Final Degree Project

Bachelor's degree in Chemical Engineering

Integration of membrane technologies in agro-industrial process stages

REPORT

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Summary

Nowadays, several applications for the treatment of individual process streams as a source of water and technical fluids reuse are emerging. One of the agro-industrial challenges, apart from obtaining the desired final product, is to be able to recover or separate intermediate and/or secondary metabolites with added value. In this sense, different membrane techniques such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and pervaporation (PV) can be used to treat these agro-industrial streams (such as milk, beer, wine, fruit juices, among others). Therefore, the industrial application of membrane technologies in some process stages could be a solution, allowing a greater efficiency as well as a circular economic concept of the process.

In this work, the state-of-the art of membrane technologies in dairy and wine industry is reviewed in order to account for possible applications of membrane filtrations and to demonstrate their feasibility. Moreover, a market overview, focused on Spain, has been realized to select the most interesting industry between dairy and wine. Then, a scaling-up for those membrane applications has been done and a real chemical process has been simulated for the wine industry.

Results showed that there are various possible applications for membrane technologies in these two industries. In addition, after the scaling-up, it has been demonstrated the feasibility to integrate the processes studied in previous works (published in the literature) into the industrial scale. The market overview showed that the most interesting industry in Spain is the wine industry because of this country is 3rd wine producer worldwide.

Finally, according to the progress reported on both scientific literature and industrial solutions commercialized it can be said that in the next years the membrane providers and the agro-industries will make a step forward in membrane technologies integration in the production processes. The main effort has been centered initially on improving process performance however a window is open on the valorization of waste streams rich on bio-active molecules of nutritional or health interest (e.g. anti-oxidants).

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1. Introduction

1.1. Objective of the project

The aim of this project is to investigate the feasible and potential applications of membrane technologies in agro-industrial process stages. Furthermore, the specific objectives are described as follows:

(i) To select the most interesting industry: dairy or wine.

(ii) To scale-up the membrane technology processes in order to simulate a real chemical process.

1.2. Scope of the project

The integration of membrane technologies has been investigated in dairy and wine industries, specifically. Although the term 'agro-industry' involves other industries such as fruit juice and beer, in this project, two big agro-industries, dairy and wine, have been selected because of their importance in Spain given that many regions of Spain are well-known producers of wine (e.g., La Rioja) and milk (e.g., Galicia).

This project includes a market overview for these two industries. The aim of this point is to compare the two industries and to select the most interesting. Nevertheless, this market analysis is focused on Spain, in order to give arguments to choose which sector is worth exploiting and selling membrane technologies in this country.

The scaling-up and the simulation of a real chemical process has been made based on studies already published, which are cited in this project, but the processing capacity and flow values are not real values of a wine producer. From this sizing, if a wine production plant provided data of its annual production, calculations could be easily adapted for such values.

The scope of the project is strictly limited by the application of membrane technologies in the current industrial processes. Despite the fact that the agro-industrial processes are described in order to understand better the whole work, it is not the aim of the project to study those processes.

Likewise, the interest of membrane technologies relies on their applications in agro-industrial processes. It is not studied in this project what types of filtration technology do exist or how each type of membrane perform the filtration.

2. Membrane technology in dairy industry

The dairy industry processes the raw milk to obtain different products such as milk for human consumption, cheese, butter and yogurt, among others. The two most important processes are milk and cheese production. Therefore, a study of the integration of membrane technologies in this two production processes has been carried out. Figure 2.1 and Figure 2.2 show the diagrams of the processes to help the reader to understand the following explanations.

2.1. Milk production process

Milk can be considered as an emulsion of fat globules in an aqueous phase. The aqueous phase consists of water with suspended and dissolved components such as casein micelles, serum proteins, lactose and salts. A typical composition of cow milk is described in Table 2.1.

Table 2.1
Average composition of cow milk [1]

	Concentration in whole milk (g/L)	**Size range**
Water	87.1	
Fat globules	4.0	0.1—15 μm
Casein	2.6	20—300 nm
Whey protein	0.7	3—6 nm
α-Lactalbumin	0.12	14 kDa
β-Lactoglobulin	0.32	18 kDa
BSA	0.04	66 kDa
Proteose-pepton	0.08	4—40 kDa
Immunoglobulin	0.08	150—900 kDa
Lactoferrin	0.01	86 kDa
Transferrin	0.01	76 kDa
Others	0.04	
Lactose	4.6	0.35 kDa
Mineral substances	0.7	
Organic acids	0.17	
Other	0.15	

The first stage in milk production is the separation of the fats from the liquid phase. Thus, fats can be eliminated if skimmed milk is going to be produced. If semi-skimmed or whole milk were produced, the subsequent mixing of skimmed milk and fats would lead to the desired composition. The usual fat content of the different types of milk that is accepted by the food regulations is shown in Table 2.2. The fat content regulation is called the standardization step.

Table 2.2
Usual accepted fat content for different types of milks [2]

Whole milk	3.5 – 3.9 %
Semi-skimmed milk	1.5 – 1.8 %
Skimmed milk	< 0.3 %

Traditionally, a gravity separation was used as first step. Fat globules have an average density around 0.93 g/cm^3 while the serum or liquid phase has a heavier density about 1.035 g/cm^3, both values at 20 ºC [3]. Due to the gravitational force milk fats can be separated from the liquid phase. However, this method is very slow and inefficient for the milk producer.

Nowadays centrifugal separators are used for this operation, in which the separation principle relies also in density differences but a centrifugal force is applied to the milk. Thus, the liquid phase moves to the outer edge of the separator because of its heavier density [3].

Milk is an extremely favourable medium for the growth of microorganisms. Therefore, after standardization the milk is treated to ensure the quality for the consumers. There are two main treatments applied to the milk to ensure microbiological limpidity: pasteurization and ultra high temperature (UHT). Pasteurization consists in heating the milk to such temperature that destroys the microorganisms whereas UHT consists in heating the milk to higher temperatures (over 138 ºC) but just for a few seconds [4]. UHT is the most used technique in dairy industry nowadays.

The last stage before bottling the milk is the homogenization. The aim of this process is to avoid the formation of milk fat layers by reducing the fat globules size. For the same fat content, homogenized milk appears sweeter and has more body than no-homogenized milk [5].

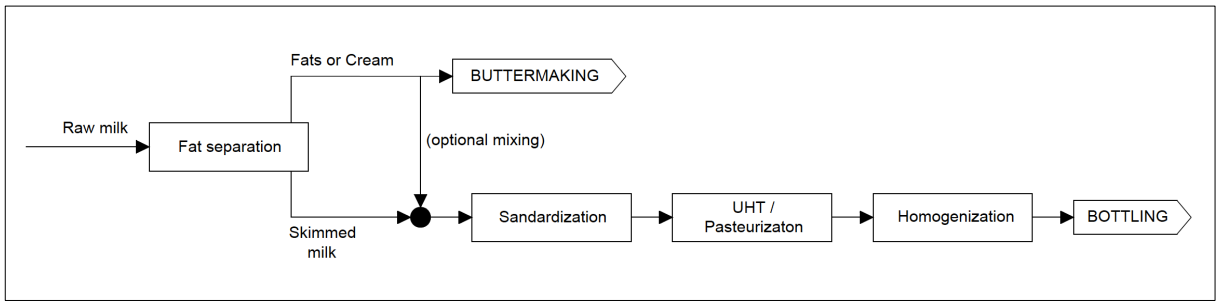

Fig. 2.1. Milk production process diagram.

2.2. Cheese production process

Cheese is a dairy food product derived from milk that is produced by coagulation of the milk casein. Cheese production starts with the standardization of the raw milk, because depending on the milk fat content and the fat globules size different cheeses are obtained in terms of texture and flavour. The standardization process is the same as for the milk production [6].

Next stage is the coagulation or curdling; milk is separated into solid curds and liquid whey, usually done by acidifying the milk and adding the enzyme rennet. Some acids can be used in the acidifying step although most commonly used starter is a bacterium, which converts milk sugars into lactic acid. Most cheeses are made with starter bacteria from *Lactococcus, Lactobacillus* and *Streptococcus* strains [7].

After coagulation, the liquid whey is separated from the solids by draining. At this point, some fresh cheeses are essentially complete: they are salted and packaged. Hard cheeses are heated to 35 – 55 ºC forcing the extraction of more whey. Then, most of cheeses are normally left to rest under controlled conditions on an aging period, also called ripening [8].

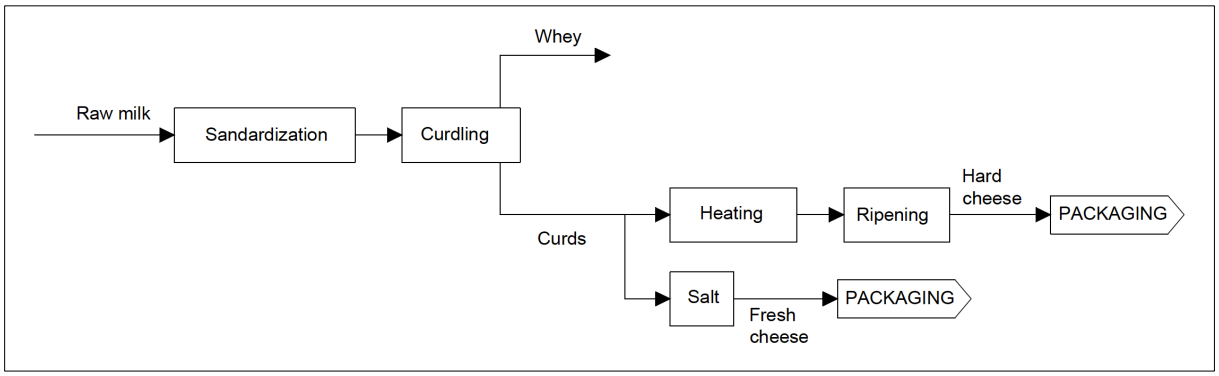

Fig. 2.2. Cheese production process diagram.

2.3. State of the art of membrane technology in dairy industry

As shown in Fig. 2.3, membrane technology allows separating the milk components (described in Table 2.1), thus enabling the optimization of dairy industry processes and the recovery or fractionation of some components with special interest for food supplements, e.g., whey protein. The pressure-driven membranes processes such as MF, UF, NF and RO are the most common membrane technologies used in the dairy industry and based on their applicability range it is possible to separate virtually every major component of milk.

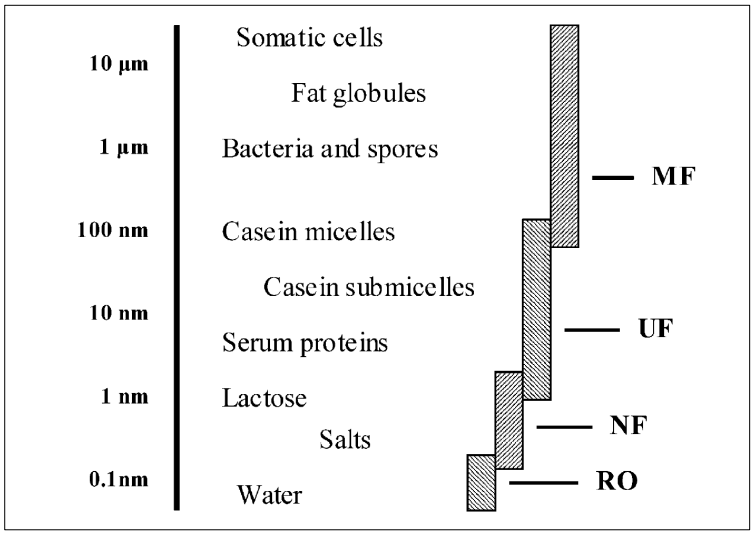

Fig. 2.3. Components in whole milk: size indication and membrane processes. MF: microfiltration, UF: ultrafiltration, NF: nanofiltration, RO: reverse osmosis. [1]

2.3.1. Milk fat fractionation by microfiltration

In milk, fat is predominantly present in spherical globules with a diameter between 0.1 – 15 µm; small globules (SG) have a diameter of less than 2 µm while large globules (LG) have a diameter over 2 µm. On average, globules below 1 µm in diameter account for 80% or more of the total fat globules, but they represent a small fraction of the total fat volume. Globules with a diameter between 1 and 8 µm represent the 90% of the total fat volume [5].

The fatty acid composition of milk fat is diverse regarding chain length and degree of saturation. This composition gives milk its specific flavour and mouth feel. Moreover, the fat globule size seems to be responsible of the texture characteristics differences between different dairy products [6]. To use the adequate fat fraction would help to achieve the desired texture and mouth feeling of the final product.

Goudédranche et al. [5] performed the fractionation of milk fat by a patented process [9] using MF technology with a ceramic membrane of 2 μm average pore size diameter and then compared the different dairy products obtained.

First, the feed solution was whole milk at 50 ºC with fat content 3.9 %, obtaining a permeate flux of 700 $l \cdot h^{-1} \cdot m^{-2}$. Then the fat content of the feed solution was increased to 12 % obtaining a permeate flux of 250 $l \cdot h^{-1} \cdot m^{-2}$. Table 2.4 shows the results.

Table 2.4
Fat content of the feed solution, retentate and permeate streams obtained.

	Experiment 1			**Experiment 2**		
	Feed Solution	Retentate	Permeate	Feed Solution	Retentate	Permeate
Fat content (%)	3.9	19.7	1.7	12	29.7	6.9

Semi-skimmed milks were prepared by mixing raw skimmed milks and reference creams and compared with MF permeate (SG milks) directly issued from the treatment of raw whole milks. Having both products the same fat content of 1.7 % it can be said that MF permeates were significantly more unctuous and more creamy than the reference milks.

In order to prepare fresh cheese, milks with fat content 4.1 % were prepared: skimmed milk was mixed either with reference cream (obtaining reference products), MF permeate (obtaining SG products) or with MF retentate (obtaining LG products). Once the cheeses were obtained, the taste, texture and shear stress were compared.

The same shear stress (450 Pa) was determined on the reference and LG cheeses, whereas SG cheese had lower shear stress (378 Pa). Despite the fact that no taste differences were found, SG fresh cheese was significantly appreciated in mouth texture as smoother and finer than the reference and LG cheeses.

Camembert cheeses were produced following the same method as for fresh cheeses, but in this case only SG fraction was used and the mixtures had a fat content of 2.8%. Firmness and shear stress of reference Camembert were 36.0 N and 5838 Pa versus 36.1 N and 5130 Pa respectively for the SG product. The SG cheese taste was qualified as less chalky than the reference one.

To produce mini-Swiss cheeses, cheese milks were prepared by mixing reference, LG and SG creams with skim milk. The reference product showed a shear stress of 58500 Pa while LG and SG cheeses showed 57600 Pa and 44500 Pa, respectively. No difference was found in taste, but the SG mini-Swiss cheese was judged smoother and more unctuous than the others.

The shear stress results obtained for different cheeses are shown in Table 2.5. As a conclusion, membrane MF allows the possibility to adjust texture of dairy products. The use of SG fraction yields more unctuous products and finer textural characteristics compared to products made from untreated or LG cream.

Table 2.5
Shear stress determined for different cheeses obtained from the experiment.

	Fresh cheeses			**Camembert cheeses**		**Mini-Swiss cheeses**		
	SG	LG	Reference	SG	Reference	SG	LG	Reference
Shear stress (Pa)	378	450	450	5130	5838	44500	57600	58500

2.3.2. Bacteria and spores removal by microfiltration

Although the UHT treatment is more effective than the pasteurization process, it can be more damaging for the properties of milk because of the temperature applied is higher. The removal of bacteria and spores from milk by MF is an alternative way to UHT.

The first commercial system of this process was developed by Alfa-Laval Co. (Sweden) [10]. In this process, the raw milk is separated into skim milk and cream. The skim milk is filtered by MF using ceramic membranes with a pore size of 1.4 μm at constant transmembrane pressure. Thereby, the retentate contains almost all the bacteria, whereas permeate contains less than 0.5% of the original value in milk. Then, the MF retentate is mixed with the desired quantity of cream (standardization process) and the mix is treated with the conventional UHT process. After UHT, this mix is reintroduced into permeate and then is pasteurized. Since less than 10% of the milk is heat-treated at high temperature (over 138 ºC), the sensory quality of the milk is significantly improved [11].

Saboya and Maubois [12] described the use of ceramic membranes with a pore size of 1.4 μm operated at a constant transmembrane pressure of 50 kPa and a cross-flow velocity of 2.7 $m \cdot s^{-1}$. The flux was $1.4x10^{-4}$ $m \cdot s^{-1}$ and reduction factor of bacteria and spores was above 3.5.

Guerra et al. [13] achieved the same flux at a cross-flow velocity of 1 $m \cdot s^{-1}$ with a reversed asymmetric membrane with pore size of 0.87 μm. Bacteria and spore reduction factor was between 4 and 5.

There are many applications in the dairy industry of bacterial-free milk. In cheese production, the use of low bacterial milk improves the quality of the cheese due to the removal of spores. Besides, in the production of whey protein concentrates and isolates the bacteria removal increases the quality of the product and keeps the heat treatment to a minimum, which preserves better the functional properties of the whey proteins [11].

2.3.3. Whey protein concentration and fractionation by membrane technologies

Whey is the liquid fraction that is drained from the curd during the manufacture of cheese, with 5.5—6.5% dry matter. Lactose represents the 70—80% of the dry matter and proteins represent the 10% [14]. If whey comes from coagulation by rennet enzyme, it is considered sweet whey. Otherwise, if an acid starter such as lactic acid has been used in the coagulation process, it is considered acid whey [15-16]. Traditionally, whey was considered useless for human and used for animal feed. Nowadays, whey is considered a source of valuable proteins widely used in food industry and nutritional supplements production [17].

First of all, once the whey is drained out of cheese vats it is defatted. The presence of fat in whey decreases its functional properties and leads to shorter time of storage. The most common process to reduce the fat content of whey was developed by Maubois et al. [18] and Fauquant et al. [19] and it uses the ability of the phospholipids to aggregate by calcium binding under moderate heat treatment for 8 min at 50 ºC. Then, as shown in Fig. 2.4, defatted whey is obtained by MF with a pore size of 1.4 μm to separate the resulting precipitation.

After being defatted, skim whey is filtrated then by a reverse osmosis (RO) process to concentrate the protein content up to 18—27% [20]. The RO retentate can be used to produce whey powder, whey protein concentrates (WPC) and isolates (WPI) or to perform whey protein fractionation.

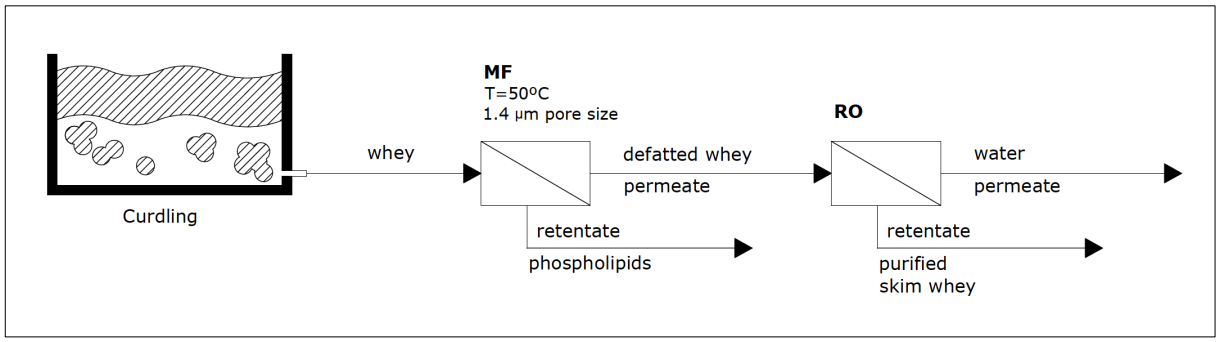

Fig. 2.4. Whey fat reduction and purification by membrane technologies.

When the purified whey is filtrated by an UF membrane (molecular weight cut-off (MWCO) 10000 Da), the retentate is WPC, with over 77% of protein concentration. A diafiltration step increases the concentration over 90%, obtaining WPI as shown in Fig. 2.5. In this stage, permeate is also a valuable stream as it has a high concentration of lactose [11][20].

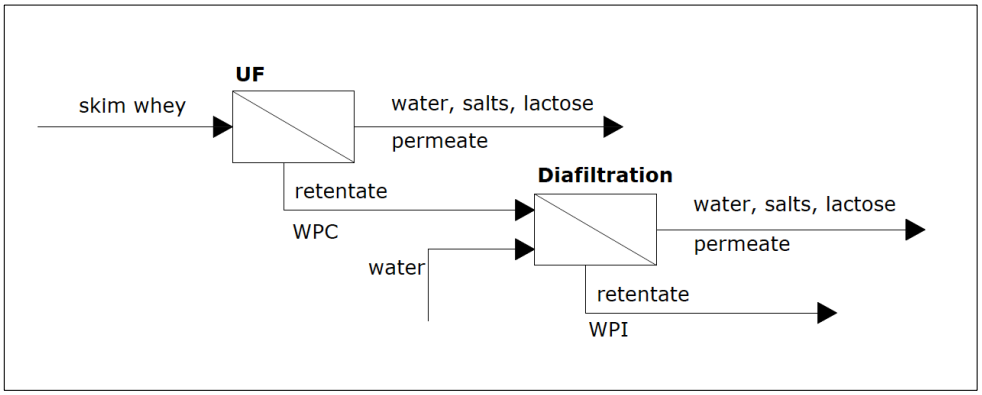

Fig. 2.5. UF and diafiltration of skim whey to obtain whey protein concentrate and isolate.

However, if the purified whey is vacuum evaporated and then spray dried, whey powder is obtained. Lactic acid whey (LAW) has a high mineralization (12 to 20 g per 100 g of dry matter) and this fact makes its processing hard by decreasing the performance of vacuum evaporators due to mineral fouling. LAW is difficult to spray dry because of the high risk of stickiness, which is attributed to high hygroscopicity of LAW powder. Consequently, a demineralization of LAW prior to spray drying is required.

Bédas et al. [21] studied the feasibility of semi-industrial scale-up, in view of the ability of NF, to improve the quality of LAW powder (see Fig. 2.6). A French food factory provided liquid lactic acid whey (5.9 g per 100 g of dry matter (DM)) and pre-concentrated whey (33 g per 100 g of DM). The liquid LAW went through a NF process carried out by a semi-industrial NF plant (GEA Processing Engineering, France) to concentrate it with a volume reduction factor of 3. Two spiral wound membranes Filmtec NF245-3840/30FF manufactured by Dow Chemical composed the plant, at operational conditions of 4 ºC, 3300 kPa and feed flow 225 $l \cdot h^{-1}$.

After the NF stage, both pre-concentrated and NF-concentrated LAW were subjected to the same semi-industrial scale-up process of vacuum evaporation and spray drying. As a conclusion, NF allowed 50-60% selective demineralization of monovalent ions (Na^+, K^+, Cl^-) while maintaining divalent ion (Ca^{2+}, Mg^{2+}, P^{2-}) content almost constant. Regarding the physico-chemical properties, the dryability of the LAW concentrate was improved by the NF stage.

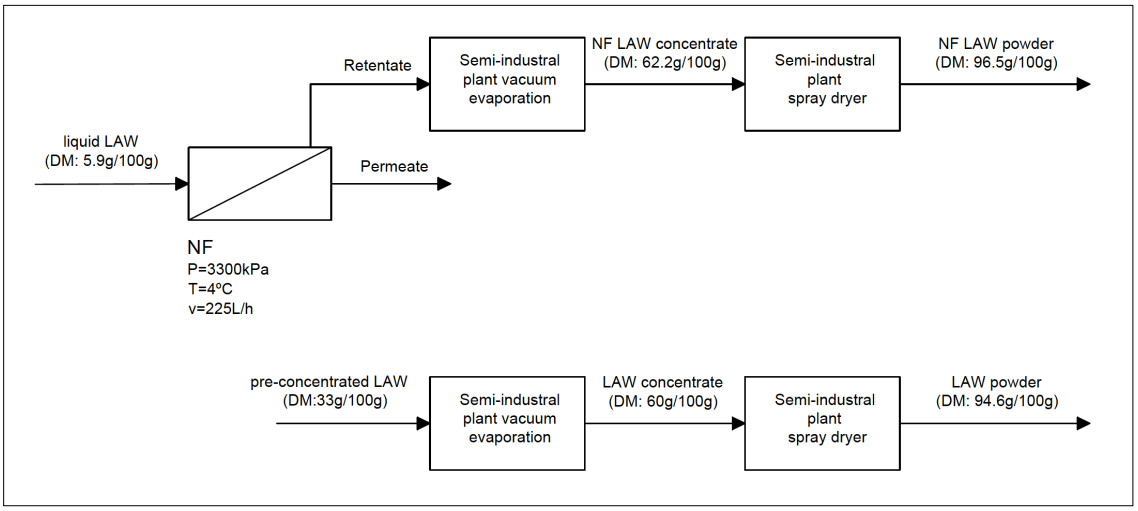

Fig. 2.6. Flowsheet for liquid and pre-concentrated LAW.

Since cheese is produced by coagulation of milk casein it is interesting to increase casein content in cheese milk. Casein enrichment significantly improves rennet coagulability and optimizes curdling process: curds are firmer and consequently lead to fewer fines in whey [20].

Milk casein content can be enriched by a MF stage. When skim milk is circulated along a MF membrane with a pore size diameter of 0.2 μm (homogeneous Al_2O_3 membrane) permeate with a composition near sweet whey is obtained. The retentate is an enriched solution of native and micellar calcium phosphocaseinate (NCPP). It is purified by diafiltration against water and then vacuum evaporated. NCPP has excellent rennet-coagulating abilities; the coagulation time of 3% NCPP solution is reduced by 53% compared to raw milk. Moreover, the partial reduction of the ratio whey proteins/caseins by MF significantly reduces the detrimental effects of heat treatment on rennet coagulability of milk. Besides, skim milk MF permeate is also valuable because it can be processed to obtain whey protein concentrates and whey protein isolates (as above mentioned in purified defatted whey (RO retentate) processing) [12][4]. Fig. 2.7 shows the MF stage in combination with UF and diafiltration.

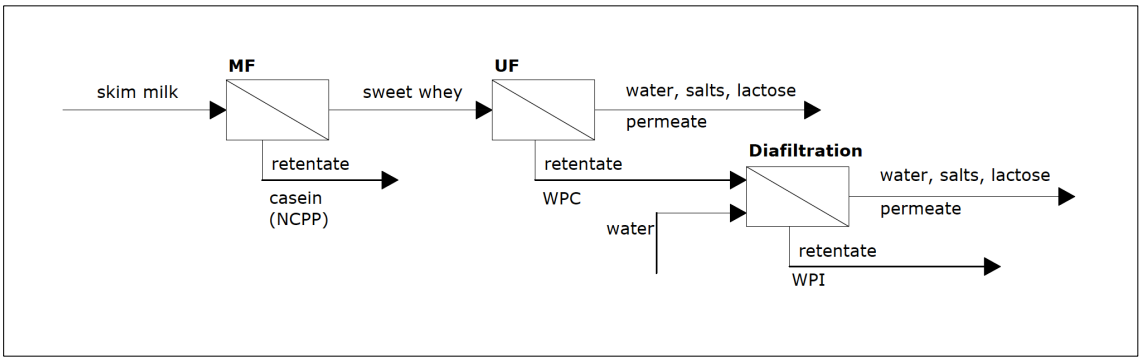

Fig. 2.7. MF of skimmed milk to obtain NCPP and UF with diafiltration of MF permeate to obtain WPC and WPI.

On the other hand, whey protein concentration is attractive in order to isolate the individual serum proteins. The most interesting whey proteins are α −Lactalbumin and β −Lactoglobulin. α −Lactalbumin has pharmaceutical applications and β −Lactoglobulin has physicochemical properties that can be used in emulsification, foaming and gelling processes, among others. These proteins can be obtained from defatted whey [1].

At low pH (4.0—4.5) and under moderate heat treatment (30 min at 55 ºC) α −Lactalbumin polymerizes reversibly with residual lipids and other whey proteins except β −Lactoglobulin.

Using a MF membrane with a pore size of 0.2 μm the β −Lactoglobulin can be separated [11]. Purification of α −Lactalbumin from the MF retentate can be achieved by solubilisation and subsequently by UF using a membrane with a MWCO 50000 Da. This process is shown in Fig. 2.8. Using polymerisation and UF steps, Gesan-Guiziou et al. [22] reported a purity of 52—83% and 85—94% for α Lactalbumin and β −Lactoglobulin, respectively.

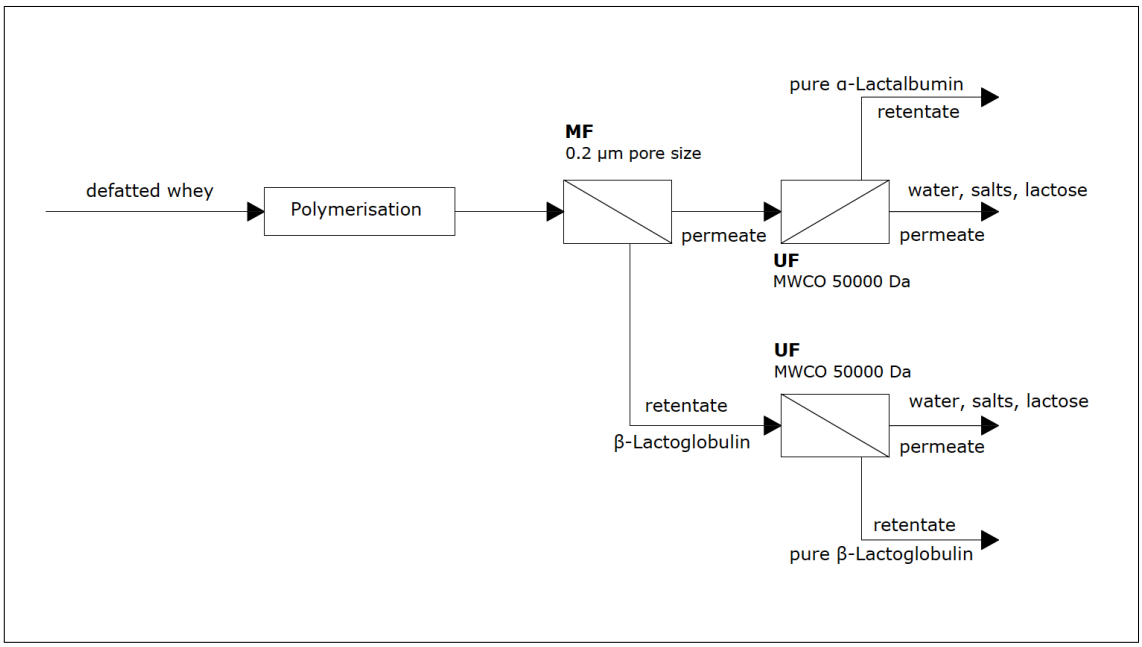

Fig. 2.8. Fractionation of whey protein to obtain α −Lactalbumin and β −Lactoglobulin.

2.3.4. Lactose recovering from whey processing by membrane technologies

As explained before, in whey processing UF is used to obtain whey protein concentrates from defatted whey. However, permeate contains lactose which is a valuable product with the possibility to concentrate and recover by a NF stage.

Hinkova et al. [14] brought data from desalination of lactose from natural salty whey obtained form Czech dairies (Fig. 2.9). Whey was purified by single UF with ceramic tubular membranes (MWCO 500 nm) provided by Membralox (USA) in which constant transmembrane pressure of 2 bar was applied. Then, the concentrated whey was filtrated by NF at 60 bar and 900 $L \cdot h^{-1}$ (maximum flow rate), using two different spiral wound membranes: NTR-7450-S2F (Nitto Denko, Japan) and FILMTEC NF270-2540 (Dow, USA).

Lactose rejections were of 1% in all experiments; therefore it was observed minimum lactose losses during UF. Higher lactose rejections were obtained on the membrane NTR-7450-S2F (85-95%) in comparison with the membrane NF270-2540 (81-87%).

On the other hand, rejections of monovalent ions (K^+ and Na^+) were very low (5—38%), especially on the membrane NTR-7450 at the pH 5—5.7 where the lactose rejection was about 95%. Under these conditions, it was possible to separate most of the monovalent salts and about 50% of calcium, whereas 95% of lactose remained in the retentate. Additionally, rejection of bovine serum albumin (BSA), which is the largest protein in whey (see Table 1), was nearly 100%. Therefore, the membrane NTR-7450 is the most suitable for whey desalination and lactose recovery.

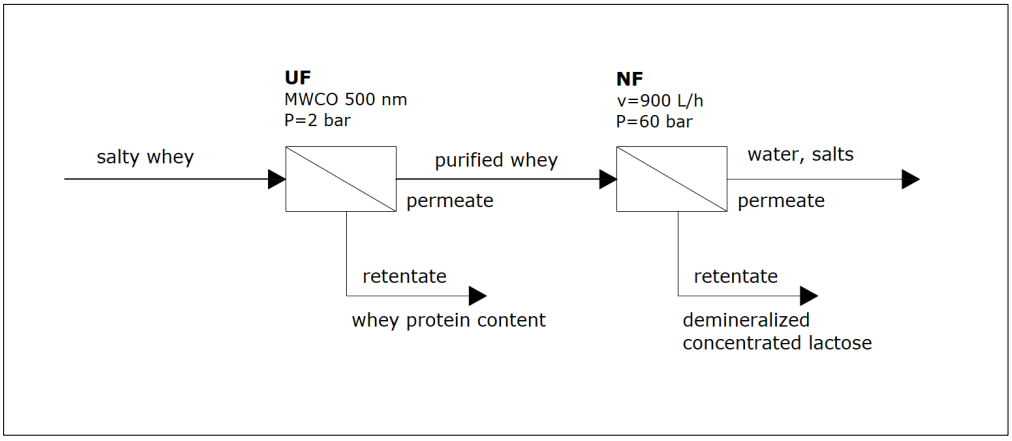

Fig. 2.9. Demineralization of a high-lactose content stream.

2.3.5. Dairy industry with integrated membrane technology

After completing the study of the state-of-the art, a flow diagram of the dairy industry integrating traditional methods and all the membrane technology explained before has been made. Fig. 2.10 shows a traditional process without membrane technologies, while Fig. 2.11 shows the integrated membrane technology process. With these membrane applications, not only the quality and texture of milk and cheese would be improved but also the whole process would be optimised as valuable by-products (whey proteins, lactose and casein) are recovered.

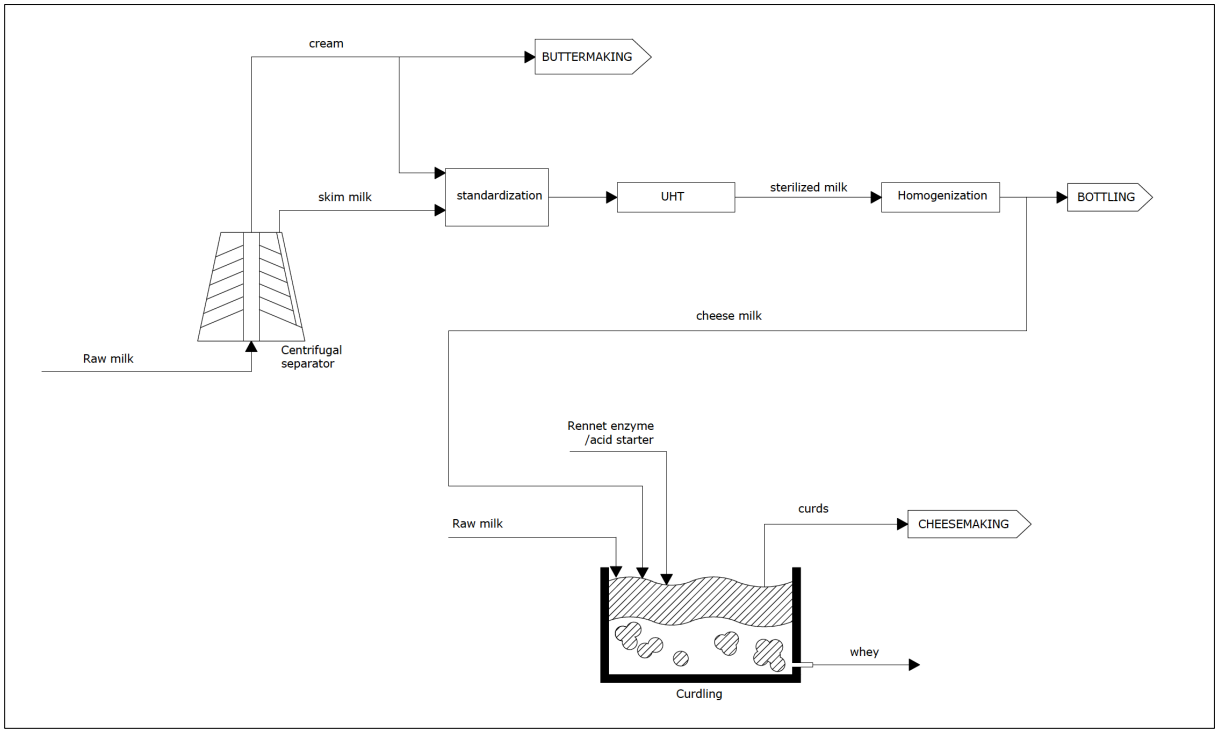

Fig. 2.10. Traditional process in dairy industry.

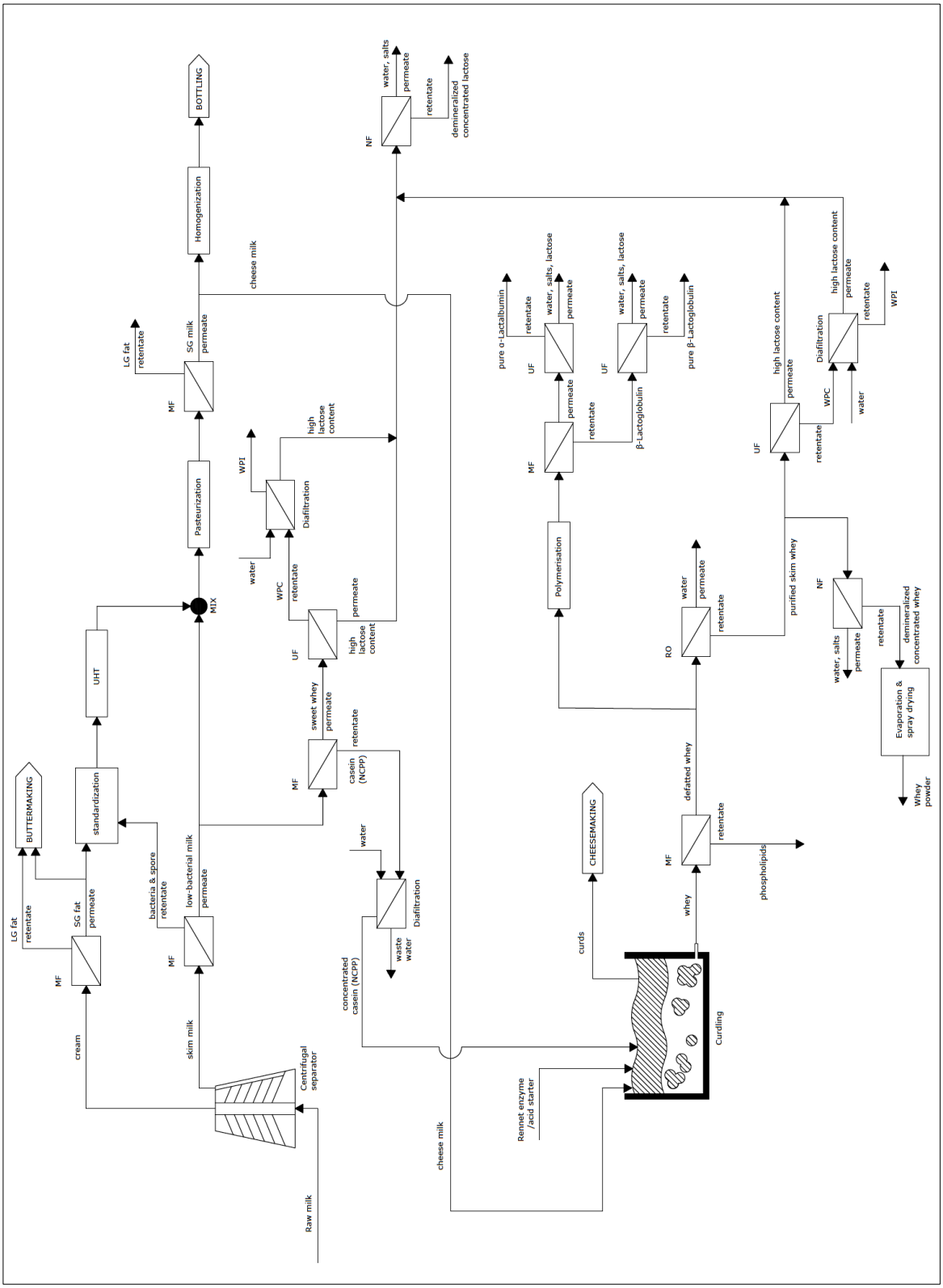

Fig. 2.11. Integrated membrane technology process in dairy industry.

3. Membrane technology in wine industry

Winemaking is the production of wine from the grapes. There are three main types of wine, red, white and rosé. These three types have very similar production processes, with the same main goal of fermenting the grape juice. However, there are little differences resulting in very different wines in terms of colour, flavour and aroma. Figure 3.1, 3.2 and 3.3 show the diagrams of the three production processes to help the reader to understand the following explanations.

Wine is an alcoholic beverage that contains some valuable compounds with beneficial effects on human health, for instance, potassium, which has a urine-beater impact, or minerals and acids that help digestion. Wine also contains polyphenols and tannins, which reduce the risk of developing high blood pressure and diseases of cardiovascular system. Regarding polyphenols, anthocyanin and flavones have special antioxidant effects [23]. An average composition of red wine is described in Table 3.1.

Table 3.1
Average composition of red wine [24]

Compound	**%**
Water	80.0 – 90.0
Ethanol	8.0 – 15.0
Glycerol	0.3 – 1.4
Carbohydrates	0.1 – 0.3
Organic acids	0.3 – 1.1
Tartaric	0.1 – 0.6
Malic	0.0 – 0.6
Citric	0.0 – 0.05
Succinic	0.05 – 0.15
Lactic	0.1 – 0.5
Acetic	0.03 – 0.05
Tannins	0.01 – 0.3
Nitrogenous compounds	0.01 – 0.09
Mineral compounds	0.15 – 0.4

3.1. Red wine production process

The red wine production (see Figure 3.1) starts with the harvesting and de-stemming of the grapes. Once grapes are separated from the stems, they are crushed to produce grape juice or must; this process is called maceration. The skins and seeds are left in contact with the juice in order to acquire the characteristic colour and flavour of red wine. This occurs because anthocyanin and tannin, which are responsible of the colour and flavour, respectively, are located in the skins and the solid parts of the grape. As a consequence, red must contains both grape juice and solid parts even during the fermentation stage [25-26].

The next stage is the fermentation process. In red wine production occurs two different fermentations called alcoholic and malolactic fermentations. First, during the alcoholic fermentation, the yeast transforms the sugar content into ethanol and carbon dioxide. Then, during the malolactic fermentation, lactic acid bacteria transform the malic acid content into lactic acid and carbon anhydride [27].

Once being fermented, the red wine is filtered (traditionally by dead-end filtration) in order to separate the skins, seeds, yeast cell sediments and other solid content present in wine. Then red wine is ready to age in oak barrels for many years before bottling.

The aging period length is determined by the wine factory in order to obtain the desired product at the end (it can vary from 1 year to more than 5 years). During the aging period the wine is moved from one barrel to another several times in order to separate it from the wine lees, namely racking. However, the aged wine usually continues containing lees. Thus, a clarification step is needed once the red wine is removed from the oak barrels. Traditionally, clarification step has been carried out by adding a fining agent, which aids to coagulate lees content [28-29].

The final stage of the wine production is to stabilize the wine. Tartaric acid is one of the most important organic acids of the wine, which provides acidity to the wine. As there are inorganic ions like potassium or calcium in the wine, potassium tartrate or calcium tartrate crystals appear and these crystals can precipitate on the bottle. To avoid it, cold stabilization is carried out; tartrate salts are forced to crystallize as they can be extracted from the wine. After tartaric stabilization the wine is ready for bottling [30].

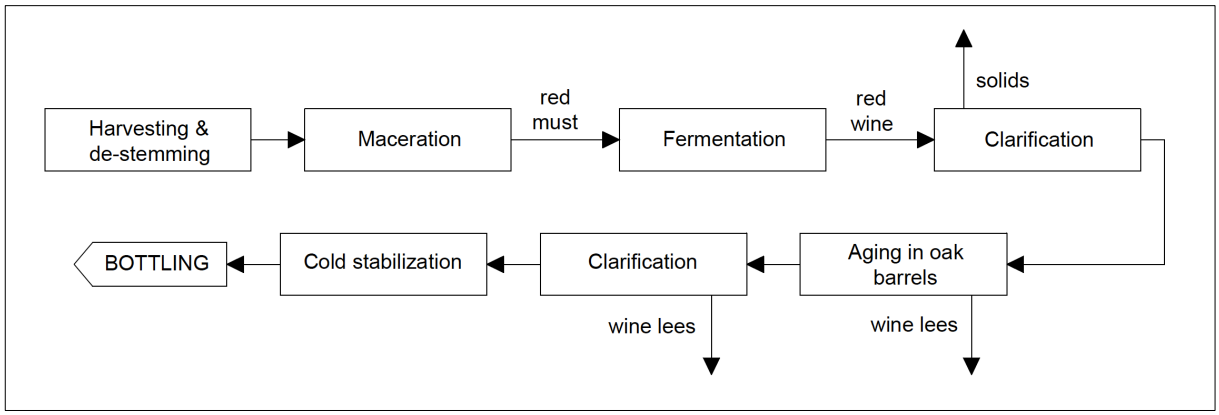

Fig. 3.1. Red wine production process diagram.

3.2. White wine production process

As in red wine production, to produce white wine (see Figure 3.2) the first three stages are harvesting, de-stemming and maceration. However, white must is quickly separated from the skins and seeds by pressing in order to prevent the acquiring of colour and flavour by leaching of anthocyanin and tannin [28-29].

After pressing, white must is fermented. Unlike red wine production, in white wine production occurs only the alcoholic fermentation. For that reason, the white wine obtained from the fermentation process is filtered to eliminate yeast cell sediments and other solid content [28-29].

White wine does not need to age in oak barrel; once fermented and clarified, it is ready to be stabilized and bottled. If white wine is required to be stored for some time, it is stored in stainless steel tanks. The stabilization process is the same as in red wine production.

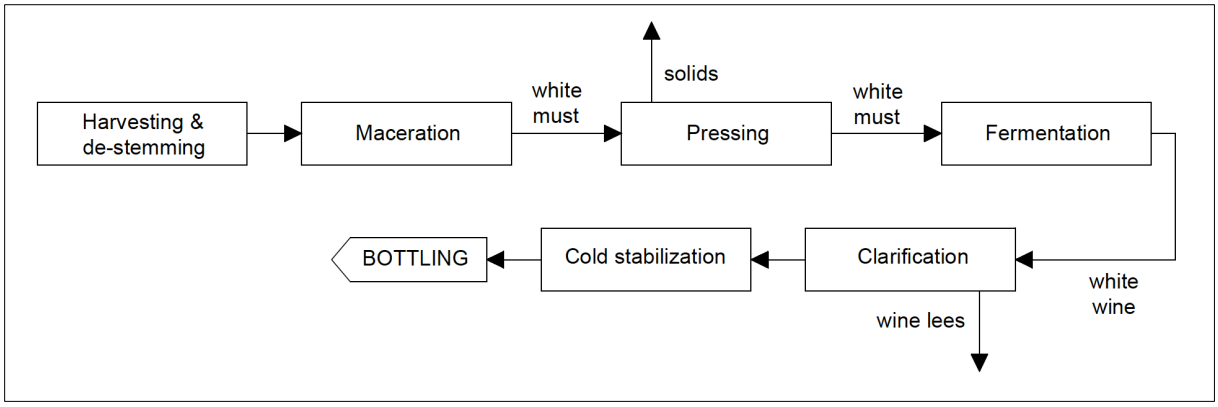

Fig. 3.2. White wine production process diagram.

3.3. Rosé wine production process

Rosé wine is between red and white wines. The first three stages of the rosé wine production process (see Figure 3.3) are harvesting, de-stemming and maceration. At this point, there are two ways to obtain this type of wine.

First option is to leave in contact the skins and seeds with the grape juice but only for 2 or 3 days. Thus, the must acquires part of the colour and flavour from anthocyanin and tannin, respectively. The result is the characteristic pinkish colour and a flavour that combines red and white wine tastes. This method is the one recommended when the wine factory produces rosé wine as the main desired final product.

The second option is to produce rosé wine as a by-product from red wine production. During the fermentation process of red wine, the must is sometimes concentrated by pressing and part of the grape juice is extracted. Thus, the must acquires more colour and flavour. The juice extracted has been in contact with skins and seeds for various days, and it can be reused to produce rosé wine by fermenting separately. This method adds value to the red wine production process but is not recommended if rosé wine is the main desired final product [31-32].

As in white wine production, only alcoholic fermentation occurs. Once fermented, the next stages are exactly the same as for the white wine; clarification, cold stabilization and bottling. No aging period is needed and if the rosé wine is required to be stored for some time, it is stored in stainless-steel tanks.

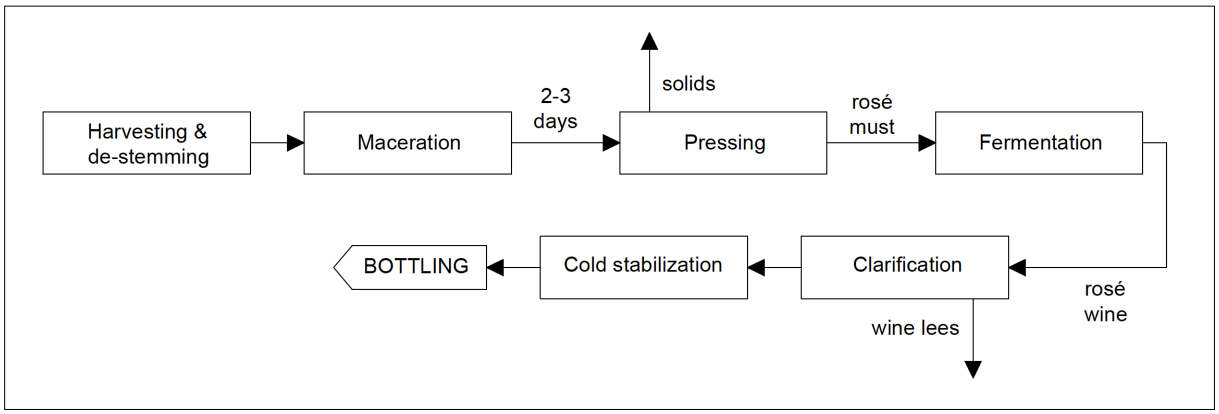

Fig. 3.3. Rosé wine production process diagram.

3.4. State of the art of membrane technology in wine industry

Membrane technologies are adopting importance in winemaking recently. The principal aim of using membranes has been to clarify wine and to ensure microbiological limpidity. Nevertheless, some other applications are emerging to improve and optimize the wine production process. Table 3.2 describes the most interesting wine compounds to separate or fractionate and their sizes.

Table 3.2
Wine compounds and sizes [11]

Component	Size
Large suspended solids	50 – 200 μm
Yeast	1 – 8 μm
Bacteria	0.5 – 1.0 μm
Polysaccharides	50,000 – 200,000 Da
Proteins, tannin, polymerized anthocyanin	10,000 – 100,000 Da
Simple phenols	500 – 2,000 Da
Ethanol, volatiles	20 – 60 Da

3.4.1. Sugar content reduction of grape must by membrane technologies

Nowadays people care much about healthy habits such as to reduce alcohol consumption. In addition, global warming has resulted in an increase of the sugar content in grapes. Therefore, fermentation leads to wines with an alcoholic degree higher than desired, with increases of 2 or 3 %vol.

A solution to the alcoholic degree increase is to reduce the sugar content in must before fermentation. Adding a NF stage in wine production process would make it possible to control sugar levels in musts, by mixing the high sugar content stream and the low sugar content stream in the required proportion.

Salgado et al. [33] tested a two-stage NF process of red and white musts before fermentation. The membrane used was a spiral wound membrane KMS SR3, supplied by Koch Membrane Systems, made of polyamide and with a molecular weight cut-off 200 Da. The active membrane area was 7.1 m^2.

As shown in Fig. 3.4, the first retentate, with high sugar content, and the second permeate, with low sugar content, were mixed regarding the expected alcoholic degree. This probable alcoholic degree was calculated on the basis of 16.83 g of total sugars per 1 %vol. of alcohol [34].

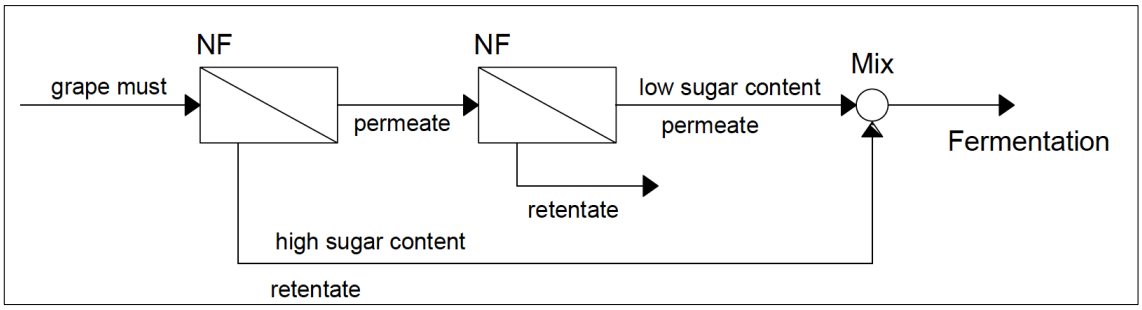

Fig. 3.4. NF of grape must before fermentation.

Red must was filtrated at 33 bar and 16 ºC with a feed flow of 0.54 $m^3 \cdot h^{-1}$, both NF stages with the same operational conditions. White must was filtrated at 35 bar and 16 ºC with a feed flow of 0.54 $m^3 \cdot h^{-1}$, also with the same operational conditions in both NF stages.

After fermentation, red wine had a lower alcoholic degree by 1.2 %vol. In case of white wine, a contamination occurred during fermentation and no alcoholic degree reduction was achieved with the two-stage NF process. However, a single-stage NF was performed to a white must sample, which ended with an alcoholic degree reduction of 1.93 %vol. After a sensory evaluation was performed to resulting wines, it can be said that the NF process did not affect the acceptance of colour and odour of red wine. However, white wine showed depletion of aroma and less overall liking.

To improve the white wine processing, Salgado et al. [35] tested a pervaporation (PV) step before NF, to separate aroma precursors and add them to the filtrated must (see Fig. 3.5). Aroma precursors compounds are mainly hexanal, isoamylalcohol, 1-hexanol, benzaldehyde, benzylalcohol and 2-phenylethanol. A PV spiral wound module commercialized by Pervatech performed PV process. As a result, the obtained wine increased the concentration of aroma precursors (more than twice if compared to the 2-stage NF without PV step). The consumers found no differences between the control wine and the PV+NF wine after sensory evaluation.

As a conclusion, a two-stage NF can be implemented to filtrate the must before being fermented, to reduce the sugar content and obtain a low-alcohol content wine. If the treated must is white, a PV step is recommended to be added to preserve the aroma and flavour.

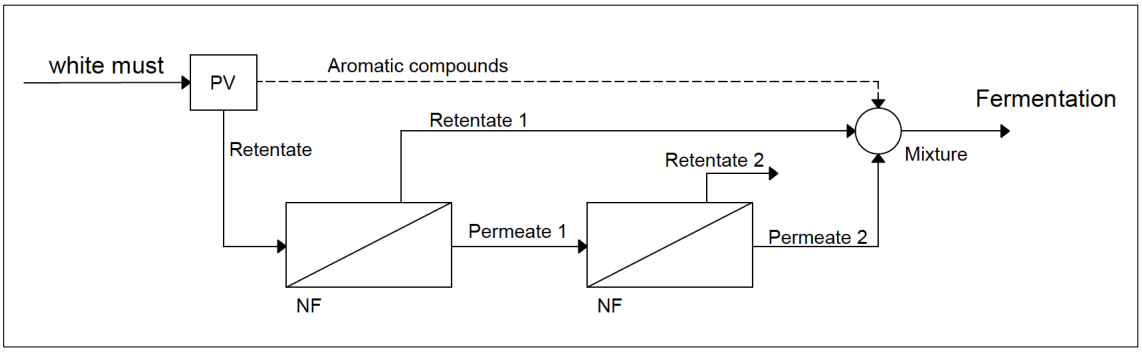

Fig. 3.5. NF of white must with previous PV step.

3.4.2. Clarification of wine by microfiltration

Once the wine is obtained from fermentation, it has to be clarified before aging. Clarification of wine means removing all colloidal or suspended matter such as skins, seeds or yeast. This process was traditionally carried out by diatomaceous-earth filtration, but nowadays is replaced by cross-flow microfiltration. MF not only provides the advantages of continuous mode of operation but also has less environmental impact in comparison with the elimination of solid wastes of diatomaceous-earth filtration media and microorganisms [36].

After aging, the wine needs to be clarified again. Traditionally, the wine was clarified by the 2nd racking and the fining step. This process can be replaced by another MF step. Thus, the use of a fining agent is avoided.

MF process can ensure microbiological limpidity in a single operation with any effect on the quality of the wine. MF is usually performed at room temperature with tubular (1.5 mm inner diameter) polysulfone membrane (0.2 µm pore diameter), cross-flow velocity of 2 $m \cdot s^{-1}$, transmembrane pressure of $2x10^5$ Pa and periodical back-flushing every 2 minutes. Long runs (10-20 h) can be operated with an average permeation flux from 50 to 100 $l \cdot h^{-1} \cdot m^{-2}$

depending on the type of wine. For unfiltrated wines or wines with high turbidity, flux must be as low as 50 $l \cdot h^{-1} \cdot m^{-2}$. For wines at final filtration before bottling, flux can be as high as 100 $l \cdot h^{-1} \cdot m^{-2}$ [20].

With regard to sensory analysis, MF is the only technique that yields limpid wines and does not lead to qualitative losses of the end product. This stage is already implemented in winemaking after fermentation. However, there are many wineries that still use the fining stage to clarify the wine after aging in oak barrels. The replacement of the fining stage by a MF process will also ensure the bacteria removal of the wine.

3.4.3. Concentration of red wine by nanofiltration

As mentioned before, red wine contains many compounds with beneficial effects on human health (potassium, minerals, polyphenols and anthocyanin, among others). Therefore, the concentration of these compounds in red wine may be interesting because the wine obtained could be sold as more healthy.

Banvolgyi et al. [23] proved that all these valuable substances can be concentrated by a NF process. After tartaric stabilization and before bottling, if wine is filtrated by a NF membrane the retentate obtained is highly enriched in those valuable compounds. Besides, the permeate stream is mainly water and ethanol, and it can be reused as raw material in alcohol industry. The ethanol content is shared in both retentate and permeate streams, therefore the alcoholic degree does not change in the wine obtained.

A wine factory has two ways to take advantage of the NF stage. If the retentate stream is bottled, the wine is enriched in valuable compounds with the same alcoholic degree. On the other hand, if the retentate is mixed with water the wine obtained has the same concentration of valuable compounds but a low-alcohol content.

3.4.4. Recovery of polysaccharides and polyphenols from wine lees

Wine lees extracted from the 2nd racking of wine and the fining or clarification stage, are a source of antioxidant compounds as there are polyphenols. Besides, the interest about natural antioxidants has increased nowadays as synthetic antioxidants are presumed to have toxicological effects [37].

Currently, phenolic compounds are recovered by extraction with organic solvents such as methanol or ethanol, which are considerably toxic, so there is a need of an environmentally friendly extraction and purification.

In this regard, Giaccobo et al. [37] realised investigated the extraction and fractionation of polysaccharides and polyphenols from wine lees generated at 2nd racking of red wine by a MF with UF and NF membrane process.

In this work it was used the MF permeate obtained in a previous study [38] as a feed solution to the UF/NF experiments. The wine lees from the second racking diluted 10 v/v were subjected to microfiltration with a 0.4 μm pore size polyimide membrane with the following operating conditions: temperature of 25 ºC, transmembrane pressure of 0.5 bar and feed flow rate of 200 $L \cdot h^{-1}$. The MF permeate composition is shown in Table 3.3.

For the UF step they tested ETNA01PP (molecular weight cut-off 1000 Da) and ETNA10PP (molecular weight cut-off 10000 Da) membranes, manufactured by Alfa Laval, while a NF270 membrane (molecular weight cut-off 200 – 300 Da), manufactured by Dow-Filmtec, was used for NF.

Table 3.3
Composition of the UF/NF feed solution. Values represent mean. [38]
GAE: Gallic acid equivalents, Mv3G: Maldivin 3-glucoside

Compound	MF permeate
Total polysaccharides ($mg \cdot l^{-1}$ glucose)	10.1
Total polyphenols ($mg \cdot l^{-1}$ GAE)	26.1
Monomeric anthocyanin ($mg \cdot l^{-1}$ Mv3G)	4.2

As a result, the NF270 membrane showed rejections greater than 90% to polyphenols, 99% to polysaccharides and full rejection to anthocyanin. Despite the two UF membranes had different molecular weight cut-off, they showed similar behaviour, rejecting more than 77% of polysaccharides and almost 50% of polyphenols. According to these results, polyphenols tend to permeate UF membranes whereas polysaccharides are mainly retained. Thus, the fractionation of polyphenols and polysaccharides becomes possible.

Therefore, an integrated membrane process (see Fig. 3.6) could be added at wineries to separate and fractionate polyphenols and polysaccharides from the wine lees.

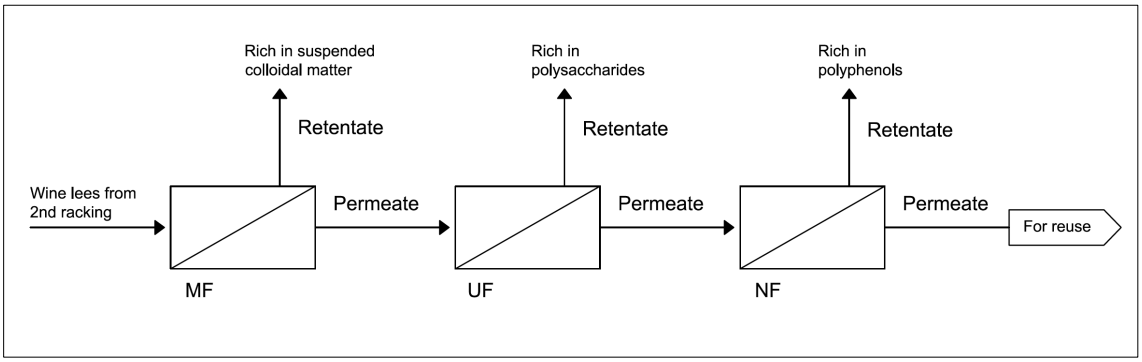

Fig. 3.6. Integrated membrane process for the fractionation of polyphenols and polysaccharides.

3.4.5. Wine industry with integrated membrane technology

After completing the study of the state-of-the art, a flow diagram of the wine production process integrating traditional methods and all the membrane technology explained before has been made. Fig. 3.7 shows a traditional process without membrane technologies, while Fig. 3.8 shows the integrated membrane technology process. With these membrane applications, the whole production process should be optimized: the quality of the wine increases as important parameters such as the must sugar content can be controlled and the recovery of valuable compounds such as polyphenols and polysaccharides add more value to the process.

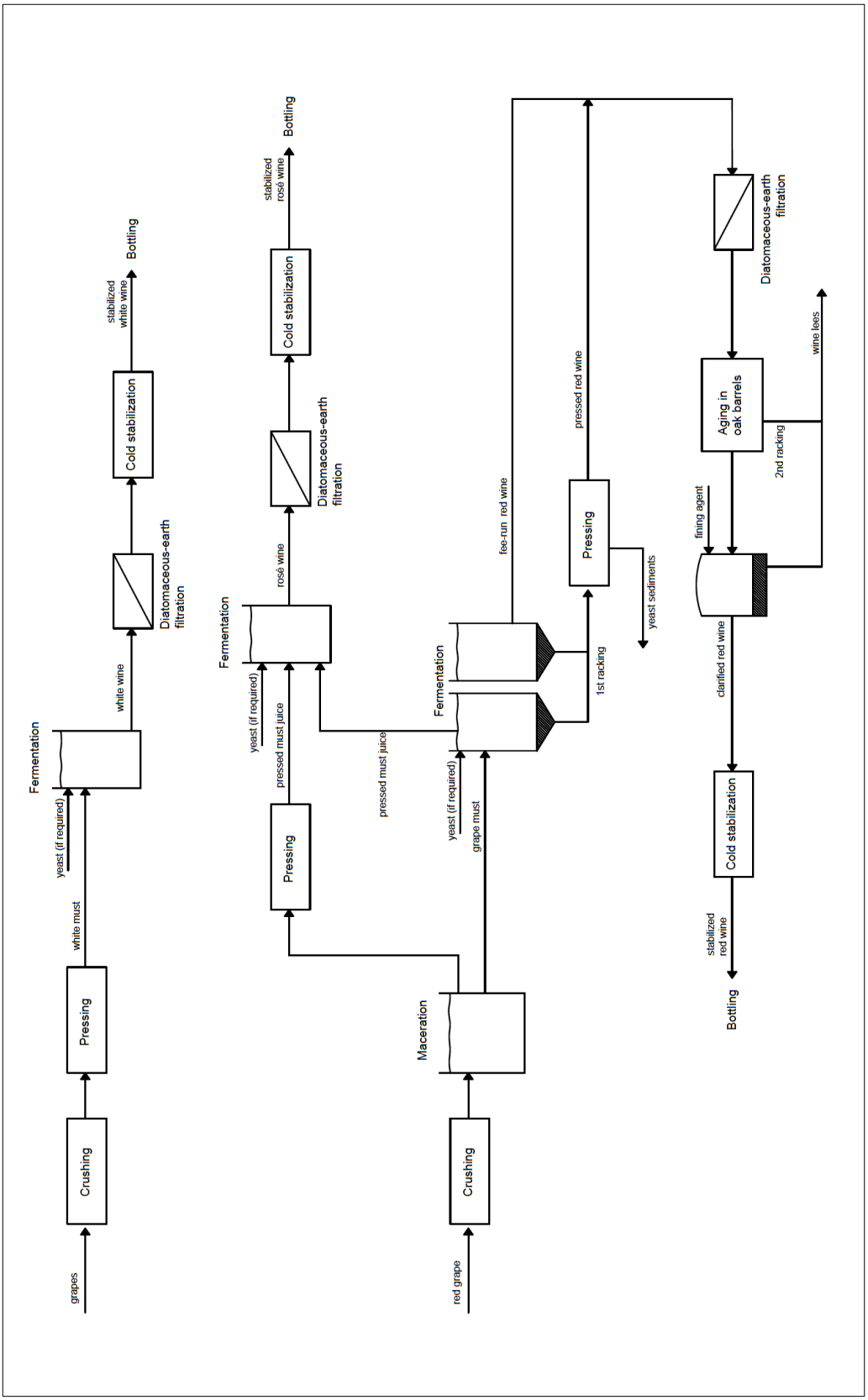

Fig. 3.7. Traditional process in wine industry.

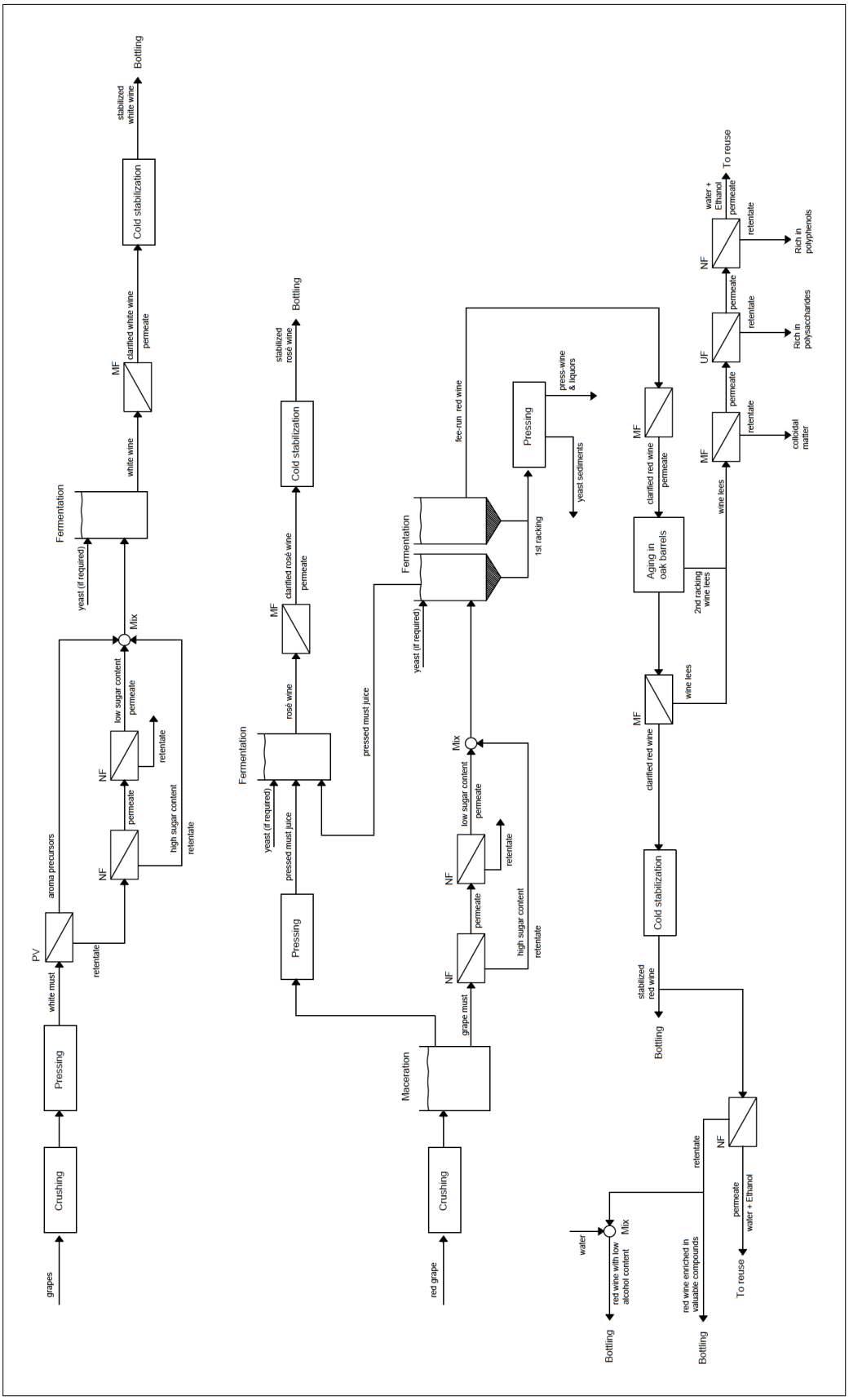

Fig. 3.8. Integrated membrane process in wine industry.

4. Market overview

4.1. Dairy industry

The dairy industry in Spain mainly produces fresh products such as drinking milk, cream and milk-based desserts. In 2015 Spain collected 6,800,000 tons of milk from cows, of which 3,687,000 tons (54%) were destined to the production of drinking milk, 117,000 tons (2%) were destined to the production of cream and 456,000 tons (7%) were destined to cheese production [39].

However, comparing these values with other European Union (EU) countries (see Table 4.1), it can be noticed that Spain is one of the top dairy producers. Spain was one of the bests EU drinking milk producers in 2015 (3rd position), although it was the 6th country when it comes to cheese production.

Table 4.1
Dairy products obtained from the biggest dairy producers EU countries. [39]

Country	Milk collected from cows (1,000 tons)	Production of drinking milk (1,000 tons)	Production of cream (1,000 tons)	Production of cheese (1,000 tons)
Spain	6,800	3,867	117	456
Germany	31,879	4,860	566	1,900
France	25,323	3,423	448	1,950
Italy	10,500	2,511	124	1,207
Poland	10,874	1,639	253	773
United Kingdom	15,191	6,883	326	403

It is considered that there are two dairy production models in Spain [40]:

(i) The green Spain model, based on territory, family manpower and smallholdings, which represent 63% of Spanish holdings and 20% of milk production.

(ii) The dry Spain model, less based on territory, with higher capacity of growth in a non-quotas horizon, which represent the 37% of the holdings and 80% of milk production.

The business structure in Spanish dairies is very different from other EU countries. The leading companies are oriented towards the processing of fresh products, and there is a remarkable absence of large multiproduct firms manufacturing different types of dairy products. The companies are dedicated only to the production of drinking milk, cheese or fresh dairy products, and there is no initiative to penetrate outside the main orientation of each industry [41].

4.2. Wine industry

The Spanish wine industry has been of great importance in Europe historically, alongside France and Italy. There are 69 denominations of origin in Spain and many of them are very well known such as La Rioja or Ribera Del Duero, among others [42].

In 2015, Spain was the 3rd principal wine producer worldwide behind Italy and France, as described in Table 4.2, producing 3,720,300 m^3 of wine (13.10% of total world wine production in 2015).

Table 4.2
Wine production in 2015 of principal world wine producers. [44]

Country	Wine production in 2015 (m^3)	Percentage of total world wine production in 2015 (%)
Italy	4,950,000	17.43
France	4,750,000	16.73
Spain	3,720,000	13.10
U.S.A.	2,975,000	10.48

In 2012, Spain had the greatest vineyards surface area of the main wine producing countries, over 1,017,000 ha ($1.017 \cdot 10^{10}$ m^2). This is the total land area planted with vines, including the areas under vines not yet in production or harvested [43].

However, Spain does not have a great wine consumption compared with other countries. In 2015, wine consumption was 1,000,000 m^3, the 8th worldwide [45]. Figure 4.1 shows the decrease of wine consumption in Spain from 2010 to 2015.

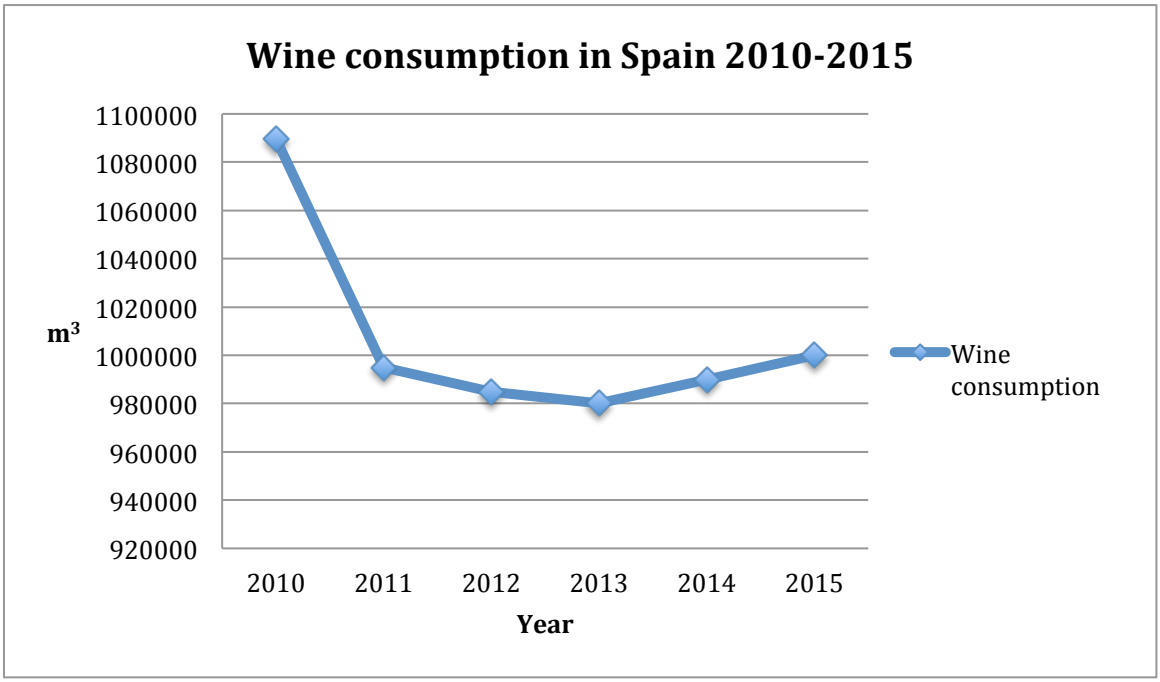

Fig. 4.1. Wine consumption in Spain from 2010 to 2015. [43-44]

In one hand, this has not affected to the production. Spain exports a great quantity of wine (2,141,100 m^3 in 2012 [43]), which makes possible that it can remain the 3rd wine producer worldwide.

In the other hand, this decrease of wine consumption and the great exports numbers, mean that people in Spain tends to consume less wine every year. If the Spanish wine industry could reactivate the wine consumption, maintaining the export, wine production would increase considerably.

4.3. Dairy versus Wine industry

After an exhaustive bibliographical search in this project about the agro-industrial processes (wine industry and the milk industry), it is observed that the wine industry presents more

chemical processes, compared to the milk industry, in which can be implemented membrane technology. For this reason it has been decided to approach in this project, from here, the scaling taking into account only the industrial processes of the wine industry.

In addition, dairy industry has not been selected for many reasons. In one hand, the fact that dairy industries in Spain are strictly focused in one type of product (being drinking milk, cheese or fresh dairy products) is an inconvenient because there are less membrane integrations feasible in each industry. If it could be a whole dairy process where milk, cheese and fresh dairy products where processed, it would be much more attractive.

In the other hand, membrane technologies are already implemented in dairy industry in process stages such as whey processing. The most novel membrane application seems to be the α − Lactalbumin and β −Lactoglobulin isolation from whey. In addition, despite the fact that this market overview is focused in Spain, it seems that in EU are other countries with a dairy industry more attractive, in terms of production, consumption and dairy industries business model.

Wine industry is the most attractive industry. The huge wine production of Spain gives this sector a great importance. Besides, wine consumption in Spain, what seems to be a weakness of this industry, can be one more reason to select this sector to sell membrane technologies. This decrease of consumption is motivated by an increase in healthy habits of the population. People nowadays, mostly in well developed countries, tend to reduce the alcohol consumption. As explained in section 3.4.1, the climate change is increasing the sugar content in grapes, what leads to obtain wines with higher alcohol content. With the novel application of NF to reduce sugar content in must before fermentation, low alcohol wines could be launched to the market. Thus, people with healthy habits could consume these wines and the whole wine production would be increased.

After this market overview, the wine industry has been considered the most interesting industry to exploit and sell membrane technologies. Therefore, the scaling-up to an industrial scale and the simulation of a real chemical process will be done regarding the integration of membrane technologies in a red wine industry.

5. Sizing membrane processes to industrial-scale in a red wine factory

5.1. Calculation basis

The red wine production process starts with the harvest and ends with bottling (see section 3.1.). To scale-up the membrane technology applications, previously explained (section 3.2.), to an industrial scale for an alleged red wine producing factory, the following calculation basis will be considered: 500,000 kg of grapes obtained from the harvest [46] and 1,067 bottles per hour on the bottling process. See calculus details in Annex A.1.

Assuming a harvest of 500,000 kg of grapes, the wine plant would obtain the same mass of red must. However, in the alleged factory the harvest would be done in 15 days, harvesting approximately 33% of total grape mass every 5 days. On average, every day the factory would receive 33,000 kg of grape, producing 33,000 kg of must.

To calculate the flow rates in all the stages, the quantity of must is required to be expressed in volume units (m^3), not mass units (kg). Taking into account that the must density is 1100 $kg \cdot m^{-3}$ [47], the factory would produce 30 m^3 of red must per day.

The first process for the red wine production is the maceration. It is assumed that this process would last 2 weeks for all the kg of grapes obtained. Therefore, after these 2 weeks, 30 m^3 of red must would be ready to be pumped to fermentation tanks every day (during 15 days). The flow rate would be 7.5 $m^3 \cdot h^{-1}$ pumping all the must in 4 hours (per day).

Once inside the fermentation tanks, must would be turned to wine during the following 15 days. After that period, the 30 m^3 of must would result in 21 m^3 of wine, assuming a yield of 70% [48]. The 85% of that wine would be considered free-run wine and easily pumped to the filtration stage, with the purpose of becoming bottled wine. The other 15% of the wine would rest in the tank sediments. These sediments are usually used to produce pressed wine and other liquors.

Therefore, only 17.85 m^3 of wine would be pumped to filtration stage and oak barrels. The flow rate is supposed to be 3.475 $m^3 \cdot h^{-1}$ pumping all the wine in about 5 hours. After filtration stage, the wine would be deposited in oak barrels to age.

After the aging period, the wine should be clarified, stabilized and bottled. The flow rate in these processes depends on the number of bottles produced per hour. With 1067 bottles per hour, containing 75 cl ($7.5 \cdot 10^{-4}$ m^3) of wine each one, the factory would pump 0.8 $m^3 \cdot h^{-1}$ of wine to the bottling machine. If the established evacuation time for the aged wine is 12 hours a day,

$$0.8 \frac{m^3\ aged\ wine}{h} \cdot \frac{12\ working\ h}{1\ day} = 9.603 \frac{m^3\ aged\ wine}{day}$$

Moreover, assuming that in the oak barrels the 3% [48] of the content becomes wine lees, the maximum m^3 of lees per day can be calculated:

$$9.603 \frac{m^3\ wine}{day} \cdot \frac{3\ m^3\ lees}{97\ m^3\ wine} = 0.297 \frac{m^3\ lees}{day}$$

To extract the lees from the barrels, the barrel content would be diluted with water at 10 V/V [37]. Establishing an extraction time of 15 hours, the flow rate would be:

$$0.297\ m^3\ lees \cdot \frac{10\ m^3\ solution}{1\ m^3\ lees} \cdot \frac{1\ process}{15\ h} = 0.198\ \frac{m^3\ lees\ solution}{h}$$

5.1.1. Required membrane surface calculation

To calculate the required membrane surface needed in each application, two values are required: the flow rate (m^3) of the treated stream (determined in section 5.1.) and the filtration rate ($m^3 \cdot h^{-1} \cdot m^{-2}$).

Therefore, to calculate the filtration rate (f_R), if needed, the following equation is used, where F is the feed flow expressed in $m^3 \cdot h^{-1}$ and A is the filtration surface expressed in m^2:

$$f_R = F \cdot \frac{1}{A}$$

Then, to calculate the filtration surface needed at industrial scale (A'), the following equation is used, where Q is the new feed flow expressed in $m^3 \cdot h^{-1}$ and f_R is the filtration ratio previously calculated:

$$A' = Q \cdot \frac{1}{f_R}$$

5.2. Cases studies: applied membrane technologies

To improve the performance of the alleged red wine factory, some membrane technologies would be integrated into the process, taking into account works and researches explained in previous sections. Fig. 5.1. and 5.2 show the red wine factory flow diagram integrating these membrane technologies, to help the reader to understand the following explanations.

a) **NF of red must before fermentation.** The aim of this process is to reduce the sugar content of the must in order to obtain low-alcohol wine. The process has two steps, both working at same operational conditions. Then, the first retentate (high sugar content) and the second permeate (low sugar content) are mixed with the desired proportion to obtain the desired sugar content. The calculation basis should be 16.83 g of total sugars per 1 %vol. [34]

b) **MF of red wine after fermentation.** The aim of this process is to perform the clarification of the red wine obtained from fermentation, eliminating suspended solids like skins and yeast cell. The clarified red wine (MF permeate) is ready to age in oak barrels.

c) **MF of red wine after aging.** The aim of this process is to ensure the microbiological limpidity in wine, while eliminating suspended solids coming from wine lees. The sterilized red wine (MF permeate) is ready to enter into the stabilization process.

Moreover, the process can be given an added value if an extra processing is integrated:

d) **MF + UF + NF of wine lees.** The aim of this process is to recover valuable compounds such as polysaccharides and polyphenols form wine lees. The process has 3 steps: (i) MF followed by (ii) UF and finally (iii) NF.

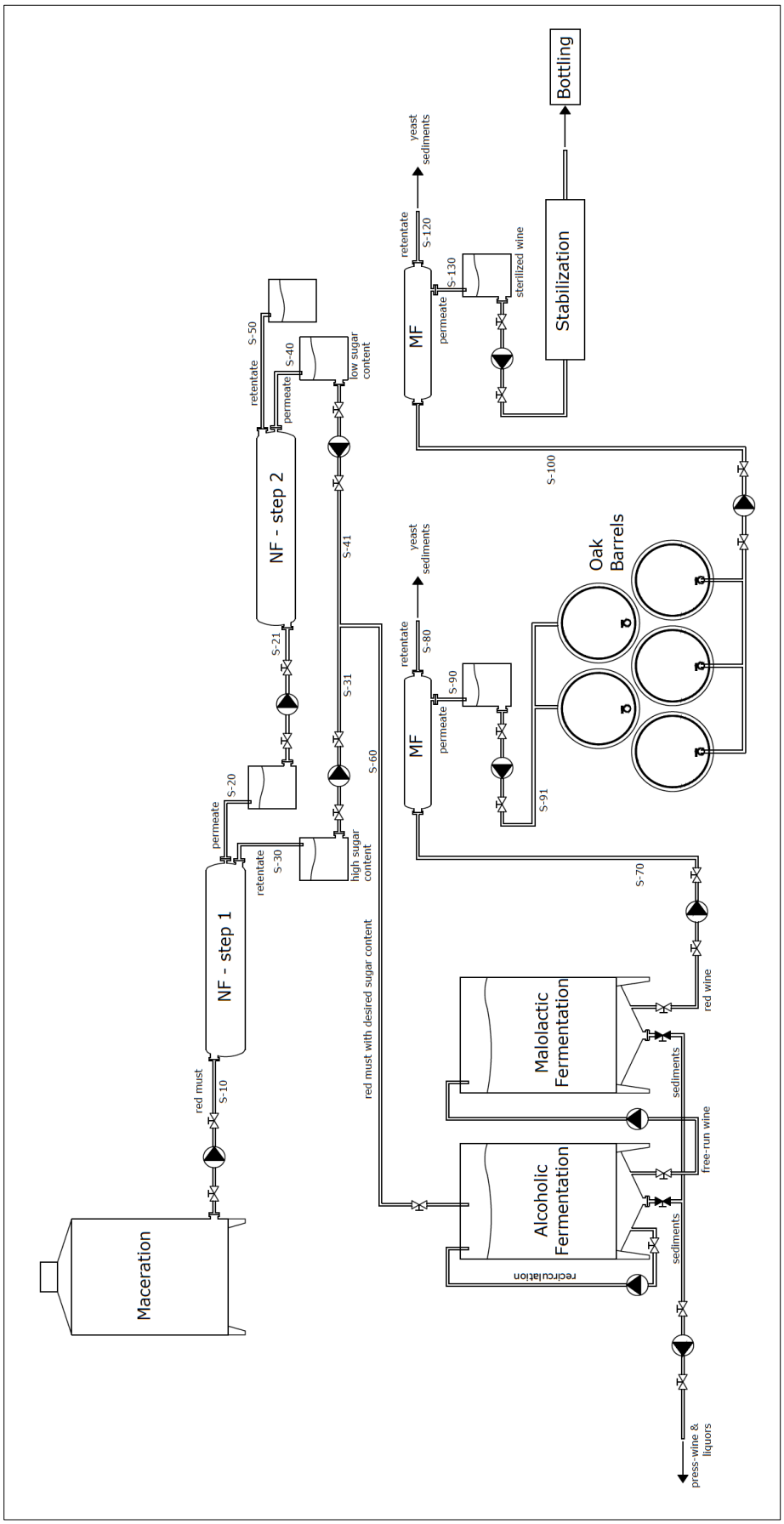

Fig. 5.1. Flow diagram of the wine production process integrating membrane technologies.

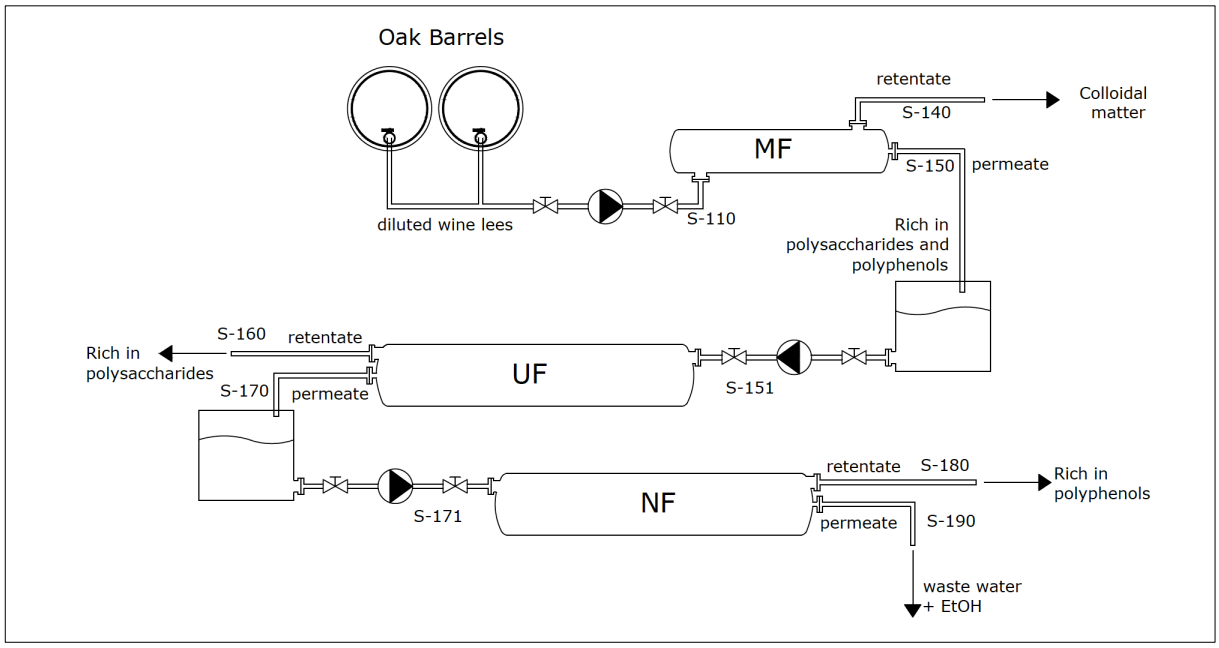

Fig. 5.2. Flow diagram of the extra processing: wine lees filtration.

5.3. Membrane selection

To select what commercial membrane would perform each filtration process, these criteria have been used: the published results mentioned in previous sections, the required filtration surface calculated for the industrial flow rates, described in Table 5.1 (see calculus in Annex A.1 and A.2), and the commercial membranes available nowadays. All selected membrane technical data are described in Table 5.2. Technical data sheets of the membranes are in the Annex B.

a) **NF of red must before fermentation.** The membrane selected is very similar to that used by Salgado et al. [33], made by the same manufacturer but with a larger surface area (34.5 m^2 instead of 7.1 m^2).

b) **MF of red wine after fermentation.** The proposed filtration equipment has been selected due to the experience in winery filters of the company (Koch Membrane Systems). The equipment selected has been designed for the wine industry, especially for wine clarification. Note that the pore size has been chosen regarding typical yeast cell size values shown in Table 3.2, because it is the smallest suspended solid in wine after fermentation.

c) **MF of red wine after aging.** The proposed filtration equipment is very similar to that selected for the MF of red wine after fermentation. Note that the pore size has been chosen regarding the typical bacteria size values shown in Table 3.2, to ensure all bacteria present in wine are removed.

d) **MF, UF & NF of wine lees.** For these membrane processes, the same membranes used in the reference experiments have been selected. The flow rate would be the same as in the experiments, so membranes should perform the filtration with success.

Table 5.1
Calculation of the required filtration surface for each application. See Annex A.2.

Membrane application	Reference	Filtration flow rate ($m^3 \cdot h^{-1} \cdot m^{-2}$)	Industrial-scale flow rate ($m^3 \cdot h^{-1}$)	Required filtration surface (m^2)
NF of red must (each step)	Salgado et al. [33]	0.0761	7.5	98.55
MF of red wine after fermentation	Daufin et al. [20]	0.05	3.475	69.50
MF of red wine after aging	Daufin et al. [20]	0.10	0.880	8.80
MF of wine lees	Giacobbo et al. [37]	3.39	0.2	0.06
UF of wine lees	Giacobbo et al. [37]	0.015	0.15	10
NF of wine lees	Giacobbo et al. [37]	0.056	0.4275	7.6

Table 5.2
Selected membrane technical data. Information provided by the manufacturers (See Annex B).
MWCO: molecular weight cut-off.

	NF red must	MF after fermentation	MF after aging	MF wine lees	UF wine lees	NF wine lees
Manufacturer	Koch Membrane Systems	Koch Membrane Systems	Koch Membrane Systems	PAM – membranas seletivas	Alfa Laval	Dow Filmtec
Model	SR3-NYV 8038	Winefilter™ MF 6060	Super-Cor® 3010	MFP5	ETNA 01PP	NF270 4040
Type of membrane	Spiral wound module	Hollow fibre	Tubular cross-flow	Hollow fibre	Spiral wound module	Spiral wound module
Membrane material	TFC® polyamide	Polyether-sulfone	Polysulfone	Polyimide	Fluoro polymer on PP	Polyamide film composite
MWCO (Da)	200 Da	-	-	-	1000	200
Pore size (µm)	-	Microporus	0.1	0.4	-	-
Active membrane area (m^2)	34.5	13.9	2.2	0.06	10	7.6
Recommended inlet pressure (bar)	13 – 31	2.7	6.2	5	1 – 10	40
Maximum temperature (ºC)	50	40	49	55	60	45
Number of membranes used	3	5	4	1	1	1
Total surface	103.5	69.5	8.8	0.06	10	7.6

5.4. Expected performance of the membranes

Each integrated membrane technology should improve and optimize the whole process. To evaluate the success of the membranes, in this section the filtration results are simulated. To help the reader understanding the following explanations, Fig. 5.1 shows the wine production process with the integrated membrane technology, in which a number has been assigned to each stream. Additionally, Table 5.3 and Table 5.4 describe each stream and all the membranes used, respectively. For more calculus details see Annex A.3.

First of all, some initial values are needed to be established. These values are: a) glucose and fructose concentration of the initial red must, and b), polyphenols and polysaccharides concentration of wine lees from barrels.

- **Glucose and fructose content in red must.** These values are assumed to be 105 $g \cdot l^{-1}$ and 106 $g \cdot l^{-1}$, respectively. It is considered the same composition as the red must used by Salgado et al. [33].

- **Polyphenols and polysaccharides in lees.** These values are assumed to be 21.6 ppm and 10.1 ppm, respectively. It is considered the same lees composition used by Giaccobo et al. [37].

Table 5.3
Numeration and description of the chemical process streams (showed in Fig. 5.1.).

Stream	Description	Stream	Description
10	Untreated red must	110	Lees from barrel
20	Membrane 1 permeate	120	Membrane 4 retentate
21	Membrane 2 inlet	130	Membrane 4 permeate
30	Membrane 1 retentate	140	Membrane 5 retentate
31	M1 retentate mixing	150	Membrane 5 permeate
40	Membrane 2 permeate	151	Membrane 6 inlet
41	M2 permeate mixing	160	Membrane 6 retentate
50	Membrane 2 retentate	170	Membrane 6 permeate
60	Mixture S31 + S41	171	Membrane 7 inlet
70	Fermented wine	180	Membrane 7 retentate
80	Membrane 3 retentatre	190	Membrane 7 permeate
90	Membrane 3 permeate		
91	Oak barrel inlet		
100	Wine from barrel		

Table 5.4
Description of membranes used in the integrated wine process showed in Fig 5.1.

Membrane	Description
1	NF of red must - step 1
2	NF of red must – step 2
3	MF of fermented wine
4	MF of aged wine
5	MF of wine lees
6	UF of wine lees
7	NF of wine lees

5.4.1. Nanofiltration of red must before fermentation

The aim of the filtration process is to control and correct the sugar content of the untreated red must. Based on Salgado et al. [33] experiments, the selected membrane to perform this filtration stage should show a rejection to glucose and fructose of 79% and 81%, respectively, in the first step. However, in the second step these rejections should be 92% and 90%, respectively.

The first step inlet flow rate, established in section 5.1., is 7.5 $m^3 \cdot h^{-1}$. The NF permeate should be 3.075 $m^3 \cdot h^{-1}$ (41%) and the NF retentate 4.425 $m^3 \cdot h^{-1}$ (59%), both values considered according with Salgado et al. [33] results.

The second step inlet flow rate, also established in section 5.1., is 7.5 $m^3 \cdot h^{-1}$. The NF permeate should be 3.785 $m^3 \cdot h^{-1}$ (50.5%) and the NF retentate 3.715 $m^3 \cdot h^{-1}$ (49.5%), both values considered with the same criterion as in the first step.

Finally, first-step retentate and second-step permeate are mixed with the required proportion. To calculate this proportion, many factors have to be considered. The first factor to consider is the desired alcohol content at the final product. This value is supposed to be 10.6 %vol. (calculation basis is 1 %vol. per 16.83 $g \cdot l^{-1}$ of total sugar [34]).

The second factor to consider is the mixture flow rate. In section 5.1., it is established a flow rate of 7.5 $m^3 \cdot h^{-1}$ in order to pump, every day, 30 m^3 of red must to fermentation tanks in 4 h. Nevertheless, with the 2-step NF process this value changes. The second-stage retentate does not have the desired sugar content and it is not considered in the final mixture. Thus, over 6 m^3 of must (20%) are not included. The final volume of must pumped to fermentation tanks is 24 m^3, changing the flow rate to 6 $m^3 \cdot h^{-1}$.

According to the results described in Table 5.5, the required mixing values are 3.6 $m^3 \cdot h^{-1}$ (60%) of first-step retentate (stream 31) and 2.4 $m^3 \cdot h^{-1}$ (40%) of second-step permeate (stream 41). Thus, the expected alcoholic degree of the final product should be 10.6 %vol. To check each stream description, see Table 5.3.

Table 5.5
Expected results of the 2-step NF process before fermentation. See calculus details in Annex A.3.

Stream	**10**	**20**	**21**	**30**	**31**	**40**	**41**	**50**	**60**	**70**
Glucose ($g \cdot l^{-1}$)	105	53.78	53.78	140.59	140.59	8.53	8.53	99.89	87.77	0
Fructose ($g \cdot l^{-1}$)	106	49.12	49.12	145.53	145.53	9.73	9.73	89.25	91.21	0
Ethanol (%vol.)	0	0	0	0	0	0	0	0	0	10.6

5.4.2. Microfiltration of red wine

There are two proposed MF of red wine: a clarification stage after fermentation and a sterilization stage after aging. The aim of the first process is to eliminate suspended solids such as yeast cell sediments, skins and seeds. This process is simple to evaluate: in the MF permeate should not be any suspended solid. The second MF stage, after aging, ensures the microbiological limpidity of the wine. Therefore, no bacteria should be found in the MF permeate. Fig. 5.2 shows both processes with a 100% of success.

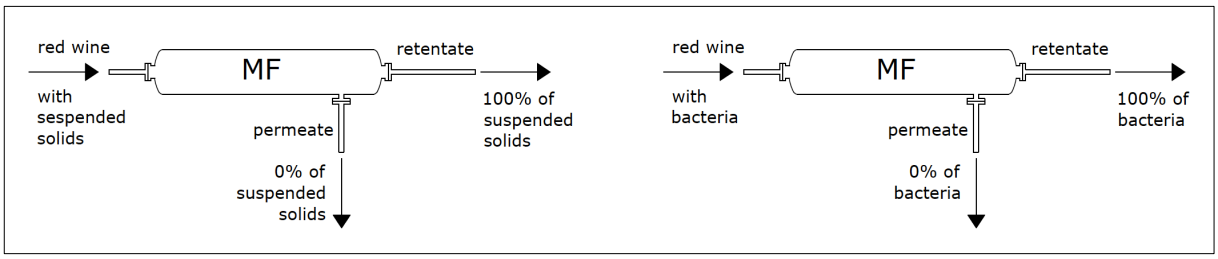

Fig. 5.2. Integrated MF processes with the expected performance.

5.4.3. Wine lees treatment by MF+UF+NF

The aim of the process is to recover polyphenols and polysaccharides from wine lees. As explained in section 5.1., wine lees are extracted diluting 10 v/v and with a flow rate of 0.2 $m^3 \cdot h^{-1}$. This dilution is considered to contain 21.6 ppm of polyphenols and 10.1 ppm of polysaccharides (see section 5.4.). The following flow rate and rejections values are all based on Giaccobo et al. [37] experiments.

The first step (MF) should eliminate the colloidal matter present in the wine lees dilution. Thus, a rejection of 100% to suspended solid content is expected as the MF permeate should have none solids remaining, while the polyphenols and polysaccharides content should not have changed.

The second step (UF) membrane should present a rejection to polyphenols and polysaccharides of 50% and 70%, respectively. The inlet flow rate, established in section 5.1., is 0.15 $m^3 \cdot h^{-1}$, while UF permeate is expected to be 0.1425 $m^3 \cdot h^{-1}$ (95%) and UF retentate 0.0075 $m^3 \cdot h^{-1}$ (5%).

The last step (NF) membrane should reject the 90% of polyphenols and the 99% of polysaccharides. The established inlet flow is 0.428 $m^3 \cdot h^{-1}$ (see section 5.1), while NF permeate flow rate should be 0.406 $m^3 \cdot h^{-1}$ (95%) and NF retentate 0.00214 $m^3 \cdot h^{-1}$ (5%).

The results (see Table 5.6) show that the recovery of polyphenols and polysaccharides is feasible. However, while polyphenols are mainly separated from polysaccharides in NF retentate (stream 180), polysaccharides are not entirely separated as part of the polyphenols pass through the UF membrane and remain in the UF retentate (stream 160). To check each stream description, see Table 5.3.

Table 5.6
Expected results of the membrane technology applied to wine lees. See calculus details in Annex A.3.

Stream	**110**	**140**	**150**	**151**	**160**	**170**	**171**	**180**	**190**
Polyphenols (ppm)	21.6	0	21.6	21.6	216	11.37	11.37	203.44	1.20
Polysaccharides (ppm)	10.1	0	10.1	10.1	155.54	2.45	2.45	48.13	0.03
Suspended solids	YES	YES	NO	NO	NO	NO	NO	NO	NO

6. Economic evaluation

The economic evaluation of this project has been done taking into account the realization of the project and the costs of the material used. The realization of the project includes the design phase, the gathering information and the writing of this document. Table 6.1 and 6.2 describe all these points and the whole project economic cost.

Table 6.1
Cost of realization of the project. [49]

Concept	Units (h)	Unit price (€/h)	Total price (€)
Design			
Project design	4	16	64
Industries selection	3	16	48
Total phase	**7**	**16**	**112**
Gathering information			
Dairy Industry production processes	20	16	320
Wine Industry production processes	20	16	320
State-of-the art review	80	16	1280
Commercial membranes selection	6	16	96
Market overview	10	16	160
Total phase	**136**	**16**	**2176**
Calculation for wine industry			
Alleged factory flow rates	14	16	224
Required m^2 of membrane	6	16	96
Performance simulation	12	16	192
Total phase	**32**	**16**	**672**
Writing the document			
Writing	90	16	1440
Technical review	25	35	875
Total phase	**115**		**2315**
TOTAL REALIZATION	**290**	**-**	**5275**

Table 6.2
Cost of material of the project.
Computer and printer costs are 10% of the estimated original value.

Concept	Units	Unit price (€/u)	Total price (€)
Office material	1	10	10
Computer	1	107	107
Printer	1	8	8
TOTAL MATERIAL	**-**	**-**	**125**

At the end, the cost of the whole project is estimated at 5,400 €, considering the material and the manpower cost, as showed in Table 6.3.

Table 6.3
Total cost of the project.

Concept	Price (€)
Manpower	5,275
Material	125
TOTAL PROJECT	**5,400**

Conclusions

After realising this scoping study on the viability and applicability of membrane technology in dairy and wine industries, it has been demonstrated that there are many feasible applications that could be upgraded. The integration of membrane technologies in these industries may improve the production processes by optimizing them and adding value by recovering some by-products (such as antioxidants, polysaccharides, among others). Traditionally, membrane technologies have been developed focused on water treatment, but both agro-industries and membrane manufacturers should deepen these applications for mutual benefits.

From the market overview focused on Spain, the conclusion is that wine industry is more attractive to exploit than dairy industry. Dairy industries in Spain have such a business plan focused on specific dairy products and this causes that less membrane technologies could be applied or sold to each industry. In Spanish wine industry is easier to see wine producing plants that processes different types of wine. Moreover, Spain is the 3rd wine producer worldwide, so it has one of the strongest wine sectors. The fact that the wine consumption has decreased last years due to the increase of populations healthy habits, among others, can be a good point to sell for instance the NF process of grape must before fermentation, in order to obtain low-alcohol wines and increase the wine consumption in Spain.

On the work carried out to evaluate the scale-up of membrane technology on the winery industry it has been demonstrated that it is feasible to integrate different membrane based solutions. Both solid liquid separation and removal or concentration of specific components were achieved by combination of MF/UF with NF. Nowadays, with available commercial membranes, in terms of chemical and physical properties, the process schemes defined to perform the filtrations stages are not fanciful but realistic.

However, the NF of grape must described in this project as an example, which is the most novel membrane application in wine industry, includes a loss of 20% of the must. To improve the process and convince the wine industry, this must loss should be reused. An alternative could be to recirculate part of the must and mix with the untreated must. Other alternatives could be to use this must to produce another beverage or to perform a filtration process, similar to that proposed in this project to recover valuable compounds from wine lees, in order to recover polyphenols and polysaccharides. The optimization of this filtration stage should be the next challenge to face.

A next step will be done next years in membrane technologies applications, integrating them in agro-industrial process stages and optimizing the production processes. Traditional production processes need to be replaced by new technologies in order to satisfy the consumers desire of better quality products and to optimize the processes. For its part, this is an attractive point of exploit for membrane manufacturers, which have historically focused their efforts and innovations towards water treatment.

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