. This configuration minimizes the conductive heat transfer across the membrane due to the low pressure on the permeate stream. According to the literature, VMD is a potential technique for gentle aroma compounds recovery from natural sources, e.g. black currant juice (Bagger-Jørgensen et al., 2004), as well as for sucrose concentration (Chen et al., 2018). According to the findings of Bagger-Jorgensen et al. (Bagger-Jørgensen et al., 2004), a linear relationship between permeate flux and the difference of the water vapour pressure can be found employing VMD. Additionally, the authors observed higher recovery rate of aromas compared to a conventional aroma recovery plant. For example, using VMD, it was possible to recover up to 83% of highly volatile compounds and 38% of poorly volatile compounds.

Despite the satisfactory quality of the concentrated juices using this technique, there are still some drawbacks limiting the use of MD in the food industry, such as temperature polarization and membrane fouling. Especially, temperature polarization causes temperatures at the membrane surfaces to differ from the bulk temperatures measured in the feed and in the distillate with significant loss in the driving force for transport regarding the imposed force. Both phenomena may provide a flux decrease as a result of membrane permeability reduction as a function of operating time. Moreover, another important issue in MD technology lies with the membrane and its long term anti-wetting performance to process liquids, which may influence the vapour transport through the pores (El-Bourawi et al., 2006). When dealing with the fouling phenomenon, enzymatic pretreatments, as well as the use of MF and UF as clarification steps for removing suspended solids and pectins from juices, allow to reduce the juice viscosity and to improve the evaporation flux during the MD concentration step.

Table 3. Overview of the latest uses of MD for the concentration of juices.

Quist-Jensen et al. (2016) evaluated the effect of an integrated two-step DCMD process on the quality of blood orange juice. Firstly, the clarification of the extract was performed by UF, in order to remove suspended solids and juice turbidity; the clarified juice, with an initial total soluble solids (TSS) content of about 9.5 °Brix, was pre-concentrated up to 24 °Brix and then concentrated up to 65 °Brix by using a MD laboratory bench plant equipped with two PP hollow fiber membrane modules (Enka Microdyn MD-020- 2N-CP) with a nominal pore size of 0.2 µm and a membrane surface area of 0.1 m^2. Such approach allowed to produce high quality concentrated juices, as in the final product the organoleptic, nutritional and antioxidant properties of the fresh juice were efficiently preserved. The performance of the DCMD operation during the concentration of the juice in the range 24–65 °Brix is depicted in **Figure 4**. Thermal gradients of about 9 °C every 9 h resulted in an evaporation flux of about 0.55 kg m^{-2} h^{-1} (Figure 4a). After this, the membrane cleaning at regular intervals (each 9 h) produced a good restoration of the initial flux. Flux decays were observed by increasing the TSS content (Figure 4b) and juice viscosity (Figure 4c) confirming that at a higher TSS content the flux decrease primarily depends on juice viscosity and, consequently, on temperature and juice concentration. The formation of fouling layers offers an additional resistance to mass transfer and heat transfer contributing to a progressive flux decline.

Figure 4. Concentration profile of blood orange juice by DCMD. (a) evaporation flux (thermal gradient at time 0, 9, 18 and 27 h), (b) total soluble solids content and (c) viscosity as a function of operating time (Quist-Jensen et al., 2016).

Kozák et al. (2009) applied MD to produce a concentrated black-currant juice using a PP membrane module in hollow fiber configuration. It was reported that the increase in driving force (from 15 to 19 ^{o}C as thermal gradient) leads to an improvement of fluxes of about 80%. The microfiltered juice with 22°Brix TSS content was pre-concentrated by reverse osmosis (RO) and then concentrated by MD up to 58.2°Brix. All the analysed parameters, including density, total acidity and anthocyanins increased proportionally to the TSS content of the juice.

Other applications of MD in the food industry comprise the ethanol removal from fermentation broths, which is usually carried out by conventional distillation. Gryta and Barancewicz (2011) used PP capillary membranes to separate ethanol by MD during the fermentation of sucrose solutions with the participation of the yeast species *Saccharomyces cerevisiae*. Besides ethanol, propionic and acetic acids were removed from the broth to the distillate. The use of MD allowed to decrease the inhibitory effect of these compounds on microbial culture and reduce the cost of further concentration of alcohol. Interestingly, Purwasasmita et al. (2015) evaluated the potential of non-porous MD membranes (thin-film composite polyamide) in the beer dealcoholization process. In selected operating conditions (300 kPa feed pressure and 58 kPa vacuum pressure) the alcohol content was reduced from 5%-vol. to 2.45%-vol. in 6 h, with minimal loss of nutrients and flavoring components such as maltose and glycerol. The whole results clearly indicate that MD is suitable for the concentration of extracts (mainly fruit juices) by selective removal of water, recovery of aromas, and the removal of ethanol from specific processed feedstocks. However, in case of the selective recovery of aromas, and/or removal of ethanol aiming the manufacture of new processed products, pervaporation technology is likely the most sought technology. The next section addresses the latest findings in the field.

4. Pervaporation

Pervaporation (PV), as a highly selective membrane separation technique, can selectively separate multicomponent azeotropic mixtures by partial vaporization using a physical barrier (so-called membrane). This perm-selective membrane can be either a non-porous polymeric or a non-porous inorganic (ceramic/zeolite) membrane. Unlike the previous membrane-based technologies, like MF, UF, NF and MD, in which porous membranes are used, PV is based on membranes with a non-porous structure. Indeed, PV uses a coupled mechanism of permeation and evaporation phenomenon (Kaippamangalath & Gopalakrishnapanicker, 2018; Wijmans & Baker, 1995). In pristine polymer-based membranes, the mass transport across the dense membrane has been well explained by the so-called solution-diffusion mechanism, in which specific properties (i.e. solubility, diffusivity) of the target molecules play a fundamental role (Wijmans & Baker, 1995).

To carry out the selective extraction of any component, the liquid azeotropic feed solution is in direct contact with the “selective” layer of the membrane, while vacuum is generally applied on other side of the membrane (i.e. permeate stream). Such permeate stream is in vapor phase and contains most of the permeating compounds with higher compatibility-affinity to the membrane (**Figure 5**). Since different species permeate through the membrane at different rates, substances at low concentration in the feed stream can be highly enriched in the permeate.

Figure 5. General schematic of a pervaporation process.

In terms of the real driving force for the PV process, the flux, J_i, of a specific compound *i* can be described by the following transport relation (Castro-Muñoz et al., 2019):

$$J_i = -L_i \frac{d\mu_i}{dz} \qquad (7)$$

where $d\mu_i/dz$ represents the chemical potential gradient of the target compound I across the membrane and L_i a phenomenological coefficient to be experimentally determined.

Taking into account the equilibrium conditions implied by the solution-diffusion model, the component J_i (expressed as kg m^{-2} h^{-1}) can be derived as:$J_i = \frac{P_i}{\delta}(p_{f,i} - p_{p,i})$ (8)

where P_i represents the permeability coefficient, θ the membrane thickness and $(p_{f,i}-p_{p,i})$ the difference in partial vapour pressure of component *i* across the membrane.

The separation efficiency of PV membranes is usually expressed by means of the separation factor $\alpha_{i,j}$, defined as:

$$\alpha_{i,j} = \frac{c_{p,i}/c_{p,j}}{c_{f,i}/c_{f,j}} \qquad (9)$$

in which c represent the concentration (wt%) of a component *i* or *j* in the feed or permeate (Castro-Muñoz & González-Valdez, 2019). The corresponding enrichment factor is expressed as:

$$\beta = \frac{c_{p,i}}{c_{f,i}} \qquad (10)$$

The choice of the membrane material in PV is strongly correlated to the temperature and composition of the feed mixture as well as to the separation/purification target and the desired performance. Hydrophilic polymeric materials, including cellulose acetate (CA), polyvinyl alcohol (PVA), sodium alginate, chitosan, poly lactic acid (PLA), facilitate the transport of highly polar compounds including water and alcohols. On the contrary, typical hydrophobic (also known as organophilic) membranes, including poly(octylmethylsiloxane) (POMS), polydimethylsiloxane (PDMS), polyether block amide (PEBA), or poly(1-(trimethylsilyl)- 1-propyne) (PTMSP), favor the preferential transport of non-polar compounds (or less polar molecules) (Castro-Muñoz et al., 2018c). Indeed, these kinds of membranes are thus preferred for the extraction of aroma molecules when they are contained in aqueous complex solutions (e.g. extract, juices, wines). Importantly, the chemistry and nature (e.g. hydrophobic or hydrophilic) of the targeted compounds will play a crucial role during the aroma extraction using PV (Baudot & Marin, 1997; Castro-Muñoz, 2019; Fouda et al., 1993). When organic molecules are concentrated and it is needed to selectively separate them from each other, it is suitable to use membranes with highly hydrophilic nature. These membranes can separate the molecules based on their polarity according to the polar functional groups, e.g. hydroxyl (-OH) groups. Nevertheless, some other aromas and complex organic compounds contained in agro-food products could also influence the extraction (Isci et al., 2006). Herein, the nature and chemistry of the molecules will have a significant effect on the yield of the process. Recent literature reviews have reported some of the primary aromas extracted and recovered from agro-food products, including extracts, wastes, by-products, fruit juices, and food processed products (e.g. wine, beer, cider, dairy products) by using different PV membranes (Castro-Muñoz, 2019).

Aroma compounds, including alcohols, esters and organic compounds, such as trans-2-hexenal, were preferentially permeated from apple juice through a hydrophobic membrane with an active layer of PDMS by Bengtsson et al. (1989). Enrichment factor (β) values were in the range of 44-125. Similarly, Cassano et al. (2006) investigated the performance of a commercial PDMS-based membrane in the recovery of aroma compounds from kiwifruit juice within an integrated membrane process where the depectinised juice was previously clarified by UF and then concentrated by osmotic distillation (OD). The enrichment factor for most of the aroma compounds detected in the permeate of the fresh juice resulted higher than that measured for the clarified and concentrated juice with the exception of 3-hexen-1-ol and (E)-2-hexen-1-ol. This result suggested the use of PV for the recovery of aroma compounds directly from the fresh juice before the clarification and concentration step. In all PV experiments, the enrichment factor of the alcohols resulted lower (10-40) than that measured for esters, such as methyl and ethyl butanoate (about 100). For all samples, the permeate flux increased linearly in the investigated range of operating temperatures (20-40 °C). For the concentrated juice the total flux resulted slightly higher than that measured for fresh and clarified juice (**Figure 6**). A similar behavior was also observed by Figoli et al. (2010) in the processing of fresh kiwifruit juice by PV with a composite membrane having an active layer made of styrene–butadiene–co-styrene (SBS) of about 40 μm coated on a commercial UF support of PVDF. For this membrane the highest recovery factor was reached at an operating temperature of 30 °C.

Figure 6. Effect of temperature on the total flux in the processing of fresh, clarified and concentrated kiwifruit juice by PV (Cassano et al., 2006).

Aroujalian and Raisi (2007) investigated the effect of key parameters such as feed temperature, permeate pressure and feed flow rate on the pervaporative recovery process of volatile aroma compounds from orange juice by using a commercial PDMS membrane. Results indicated that increasing of Reynolds number from 500 to 2500 had a very slight increasing in flux and enrichment factor of aroma compounds in the permeate. On the other hand, total and partial fluxes increased significantly when feed temperature was increased from 25 to 50°C: this phenomenon was attributed to an increase of the free volume in the PV membrane which in turn increases the diffusion rate of individual permeating molecules and high permeation fluxes. The selectivity of all aroma compounds increased also with temperature and this change was attributed to the activation energy of each component. As expected, an increasing of permeate pressure decreased the driving force of the permeation through the membranes leading to a reduction in the permeation flux. For some aroma compounds, such as hexanal, ethyl acetate and ethyl butyrate, the enrichment factor increased when vacuum pressure was raised.

Similar results were also obtained by Raisi et al. (2008) in the recovery of aroma compounds from pomegranate juice by using POMS and PDMS membranes. The

POMS membranes produced a higher aroma enrichment factor but lower permeation flux compared to the PDMS membranes.

Additionally, the influence of the feed temperature on the PV recovery was analyzed using the Arrhenius model. It was found out that the activation energy (E_a) of the molecules was positive, which reveals that any feed temperature increase must cause higher permeation flux values. Interestingly, the apparent E_a of the recovered aromas was higher than water molecules, indicating that the transport of these specific aromas across the membrane is higher temperature dependent comparing to water molecules. In general, when activation energy parameter is high, the permeation flux will be more sensitive to temperature variations; therefore, aroma molecules are likely more sensitive to this parameter (Raisi et al., 2008; Raisi et al., 2009). Importantly, the feed operating temperature plays a key role for the performance of a PV membrane since primarily influences the solubility and diffusion coefficients of the components across membrane (Wijmans & Baker, 1995). In addition to this, the separation of thermolabile molecules is more recommendable at lower operating temperatures, in order to prevent their thermal degradation.

Coffee is well recognized for its characteristic perfume notes related to several molecules, e.g. 2-methylbutanoic acid, 2-methylpropanal, hexanal, (E)-2-nonenal, to mention just a few. Thereby, it has been also used for the separation of key flavor and aroma molecules. Organic molecules, like 2-5-dimethyl pyrazine, and 2,3-butanedione, that give sensorial features (e.g. creamy, sweet, nutty-like, buttery, and milky) were recovered using a commercial Pervatech BV membrane (Weschenfelder et al., 2015). This commercially available PDMS membrane had a high selectivity towards 2,3-butanedione (β=45) and 2-5-dimethyl pyrazine (β=42). Additionally, such membranes offered relatively moderate organic permeation flux (of about 0.432 kg m^{-2} h^{-1}).

Within the food beverage production, valuable aromas are normally recovered and then concentrated using traditional distillation, and finally blended to clarified juice (De Vasconcelos Facundo et al., 2009). Some agro-food effluents are potentially considered as new feedstock of aroma molecules. For example, Souchon et al. (2002) applied the PV process to the deodorization of a cauliflower blanching effluent in order to recover valuable food flavouring compounds such as dimethyl disulfide, dimethyl trisulfide and S-methyl thio-butyrate. Hydrophobic PDMS and PEBA membranes showed high selective affinity for S-methyl thio-butyrate, with enrichment factors of 307 and 1200, respectively, when a model solution with three sulfur compounds was tested. In fact, this membrane was selected for PV experiments on the industrial effluent. In this case the selectivity resulted five times lower than the one obtained on model solution probably due to the formation of an important boundary layer. However, the odour quality of the permeate was completely modified and the retentate was significantly deodorized regards to the feed.

Recently, Dawiec-Liśniewska et al. (2018a) evaluated the extraction of aromas from fruit juice hydrolates by using PV on both laboratory and semi-technical scale. The hydrolate derivatives were obtained from several horticultural products (e.g. blackcurrant, plum, cherry and apple fruits), which usually contain a wide category of aromatic-based compounds. 37 different aroma compounds were identified and quantified in the blackcurrant hydrolate, while 14 and 20 organic compounds were identified in cherry and apple derivatives, respectively. Commercial hydrophobic PDMS membranes (Pervap 4060, Sulzer, Germany) used in both laboratory and semi-technical scale, exhibited extremely high separation affinity for organic molecules, like heptan-1-ol (β~1131), hexanal (β~3678), pentan-1-ol (β~5800), and butyl acetate (β~8602). These membranes displayed a total permeate flux of at least 0.180 kg m^{-2} h^{-1} that can be further increased up to 0.450 kg m^{-2} h^{-1}, depending on operating temperature. The results of the economic analysis demonstrated that PV is a profitable and feasible option for aroma recovery from fruit hydrolates.

Some processed products from the food beverage industry, including beer, cider and wine, are also currently explored for the recovery of aroma compounds (Catarino et al., 2009; Catarino & Mendes, 2011a; Paz et al., 2017). Catarino et al. (2009) evaluated a commercial brand beer as a candidate for extracting a wide range of esters (e.g. isomyl acetate, ethyl acetate), alcohols (e.g. isoamyl alcohol, propanol, isobutanol,) and aldehydes (e.g. acetaldehyde). The extraction of aromas was aimed to achieve the sensorial properties of low-alcoholic content beer, which is prone to lose some of these aromas caused by ethanol removal (Castro-Muñoz, 2019). PV experiments were performed by using a polyoctylmethylsiloxane/polyetherimide (POMS/PEI) composite asymmetric membrane and the effect of operating conditions on the process performance was analysed according to the response surface methodology (RSM) approach. In optimized conditions of feed temperature, feed velocity and permeate pressure (12.4 °C, 0.45 m s^{-1} and 1.0 mbar, respectively) the permeate flux was predicted to be 7.26 kg m^{-2} s^{-1}, while alcohols and esters selectivity was in the range 1.31-3.39

and 14.46-17.10, respectively. Experimental results, obtained in optimized operating conditions, resulted in a good agreement with the predicted values of the regression model. Experimental results for the runs performed at the optimal operating conditions mostly agreed with the predicted values.

In another approach Catarino & Mendes (2011b) investigated the manufacture of non-alcoholic beer with a corrected natural flavour profile by using an industrial set-up. Firstly, the aroma compounds were extracted from the original beer by using a POMS/PEI membrane, and later mixed with the previously dealcoholized beer. Such integrated methodology permitted to achieve a flavored non-alcoholic beer with minimal content of alcohol (<0.5 vol.% ethanol). A similar approach was used to improve the aroma profile of dealcoholized wine samples (Catarino & Mendes, 2011a).

Two different commercial beers differing in ethanol concentration (a special beer ~5.5% ABV and a reserve beer ~6.5% ABV) were processed by using a hydrophobic PDMS Pervatech membrane to extract aroma molecules which were then mixed to a low-alcohol beer (less than 1% ABV) and an alcohol-free beer (less than 0.1% ABV) to enhance their sensorial and organoleptic quality (Olmo et al. 2014). Three individual flavor components were analysed in detail (ethyl acetate, isoamyl acetate, isobutyl alcohol) and selectivities were predicted considering solubility parameters of polymer and compounds. The theoretical calculation of relative selectivities from solubility parameters can provide useful information about the design of the process and the selection of the membrane in order to reach high productivities and selectivities. Similarly, Salgado et al. (2017) used a PV spiral-wound membrane module with a PDMS based membrane (PV-

SR1, Pervatech) for the extraction of aroma precursors (i.e. hexanal, isoamylalcohol,1-hexanol, benzaldehyde, benzyl alcohol and 2-phenylethanol) from grape must. Such aromas were recovered and then blended into low alcohol white wines obtained by reducing the sugar content in grape must through NF membranes, in order to produce a full flavored white wine with reduced alcohol content. The PV membrane did not offer high permeation rates (~0.073 kg m^{-2} h^{-1}), however, the final product showed an aroma content similar to the original grape must with the exception of benzaldehyde and 1-hexanol.

All these studies confirm the great potential of PV-based membrane processes for recovering/extracting aromatic-based compounds from different natural feedstocks by means of non-porous membranes. Furthermore, PV can also assist other types of food processing processes, e.g. when dealing with the removal of ethanol to produce non-alcoholic drinks and beverages based on wine and beer.

5. Conclusions and future trends

Membrane-based processes, including MF, UF, NF, MD, and PV, have demonstrated to meet the recovery and extraction requirements of biologically active compounds, such as phenolic-based molecules and their specific derivatives, as well as aroma compounds from natural products and agro-food by-products.

In general, MF technology finds its main application as a pre-treatment technique to separate macromolecules, colloids and suspended solids from solutions, which subsequently are processed by UF and NF technologies for a better reclamation of smaller high-added-value molecules. Particularly, PV proved its ability to recover different types of aromatic-based compounds, in which the membrane nature, as well as the polarity of the target solutes, play a key role on both productivity and selectivity of the process. In addition, MD and PV processes have been also addressed as potential candidates for the production of non-alcoholic beverages. Comparing with conventional techniques, membrane-based separation operations are economically profitable not only in terms of extraction but also because these emerging processes do not demand the usage of further agents or/and destructive compounds. Thus, the extraction and recovery of valuable molecules from different sources are both industrially sustainable and environmentally friendly, making membrane-based processes meaningful for the integral management of products and by-products derived from the food industry. It is likely that the prominent raising worldwide demand towards these valuable solutes will promote a wider application of such membrane-based operations in this field.

Concluding remarks related to the different processes analysed in this context are reported in the following.

- *Microfiltration, ultrafiltration and nanofiltration*: Scientists in the field should put an effort into treating real feed solutions in order to provide a more real proximity performance of membranes. In such a way, future developments will provide relevant insights into the possibility of considering these processes for large scale applications. Importantly, fouling phenomena represent the main drawback when real complex solutions (e.g. agro-food by-products and wastewaters) are processed. At this purpose, "membranologists" are looking for novel membrane materials in membrane preparation, as well as facing the weakness of the existing ones, to develop and manufacture new smart membranes that could mitigate membrane fouling and therefore less prone to be fouled. Another important aspect regards to the purity of the recovered solutes, which will primarily need further purification for a specific application.

- *Membrane distillation*: This process can overcome the limits of thermal processes (e.g. evaporation, distillation). Thanks to the effective operation at low temperatures, MD can be integrated with alternative energy sources for example waste energy or solar energy. This feature may make it more promising for industrial implementation. On the other hand, most of MD studies regard the concentration of aqueous model solutions at lab scale; thereby, investigations on complex feed solutions are encouraged. There are still some issues that must be overcome, such as scaling, fouling and pore wetting in a long-term MD processing. At this point, the main research challenge is to create new membrane materials with improved porosity and higher hydrophobicity using low-thermal conductive polymers to minimize heat loss.
- *Pervaporation*: This process finds the low permeation rate as its main drawback compared to other membrane-based technologies (e.g. MF, UF and NF), while its strength comprises the high selectivity. Importantly, two main issues should be addressed by future studies in the field. The first one, real feed solutions (e.g. agro-food products and by-products) should be tested in order to provide a more realistic approximation of membranes' performance over long-term operation. On the other hand, as a second issue, scientists should preferentially report the PV performance data based

on permeance and selectivity. Such parameters are a preferred way of reporting pervaporation results, in which membrane' performance does not depend on the operating parameters (including driving force). In this way, a fair comparison of different studies can be given.

Conflict of Interest

The authors declare no conflict of interest.

References

Aroujalian, A., & Raisi, A. (2007). Recovery of volatile aroma components from orange juice by pervaporation. *Journal of Membrane Science*, *303*(1–2), 154–161. https://doi.org/10.1016/j.memsci.2007.07.004

Astudillo-Castro, C. L. (2015). Limiting flux and critical transmembrane pressure determination using an exponential model: The effect of concentration factor, temperature, and cross-flow velocity during casein micelle concentration by microfiltration. *Industrial and Engineering Chemistry Research*, *54*(1), 414–425. https://doi.org/10.1021/ie5033292

Bacchin, P., Si-hassen, D., Starov, V., Clifton, M. J., & Aimar, P. (2002). A unifying model for concentration polarization , gel-layer formation and particle deposition in cross- flow membrane filltration of colloidal suspensions. *Chemical Engineering Science*, *57*, 77–91. https://doi.org/http://dx.doi.org/10.1016/S0009-2509(01)00316-5

Bagger-Jørgensen, R., Meyer, A. S., Varming, C., & Jonsson, G. (2004). Recovery of volatile aroma compounds from black currant juice by vacuum membrane distillation. *Journal of Food Engineering*, *64*(1), 23–31. https://doi.org/10.1016/j.jfoodeng.2003.09.009

Baudot, A., & Marin, M. (1997). Pervaporation of aroma compounds: Comparison of Membrane Performances with Vapour-Liquid Equilibria and Engineering Aspects of Process Improvement. *Food and Bioproducts Processing: Transactions of the Institution of of Chemical Engineers, Part C*, *75*(2), 117–142. https://doi.org/10.1205/096030897531432

Belessiotis, V., Kalogirou, S., & Delyannis, E. (2016). Membrane Distillation. In V. Belessiotis, S. Kalogirou, & E. Delyannis (Eds.), *Thermal Solar Desalination: Methods and Systems* (First Edit, pp. 191–251). https://doi.org/https://doi.org/10.1016/B978-0-12-809656-7.00004-0

Bengtsson, E., Trägårdh, G., & Hallström, B. (1989). Recovery and concentration of apple juice aroma compounds by pervaporation. *Journal of Food Engineering*, *10*(1), 65–71. https://doi.org/10.1016/0260-8774(89)90021-6

Blanco Gálvez, J., García-Rodríguez, L., & Martín-Mateos, I. (2009). Seawater desalination by an innovative solar-powered membrane distillation system: the MEDESOL project. *Desalination*, *246*(1–3), 567–576. https://doi.org/10.1016/j.desal.2008.12.005

Blanco, J. F., Sublet, J., Nguyen, Q. T., & Schaetzel, P. (2006). Formation and morphology studies of different polysulfones-based membranes made by wet phase inversion process. *Journal of Membrane Science*, *283*(1–2), 27–37. https://doi.org/10.1016/j.memsci.2006.06.011

Cartalade, D., & Vernhet, A. (2006). Polar interactions in flavan-3-ol adsorption on solid surfaces. *Journal of Agricultural and Food Chemistry*, *54*(8), 3086–3094. https://doi.org/10.1021/jf0514928

Cassano, A., Conidi, C., & Drioli, E. (2011). Comparison of the performance of UF membranes in olive mill wastewaters treatment. *Water Research*, *45*(10), 3197–3204. https://doi.org/10.1016/j.watres.2011.03.041

Cassano, A., Conidi, C., Galanakis, C. M., & Castro-Muñoz, R. (2016). Recovery of polyphenols from olive mill wastewaters by membrane operations. In *Membrane Technologies for Biorefining*. https://doi.org/10.1016/B978-0-08-100451-7.00007-4

Cassano, A., Figoli, A., Tagarelli, A., Sindona, G., & Drioli, E. (2006). Integrated membrane process for the production of highly nutritional kiwifruit juice. *Desalination*, *189*(1-3 SPEC. ISS.), 21–30. https://doi.org/10.1016/j.desal.2005.06.009

Cassano, Alfredo, Cabri, W., Mombelli, G., Peterlongo, F., & Giorno, L. (2016). Recovery of bioactive compounds from artichoke brines by nanofiltration. *Food and Bioproducts Processing*, *98*, 257–265. https://doi.org/10.1016/j.fbp.2016.02.004

Cassano, Alfredo, Conidi, C., & Castro-Muñoz, R. (2019). Current and Future Applications of Nanofiltration in Food Processing. In *Separation of Functional Molecules in Food by Membrane Technology*. https://doi.org/10.1016/b978-0-12-815056-6.00009-7

Cassano, Alfredo, Conidi, C., Giorno, L., & Drioli, E. (2013). Fractionation of olive mill wastewaters by membrane separation techniques. *Journal of Hazardous*

Materials, *248–249*(1), 185–193. https://doi.org/10.1016/j.jhazmat.2013.01.006

Cassano, Alfredo, Conidi, C., & Ruby-Figueroa, R. (2014). Recovery of flavonoids from orange press liquor by an integrated membrane process. *Membranes*, *4*(3), 509–524. https://doi.org/10.3390/membranes4030509

Cassano, Alfredo, Conidi, C., Ruby-Figueroa, R., & Castro-Muñoz, R. (2015). *A Two-Step Nanofiltration Process for the Production of Phenolic-Rich Fractions from Artichoke Aqueous Extracts*. 8968–8987. https://doi.org/10.3390/ijms16048968

Cassano, Alfredo, Conidi, C., Ruby-Figueroa, R., & Castro-Muñoz, R. (2018). Nanofiltration and Tight Ultrafiltration Membranes for the Recovery of Polyphenols from Agro-Food By-Products. *International Journal of Molecular Sciences*, *19*(2), 351. https://doi.org/10.3390/ijms19020351

Castro-Muñoz, R. (2019). Pervaporation-based membrane processes for the production of non-alcoholic beverages. *Journal of Food Science and Technology*, *56*(5), 2333–2344. https://doi.org/10.1007/s13197-019-03751-4

Castro-Muñoz, R., Buera-Gonzalez, J., de la Iglesia, O., Galiano, F., Fíla, V., Malankowska, M., … Coronas, J. (2019). Towards the dehydration of ethanol using pervaporation cross-linked poly(vinyl alcohol)/graphene oxide membranes. *Journal of Membrane Science*, *582*, 423–434. https://doi.org/https://doi.org/10.1016/j.memsci.2019.03.076

Castro-Muñoz, R., Conidi, C., & Cassano, A. (2018). Membrane-based technologies for meeting the recovery of biologically active compounds from foods and their by-products. *Critical Reviews in Food Science and Nutrition*, *0*(0), 1–22. https://doi.org/10.1080/10408398.2018.1478796

Castro-Muñoz, R., Galiano, F., Fíla, V., Drioli, E., & Figoli, A. (2018). Mixed matrix membranes (MMMs) for ethanol purification through pervaporation: Current state of the art. *Reviews in Chemical Engineering Https://Doi.Org/10.1515/Revce-2017-0115*. https://doi.org/https://doi.org/10.1515/revce-2017-0115

Castro-Muñoz, Roberto. (2018). Pressure-driven membrane processes involved in waste management in agro-food industries: A viewpoint. *AIMS Energy*, *6*(6), 1025–1031. https://doi.org/10.3934/energy.2018.6.1025

Castro-Muñoz, Roberto. (2019a). Pervaporation: The emerging technique for extracting aroma compounds from food systems. *Journal of Food Engineering*, *253*(February), 27–39. https://doi.org/10.1016/j.jfoodeng.2019.02.013

Castro-Muñoz, Roberto. (2019b). Retention profile on the physicochemical properties of maize cooking by-product using a tight ultrafiltration membrane. *Chemical Engineering Communications*, *0*(0), 1–9. https://doi.org/10.1080/00986445.2019.1618844

Castro-Muñoz, Roberto, Barragán-Huerta, B. E., Fíla, V., Denis, P. C., & Ruby-Figueroa, R. (2018). Current Role of Membrane Technology: From the Treatment of Agro-Industrial by-Products up to the Valorization of Valuable Compounds. *Waste and Biomass Valorization*, *9*(4), 513–529. https://doi.org/10.1007/s12649-017-0003-1

Castro-Muñoz, Roberto, Barragán-Huerta, B. E., & Yáñez-Fernández, J. (2016). The Use of Nixtamalization Waste Waters Clarified by Ultrafiltration for Production of a Fraction Rich in Phenolic Compounds. *Waste and Biomass Valorization*, *7*(5), 1167–1176. https://doi.org/10.1007/s12649-016-9512-6

Castro-Muñoz, Roberto, & Fíla, V. (2018). Membrane-based technologies as an emerging tool for separating high-added-value compounds from natural products. *Trends in Food Science and Technology*, *82*(September), 8–20. https://doi.org/10.1016/j.tifs.2018.09.017

Castro-Muñoz, Roberto, & González-Valdez, J. (2019). New Trends in Biopolymer-Based Membranes for Pervaporation. *Molecules*, *24*(19), 3584. https://doi.org/10.3390/molecules24193584

Castro-Muñoz, Roberto, & Yáñez-Fernández, J. (2015). Valorization of Nixtamalization wastewaters (Nejayote) by integrated membrane process. *Food and Bioproducts Processing*, *95*, 7–18. https://doi.org/10.1016/j.fbp.2015.03.006

Castro-Muñoz, Roberto, Yáñez-Fernández, J., & Fíla, V. (2016). Phenolic compounds recovered from agro-food by-products using membrane technologies: An overview. *Food Chemistry*, *213*, 753–762. https://doi.org/10.1016/j.foodchem.2016.07.030

Catarino, M., Ferreira, A., & Mendes, A. (2009). Study and optimization of aroma recovery from beer by pervaporation. *Journal of Membrane Science*, *341*(1–2), 51–59. https://doi.org/10.1016/j.memsci.2009.05.038

Catarino, M., & Mendes, A. (2011a). Dealcoholizing wine by membrane separation processes. *Innovative Food Science and Emerging Technologies*, *12*(3), 330–337. https://doi.org/10.1016/j.ifset.2011.03.006

Catarino, M., & Mendes, A. (2011b). Non-alcoholic beer - A new industrial process. *Separation and Purification Technology*, *79*(3), 342–351. https://doi.org/10.1016/j.seppur.2011.03.020

Chen, Y. R., Chen, L. H., Chen, C. H., Ko, C. C., Huang, A., Li, C. L., … Tung, K. L. (2018). Hydrophobic alumina hollow fiber membranes for sucrose concentration by vacuum membrane distillation. *Journal of Membrane Science*, *555*(March), 250–257. https://doi.org/10.1016/j.memsci.2018.03.048

Conidi, C., Cassano, A., & Garcia-Castello, E. (2014). Valorization of artichoke wastewaters by integrated membrane process. *Water Research*, *48*(1), 363–374. https://doi.org/10.1016/j.watres.2013.09.047

Conidi, C., Rodriguez-Lopez, A. D., Garcia-Castello, E. M., & Cassano, A. (2015). Purification of artichoke polyphenols by using membrane filtration and polymeric resins. *Separation and Purification Technology*, *144*, 153–161. https://doi.org/10.1016/j.seppur.2015.02.025

Conidi, Carmela, Cassano, A., & Drioli, E. (2012). Recovery of phenolic compounds from orange press liquor by nanofiltration. *Food and Bioproducts Processing*, *90*(4), 867–874. https://doi.org/10.1016/j.fbp.2012.07.005

Crespo, J., & Brazinha, C. (2015). Fundamentals of pervaporation. In A. Basile, A. Figoli, & M. Khayet (Eds.), *Pervaporation, vapour permeation and membrane distillation* (pp. 1–17). Cambridge UK: Elsevier Ltd.

Crespo, J. G., & Brazinha, C. (2010). Membrane processing: Natural antioxidants from winemaking by-products. *Filtration and Separation*, *47*(2), 32–35. https://doi.org/10.1016/S0015-1882(10)70079-3

Dawiec-Liśniewska, A., Szumny, A., Podstawczyk, D., & Witek-Krowiak, A. (2018). Concentration of natural aroma compounds from fruit juice hydrolates by pervaporation in laboratory and semi-technical scale. Part 1. Base study. *Food Chemistry*, *258*, 63–70. https://doi.org/10.1016/j.foodchem.2018.03.023

De Vasconcelos Facundo, H., De Souza Neto, M., Arraes Maia, G., Narain, N., & Dos Santos, D. (2009). Changes in flavor quality of pineappled juice during processing. *Journal of Food Processing and Preservation*, *34*, 508–519. https://doi.org/10.1111/j.1745-4549.2008.00356.x

Deshmukh, S. K., Sapkal, V. S., & Sapkal, R. S. (2011). Evaluation of Direct Contact Membrane Distillation for Concentration of Orange Juice. *Int. J. Chem. Res.*, *01*(2), 39–48.

Dhillon, G. S., Kaur, S., & Brar, S. K. (2013). Perspective of apple processing wastes as low-cost substrates for bioproduction of high value products: A review. *Renewable and Sustainable Energy Reviews*, *27*, 789–805. https://doi.org/10.1016/j.rser.2013.06.046

Díaz-Reinoso, B., González-López, N., Moure, A., Domínguez, H., & Parajó, J. C. (2010). Recovery of antioxidants from industrial waste liquors using membranes and polymeric resins. *Journal of Food Engineering*, *96*(1), 127–133. https://doi.org/10.1016/j.jfoodeng.2009.07.007

Díaz-Reinoso, B., Moure, A., Domínguez, H., & Parajó, J. C. (2009). Ultra- and nanofiltration of aqueous extracts from distilled fermented grape pomace. *Journal of Food Engineering*, *91*(4), 587–593. https://doi.org/10.1016/j.jfoodeng.2008.10.007

Díaz-Reinoso, B., Moure, A., González, J., & Domínguez, H. (2017). A membrane process for the recovery of a concentrated phenolic product from white vinasses. *Chemical Engineering Journal*, *327*, 210–217. https://doi.org/10.1016/j.cej.2017.06.088

El-Bourawi, M. S., Ding, Z., Ma, R., & Khayet, M. (2006). A framework for better understanding membrane distillation separation process. *Journal of Membrane Science*, *285*(1–2), 4–29. https://doi.org/10.1016/j.memsci.2006.08.002

Evans, P. J., Bird, M. R., Pihlajamäki, A., & Nyström, M. (2008). The influence of hydrophobicity, roughness and charge upon ultrafiltration membranes for black tea liquor clarification. *Journal of Membrane Science*, *313*(1–2), 250–262. https://doi.org/10.1016/j.memsci.2008.01.010

Fane, A. G., & Fell, C. J. D. (1987). A review of fouling and fouling control in ultrafiltration. *Desalination*, *62*(C), 117–136. https://doi.org/10.1016/0011-9164(87)87013-3

Fawzy, M. K., Varela-Corredor, F., & Bandini, S. (2019). On the Morphological Characterization Procedures of Multilayer Hydrophobic Ceramic Membranes for Membrane Distillation Operations. *Membranes*, *9*(10), 125. https://doi.org/10.3390/membranes9100125

Figoli, A., Tagarelli, A., Cavaliere, B., Voci, C., Sindona, G., Sikdar, S. K., & Drioli, E. (2010). Evaluation of pervaporation process of kiwifruit juice by SPME-GC/Ion Trap Mass Spectrometry. *Desalination*, *250*(3), 1113–1117. https://doi.org/10.1016/j.desal.2009.09.120

Figoli, A., Tagarelli, A., Mecchia, A., Trotta, A., Cavaliere, B., Lavecchia, R., … Drioli, E. (2006). Enzyme-assisted pervaporative recovery of concentrated bergamot peel oils. *Desalination*, *199*(1–3), 111–112. https://doi.org/10.1016/j.desal.2006.03.025

Fouda, A., Bai, J., Zhang, S. Q., Kutowy, O., & Matsuura, T. (1993). Membrane separation of low volatile organic compounds by pervaporation and vapor permeation. *Desalination*, *90*(1–3), 209–233. https://doi.org/10.1016/0011-

9164(93)80177-O

Galanakis, C. M. (2013). Emerging technologies for the production of nutraceuticals from agricultural by-products: A viewpoint of opportunities and challenges. *Food and Bioproducts Processing*, *91*(4), 575–579. https://doi.org/10.1016/j.fbp.2013.01.004

Galanakis, C. M. (2015a). Chapter 3 – The universal recovery strategy. In *Food Waste Recovery*. https://doi.org/10.1016/B978-0-12-800351-0.00003-1

Galanakis, C. M. (2015b). Separation of functional macromolecules and micromolecules: From ultrafiltration to the border of nanofiltration. *Trends in Food Science and Technology*, *42*(1), 44–63. https://doi.org/10.1016/j.tifs.2014.11.005

Galanakis, C. M., Markouli, E., & Gekas, V. (2013). Recovery and fractionation of different phenolic classes from winery sludge using ultrafiltration. *Separation and Purification Technology*, *107*, 245–251. https://doi.org/10.1016/j.seppur.2013.01.034

Galanakis, C. M., Tornberg, E., & Gekas, V. (2010). Clarification of high-added value products from olive mill wastewater. *Journal of Food Engineering*, *99*(2), 190–197. https://doi.org/10.1016/j.jfoodeng.2010.02.018

Galiano, F., Mecchia, A., Castro-Muñoz, R., Tagarelli, A., Lavecchia, R., & Figoli, A. (2019). Enzyme-Mediated Extraction of Limonene , Linalool and Linalyl Acetate from Bergamot Peel Oil by Pervaporation Graphical abstract Keywords. *Journal of Membrane Science & Research*, *5*, 187–193. https://doi.org/10.22079/JMSR.2018.95080.1221

Garcia-Castello, E., Cassano, A., Criscuoli, A., Conidi, C., & Drioli, E. (2010).

Recovery and concentration of polyphenols from olive mill wastewaters by integrated membrane system. *Water Research*, *44*(13), 3883–3892. https://doi.org/10.1016/j.watres.2010.05.005

Giacobbo, A., Bernardes, A. M., & de Pinho, M. N. (2017). Sequential pressure-driven membrane operations to recover and fractionate polyphenols and polysaccharides from second racking wine lees. *Separation and Purification Technology*, *173*, 49–54. https://doi.org/10.1016/j.seppur.2016.09.007

Giacobbo, A., Do Prado, J. M., Meneguzzi, A., Bernardes, A. M., & De Pinho, M. N. (2015). Microfiltration for the recovery of polyphenols from winery effluents. *Separation and Purification Technology*, *143*, 12–18. https://doi.org/10.1016/j.seppur.2015.01.019

Giacobbo, A., Meneguzzi, A., Bernardes, A. M., & de Pinho, M. N. (2017). Pressure-driven membrane processes for the recovery of antioxidant compounds from winery effluents. *Journal of Cleaner Production*, *155*, 172–178. https://doi.org/10.1016/j.jclepro.2016.07.033

Gryta, M., & Barancewicz, M. (2011). Separation of volatile compounds from fermentation broth by membrane distillation. *Polish Journal of Chemical Technology*, *13*(3), 56–60. https://doi.org/10.2478/v10026-011-0038-1

Gunko, S., Verbych, S., Bryk, M., & Hilal, N. (2006). Concentration of apple juice using direct contact membrane distillation. *Desalination*, *190*(1–3), 117–124. https://doi.org/10.1016/j.desal.2005.09.001

Isci, A., Sahin, S., & Sumnu, G. (2006). Recovery of strawberry aroma compounds by pervaporation. *Journal of Food Engineering*, *75*(1), 36–42. https://doi.org/10.1016/j.jfoodeng.2005.03.048

Kaippamangalath, N., & Gopalakrishnapanicker, U. (2018). Chapter 8 - Transport Properties Through Polymer Membranes. In S. Thomas, A. Kumar, R. Wilson, & S. George (Eds.), *Transport Properties of Polymeric Membranes* (First edit). https://doi.org/10.1016/B978-0-12-809884-4.00008-2

Kanani, D. (2015). Membrane fouling: A challenge during dairy ultrafiltration. *Membrane Processes for Dairy Ingredient Separation*, 67–85. https://doi.org/10.1002/9781118590331.ch3

Kozák, Á., Békássy-Molnár, E., & Vatai, G. (2009). Production of black-currant juice concentrate by using membrane distillation. *Desalination*, *241*(1–3), 309–314. https://doi.org/10.1016/j.desal.2008.02.033

Lawson, K. W., & Lloyd, D. R. (1997). Membrane distillation. *Journal of Membrane ScienceMembrane Science*, *124*, 1–25.

Le, N. L., & Nunes, S. P. (2016). Materials and membrane technologies for water and energy sustainability. *Sustainable Materials and Technologies*, *7*, 1–28. https://doi.org/10.1016/j.susmat.2016.02.001

Mirabella, N., Castellani, V., & Sala, S. (2014). Current options for the valorization of food manufacturing waste: a review. *Journal of Cleaner Production*, *65*, 28–41. https://doi.org/10.1016/J.JCLEPRO.2013.10.051

Nene, S., Kaur, S., Sumod, K., Joshi, B., & Raghavarao, K. S. M. S. (2002). Membrane distillation for the concentration of raw cane-sugar syrup and membrane clarified sugarcane juice. *Desalination*, *147*(1–3), 157–160. https://doi.org/10.1016/S0011-9164(02)00604-5

Ochando-Pulido, J. M., & Martínez-Férez, A. (2017). About the recovery of the phenolic fraction from olive mill wastewater by micro and ultracentrifugation membranes. *Chemical Engineering Transactions*, *60*, 271–276. https://doi.org/10.3303/CET1760046

Olmo, Á. Del, Blanco, C. A., Palacio, L., Prádanos, P., & Hernández, A. (2014). Pervaporation methodology for improving alcohol-free beer quality through aroma recovery. *Journal of Food Engineering*, *133*, 1–8. https://doi.org/10.1016/j.jfoodeng.2014.02.014

Paz, A. I., Blanco, C. A., Andrés-Iglesias, C., Palacio, L., Prádanos, P., & Hernández, A. (2017). Aroma recovery of beer flavors by pervaporation through polydimethylsiloxane membranes. *Journal of Food Process Engineering*, *40*(6). https://doi.org/10.1111/jfpe.12556

Prudêncio, A. P. A., Prudêncio, E. S., Amboni, R. D. M. C., Murakami, A. N. N., Maraschin, M., Petrus, J. C. C., … Leite, R. S. (2012). Phenolic composition and antioxidant activity of the aqueous extract of bark from residues from mate tree (Ilex paraguariensis St. Hil.) bark harvesting concentrated by nanofiltration. *Food and Bioproducts Processing*, *90*(3), 399–405. https://doi.org/10.1016/j.fbp.2011.12.003

Purwasasmita, M., Kurnia, D., Mandias, F. C., Khoiruddin, & Wenten, I. G. (2015). Beer dealcoholization using non-porous membrane distillation. *Food and Bioproducts Processing*, *94*, 180–186. https://doi.org/10.1016/j.fbp.2015.03.001

Qtaishat, M. R., & Banat, F. (2013). Desalination by solar powered membrane distillation systems. *Desalination*, *308*, 186–197. https://doi.org/10.1016/j.desal.2012.01.021

Quist-Jensen, C. A., Macedonio, F., Conidi, C., Cassano, A., Aljlil, S., Alharbi, O.

A., & Drioli, E. (2016). Direct contact membrane distillation for the concentration of clarified orange juice. *Journal of Food Engineering*, *187*, 37–43. https://doi.org/10.1016/j.jfoodeng.2016.04.021

Raisi, A., Aroujalian, A., & Kaghazchi, T. (2008). Multicomponent pervaporation process for volatile aroma compounds recovery from pomegranate juice. *Journal of Membrane Science*, *322*(2), 339–348. https://doi.org/10.1016/j.memsci.2008.06.001

Raisi, A., Aroujalian, A., & Kaghazchi, T. (2009). A predictive mass transfer model for aroma compounds recovery by pervaporation. *Journal of Food Engineering*, *95*(2), 305–312. https://doi.org/10.1016/j.jfoodeng.2009.05.004

Ramli, R., & Bolong, N. (2016). Effects of pressure and temperature on ultrafiltration hollow fiber membrane in mobile water treatment system. *Journal of Engineering Science and Technology*, *11*(7), 1031–1040.

Russo, F., Castro-Muñoz, R., Galiano, F., & Figoli, A. (2019). Unprecedented preparation of porous Matrimid ® 5218 membranes. *Journal of Membrane Science*, *585*(March), 166–174. https://doi.org/10.1016/j.memsci.2019.05.036

Salgado, C. M., Fernández-Fernández, E., Palacio, L., Carmona, F. J., Hernández, A., & Prádanos, P. (2017). Application of pervaporation and nanofiltration membrane processes for the elaboration of full flavored low alcohol white wines. *Food and Bioproducts Processing*, *101*, 11–21. https://doi.org/10.1016/j.fbp.2016.10.001

Sánchez, A. M., Carmona, M., Prodanov, M., & Alonso, G. L. (2008). Effect of centrifugal ultrafiltration on the composition of aqueous extracts of saffron spice (Crocus sativus L.). *Journal of Agricultural and Food Chemistry*, *56*(16), 7293–7301. https://doi.org/10.1021/jf801105x

Santamaría, R. I., Reyes-Duarte, M. D., Bárzana, E., Fernando, D., Gama, F. M., Mota, M., & López-Munguía, A. (2000). Selective enzyme-mediated extraction of capsaicinoids and carotenoids from chili guajillo puya (Capsicum annuum L.) using ethanol as solvent. *Journal of Agricultural and Food Chemistry*, *48*(7), 3063–3067. https://doi.org/10.1021/jf991242p

Servili, M., Esposto, S., Veneziani, G., Urbani, S., Taticchi, A., Maio, I. Di, … Montedoro, G. (2011). Improvement of bioactive phenol content in virgin olive oil with an olive-vegetation water concentrate produced by membrane treatment. *Food Chemistry*, *124*(4), 1308–1315. https://doi.org/10.1016/j.foodchem.2010.07.042

Souchon, I., Pierre, F. X., Athes-Dutour, V., & Marin, M. (2002). Pervaporation as a deodorization process applied to food industry effluents: Recovery and valorisation of aroma compounds from cauliflower blanching water. *Desalination*, *148*(1–3), 79–85. https://doi.org/10.1016/S0011-9164(02)00657-4

Susanto, H., Feng, Y., & Ulbricht, M. (2009). Fouling behavior of aqueous solutions of polyphenolic compounds during ultrafiltration. *Journal of Food Engineering*, *91*(2), 333–340. https://doi.org/10.1016/j.jfoodeng.2008.09.011

Uyttebroek, M., Vandezande, P., Van Dael, M., Vloemans, S., Noten, B., Bongers, B., … Lemmens, B. (2018). Concentration of phenolic compounds from apple pomace extracts by nanofiltration at lab and pilot scale with a techno-economic assessment. *Journal of Food Process Engineering*, *41*(1), 1–10. https://doi.org/10.1111/jfpe.12629

Van Der Bruggen, B., Lejon, L., & Vandecasteele, C. (2003). Reuse, treatment, and discharge of the concentrate of pressure-driven membrane processes. *Environmental Science and Technology*, *37*(17), 3733–3738. https://doi.org/10.1021/es0201754

Wei, X., Bao, X., Wu, J., Li, C., Shi, Y., Chen, J., … Zhu, B. (2018). Typical pharmaceutical molecule removal behavior from water by positively and negatively charged composite hollow fiber nanofiltration membranes. *RSC Advances*, *8*(19), 10396–10408. https://doi.org/10.1039/c8ra00519b

Weschenfelder, T. A., Lantin, P., Viegas, M. C., De Castilhos, F., & Scheer, A. D. P. (2015). Concentration of aroma compounds from an industrial solution of soluble coffee by pervaporation process. *Journal of Food Engineering*, *159*, 57–65. https://doi.org/10.1016/j.jfoodeng.2015.03.018

Wijmans, J. G., & Baker, R. W. (1995). The solution-diffusion model: a review. *Journal of Membrane Science*, *107*(1–2), 1–21. https://doi.org/10.1016/0376-7388(95)00102-I

Winter, J., Barbeau, B., & Bérubé, P. (2017). Nanofiltration and tight ultrafiltration membranes for natural organic matter removal–Contribution of fouling and concentration polarization to filtration resistance. *Membranes*, *7*(3). https://doi.org/10.3390/membranes7030034

Figure 1. General description of pressure-driven membrane process.

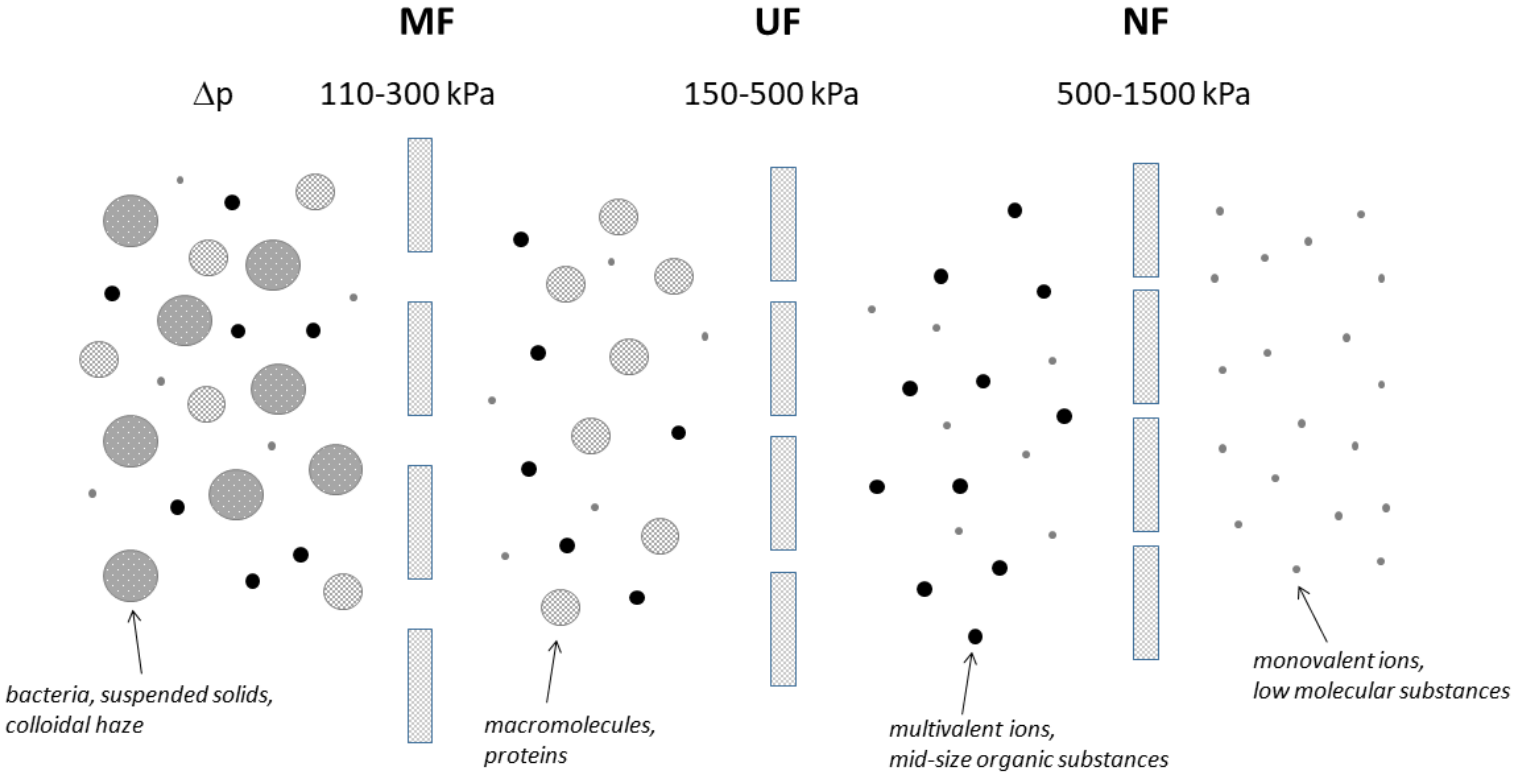


Figure 2. Layout scheme and overall mass balance of the developed process for the recover and concentration of polyphenols from white wine vinasses (Díaz-Reinoso et al., 2017).

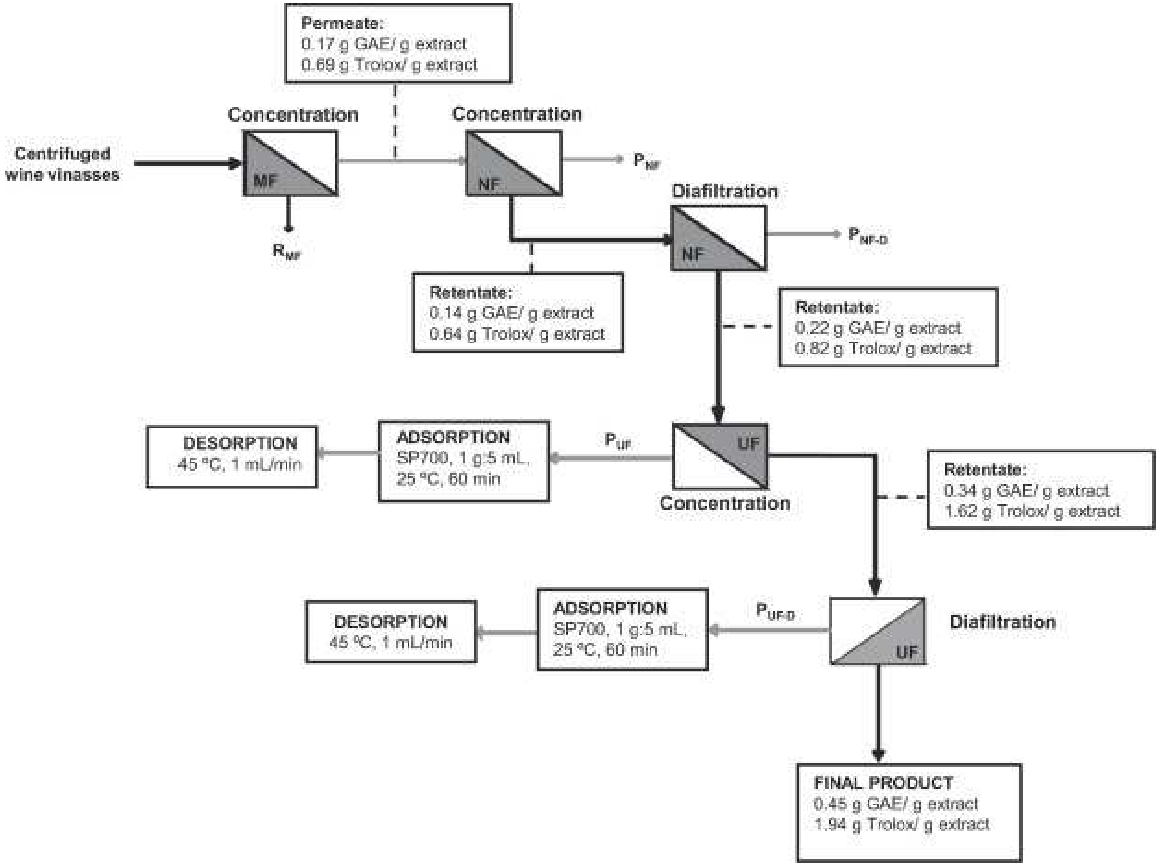


Figure 3. General drawing of a membrane distillation process.

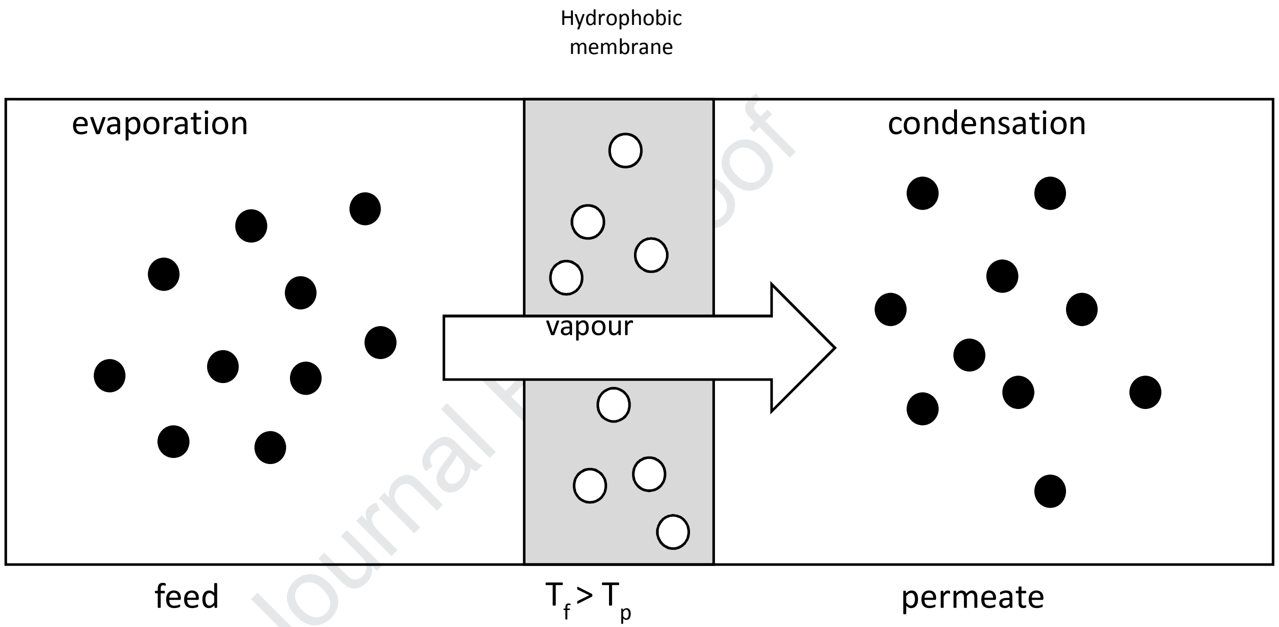


Figure 4. Concentration profile of blood orange juice by DCMD. (a) evaporation flux (thermal gradient at time 0, 9, 18 and 27 h), (b) total soluble solids content and (c) viscosity as a function of operating time (Quist-Jensen et al., 2016).

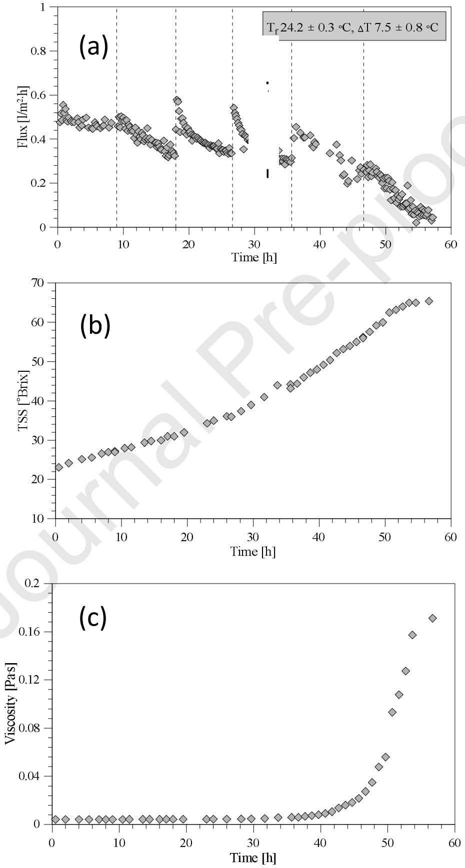


Figure 5. General schematic of a pervaporation process.

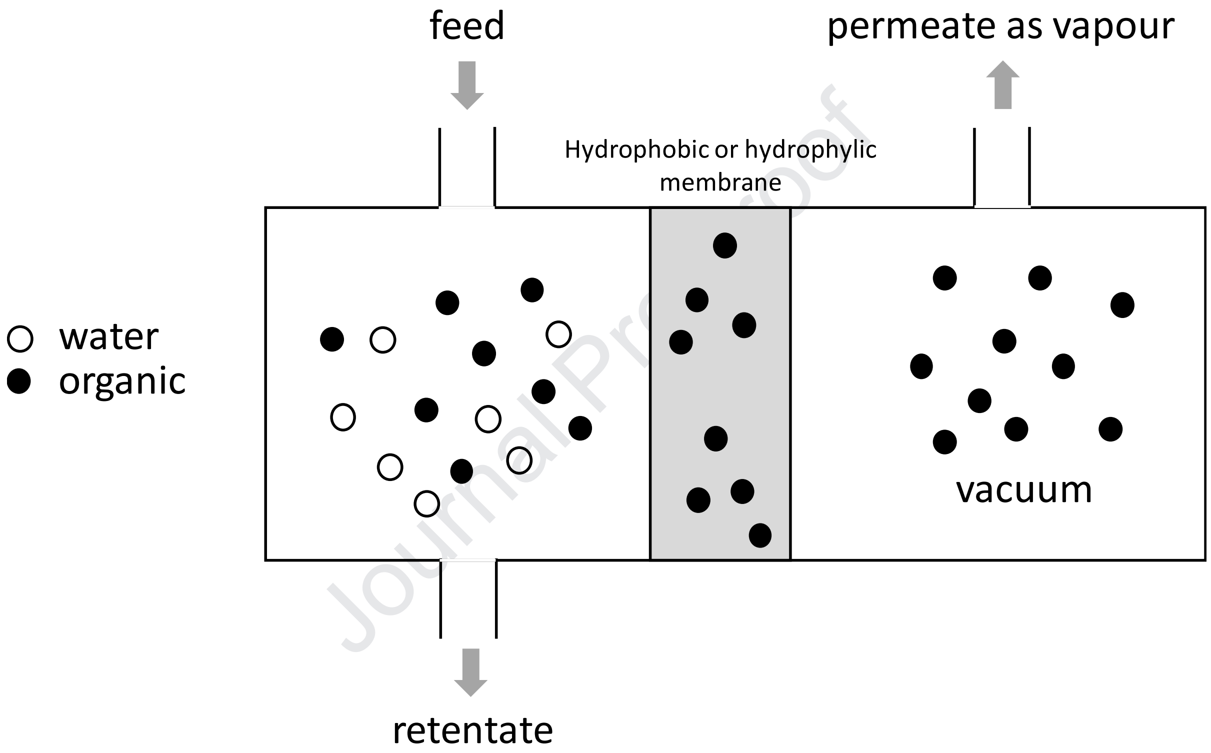
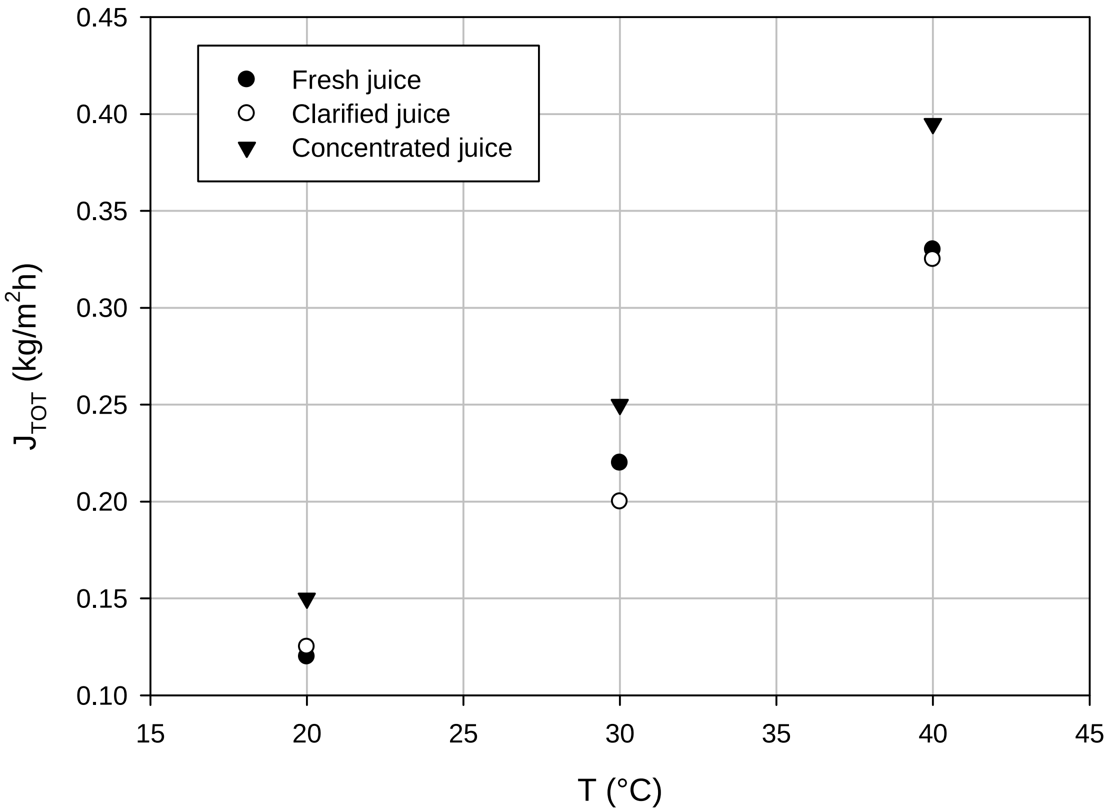


Figure 6. Effect of temperature on the total flux in the processing of fresh, clarified and concentrated kiwifruit juice by PV



(Cassano et al., 2006).

Table 1. Main characteristics of MF, UF, NF, MD and PV processes.

Membrane process	Driving force	Mass transfer mechanism	Membrane	Water permeation flux (L/m^{2}h)	Applications
Microfiltration	Pressure difference, 110-300 kPa	Convection	Porous; pore size 0.1-10 μm	500-10,000	Clarification, pre-treatment, sterilization
Ultrafiltration	Pressure difference, 150-500 kPa	Convection	Porous; pore size 1-100 nm	100-2,000	Concentration, fractionation of macromolecular solutions
Nanofiltration	Pressure difference, 500-1500 kPa	Diffusion/convection	Porous; pore size <2 nm	20-200	Concentration, purification of low molecular weight organic compounds, removal of multivalent ions
Membrane distillation	Partial pressure gradient	Evaporation diffusion/condensation	Hydrophobic micropores	0.1-30	Desalination, concentration
Pervaporation	Chemical potential or concentration difference	Adsorption/diffusion/desorption	Non-porous thin film	0.1-5	Separation of mixtures of volatile liquids

Table 2. Bioactive molecules recovered from agro-food by-products and wastewaters using membrane technologies.

Recovered molecule	*Recovery rate*	*Agro-food waste*	*Membrane process*	*MWCO/Material/ Configuration*	*Membrane nature:*	*Reference*
Phenolic compounds	45.7 %	Nixtamalization wastewaters	Integrated membrane process:			Castro-Muñoz et al., 2016; Castro-Muñoz & Yáñez-Fernández, 2015)
			MF	0.2 μm / Polysulfone / Hollow fiber	Hydrophobic	
			UF	100 kDa / Polysulfone / Hollow fiber	Hydrophobic	
			UF	1 kDa / Polysulfone / Hollow fiber	Hydrophobic	
Phenolic compounds	> 70 %	Fermented grape pomace	UF	1000 Da / Thin-film / Spiral wound	Hydrophilic	Díaz-Reinoso et al. (2009); Díaz-Reinoso et al. (2010)
	> 80 %		UF	1000 Da / Ceramic (titania) / Tubular	Hydrophilic	
	> 30 %		NF	250 Da / Polyamide-polysulfone / Spiral wound	Hydrophilic	
	> 60 %		NF	350 Da / Polyamide-polysulfone / Spiral wound	Hydrophilic	
	> 80 %		NF	150-300 Da / Thin-film / Spiral wound	Hydrophilic	
Hydroxytyrosol, protocatechuic acid, caffeic acid, tyrosol and p-cumaric acid	48.3 %	Olive mill wastewaters	UF	4 kDa / polyethersulphone / Flat sheet	Hydrophobic	Cassano et al. (2011)
	8.7 %		UF	10 kDa / Regenerated cellulose / Flat sheet	Hydrophilic	
	33.5 %		UF	10 kDa / Polyethersulphone / Flat sheet	Hydrophobic	
Hydroxycinnamic acids, o-diphenols	81 %	Winery sludge from red grapes	UF	100 kDa / Polysulfone / Flat sheet	Hydrophobic	Galanakis et al. (2013)
	77 %		UF	20 kDa / Polysulfone / Flat sheet	Hydrophobic	
	56 %		UF	1 kDa / Composite fluoropolymer / Flat sheet	Hydrophobic	
3,4-DHPEA, p-HPEA, 3,4-DHPEA-EDA, verbascoside, and total phenols	--	Olive mill wastewater	Integrated membrane process:			Servili et al. (2011)
			MF	0.3 μm / Polypropylene / Tubular	Hydrophilic	
			UF	7 kDa / Polyamide-polysulfone / Spiral wound	Hydrophilic	

Chlorogenic acid, Cynarin, Apigenin-7-O-glucoside	100 %	Artichoke wastewaters	Integrated membrane process:			Conidi et al. (2014)
			UF	50 kDa / Polysulfone / Hollow fiber	Hydrophobic	
			NF	400 Da / Polyethersulfone / Spiral wound	Hydrophobic	
			NF	150-300 Da / Polyamide / Spiral wound	Hydrophilic	
	> 85 %	Artichoke wastewaters	NF	400 Da / Polyethersulphone / Spiral wound	Hydrophobic	Cassano et al. (2015)
Gallic acid, chlorogenic acid and epigallocatechin gallate	100 %	Residues from mate tree	NF	150-300 Da / Thin-film/ Spiral wound	Hydrophobic	Prudêncio et al. (2012)
Hydroxytyrosol, protocatechuic acid, catechol, tyrosol, caffeic acid, and p-cumaric acid	100 %	Olive mill wastewaters	Integrated membrane process:			Cassano et al. (2013)
			UF	0.02 μm / PVDF / Hollow fiber	Hydrophobic	
			UF	1 kDa / Composite fluoropolymer / Flat sheet	Hydrophobic	
			NF	Salt rejection >97% / Thin-film / Spiral wound	Hydrophobic	
Hydroxytyrosol, procatechin acid, tyrosol, caffeic acid, p-cumaric acid, oleuropein and some other low MW polyphenols.	78 %	Olive mill wastewaters	Integrated membrane process:			Garcia-Castello et al. (2010)
			UF	200 nm / Al_2O_3 / Tubular	Hydrophobic	
			NF	578 Da / Polyethersulphone / Spiral wound	Hydrophobic	
Hydroxycinnamic acids and flavonols.	40 %	Olive mill wastewaters	UF	25 kDa / Polysulfone / Spiral wound	Hydrophobic	Galanakis et al. (2010)
	71 %		UF	10 kDa / Polyethersulfone / Spiral wound	Hydrophobic	
	81 %		UF	2 kDa / Polyethersulfone / Spiral wound	Hydrophobic	
	99 %		NF	120 Da / Polypiperazine/ Spiral wound	Hydrophilic	
Anthocyanins, flavonoids	> 90 %	Orange press liquor	NF	180 Da / Polyamide-polysulfone / Spiral wound	Hydrophilic	Conidi et al. (2012)
	> 80 %		NF	300 Da / Polypiperazine amide thin-film composite / Spiral wound	Hydrophilic	
	> 80 %		NF	400 Da / Polyethersulfone / Spiral wound	Hydrophobic	
	> 70 %		NF	1000 Da / Polyethersulfone / Spiral wound	Hydrophobic	
Anthocyanins (cyanidin-3-glucoside chloride, myrtillin chloride and peonidin-3-	> 65 %	Orange press liquor	NF	Na_2SO_4 rejection > 25-50 % / Polyethersulfone / Spiral wound	Hydrophobic	Cassano et al. (2014)

glucoside chloride), flavanones						
Chlorogenic acid, Apigenin-7-O-glucoside	100 %	Artichoke wastewaters	NF	200-300 Da / Polyamide / Spiral wound	Hydrophilic	Conidi et al. (2015)
Caffeoylquinic acid, flavonoids, chlorogenic acid, cynarin	> 40 %	Artichoke brines	NF	1000 Da / Polyethersulfone / Spiral wound	Hydrophobic	Cassano et al. (2016b)
	> 62 %		NF	400 Da / Polyethersulfone / Spiral wound	Hydrophobic	
	> 99 %		NF	300 Da / Piperazineamide / Spiral wound	Hydrophobic	
	> 95 %		NF	150-300 Da / Cross-linked polyamide/ Spiral wound	Hydrophilic	
	> 93 %		NF	150-300 Da / Cross-linked polyamide/ Spiral wound	Hydrophilic	
Phenolic compounds	> 80 %	White vinasses	NF	200 Da / Polyethersulfone / Spiral wound	Hydrophobic	Díaz-Reinoso et al. (2017)
Phenolic compounds	21 %	Winery effluents	MF	0.4 μm / Polyimide / Hollow fiber	Hydrophilic	Giacobbo et al. (2015)
	5 %	Winery effluents	MF	0.2 µm / PVDF / Hollow fiber	Hydrophobic	Giacobbo et al. (2017a)
Phenolic compounds	>90 %	Racking wine lees	Integrated membrane process:			Giacobbo et al. (2017b)
			UF	10 kDa/Fluoropolymer/Tubular	Hydrophilic	
			UF	1000 Da/ Fluoropolymer /Tubular	Hydrophilic	
			NF	200-300 Da/Polypiperazine/Tubular	Hydrophilic	
	57 %	Olive mill wastewaters	UF	3 kDa/Regenerated cellulose/Flat sheet	Hydrophilic	Ochando-Pulido & Martínez-Férez (2017)
Phenolic compounds	97-98 %	Apple pomace extract	NF	150-300 Da/Polyamide thin film composite/Spiral wound	Hydrophilic	Uyttebroek et al. (2018)
Quinic acid	92 %	Apple pomace extract	NF	150-300 Da/Polyamide thin film composite/Spiral wound	Hydrophilic	
Catechin	78 %	Apple pomace extract	NF	150-300 Da/Polyamide thin film composite/Spiral wound	Hydrophilic	
Epicatechin	87 %	Apple pomace extract	NF	150-300 Da/Polyamide thin film composite/Spiral wound	Hydrophilic	

Table 3. Overview of the latest uses of MD for the concentration of juices.

Type of application:	*Membrane configuration:*	*Pretreatment step:*	*Operating conditions:*	*Highlighted inputs:*	*MD configuration:*	*Membrane material:*	*Reference:*
Apple juice concentration	Flat sheet	Enzyme treatment, UF as prefiltration	Feed: 50-70°C Permeate:10-30°C	Maximum concentration for solids content of 50%.	DCMD	PVDF	(Gunko et al., 2006)
Sugarcane concentration	Flat sheet	-	Feed: 75°C Permeate:25°C	Continuous removal of water (10 kg/m^2h).	DCMD	PP	(Nene et al., 2002)
Orange juice concentration	Flat sheet	Prefiltration	Feed: 40-70°C Permeate:20-30 °C	Increase in feed flow rate reduces concentration polarization and fouling phenomenon.	DCMD	PTFE	(Deshmukh et al., 2011)
Aroma recovery	Flat sheet	UF as pre-filtration	Feed: 10-45°C Pressure:0.7-3 kPa	Recovery of highly volatile aroma compounds (ranged from 68 to 83%) from black-currant juice.	VMD	PTFE	(Bagger-Jørgensen et al., 2004)
Sucrose concentration	Hollow fiber	-	Feed:70°C Permeate:100 kPa	Maximum sucrose concentration of 50°Brix (from a feed starting solution of 10°Brix solution).	VMD	alumina	(Chen et al., 2018)
Black-currant juice concentration	Hollow fiber	Enzyme treatment MF as pre-filtration RO as pre-	Feed:26-30°C Permeate:11°C	Concentration from 22 up to 58.2 °Brix.	DCMD	PP	(Kozák et al., 2009)

		concentration				
Orange juice concentration	Hollow fiber	UF as pre-filtration	Concentration from 24^{o}Brix up to 65 ^{o}Brix.	DCMD	PP	(Quist-Jensen et al., 2016)

Vacuum membrane distillation (VMD), direct contact membrane distillation (DCMD).

Highlights

Membrane-based technologies as emerging tool to recovering functional molecules.

Tight UF and NF membranes as the high efficiency extraction of phenolic molecules.

Membrane distillation assists the concentration of valuable molecules.

Pervaporation meets the requirements for the selective extraction of aromas.