Paper-2: Principles of the Food Processing and Preservation

Module 34: Membrane Processing in Food Processing

34.1 Introduction: Among the wide range of the available separation processes, membrane technology is defined as abroad term that contains several separation processes on molecular level i.e. membrane separation usually applied on<10 µm size molecules while conventional separation is used for >10 µm size molecules. It is among the vital fields of food science**(Kotsanopoulos and Arvanitoyannis, 2013)**. A set of specialized equipments is used for a particular membraneprocess that enable it to show itstypical separation characteristics as well as,makeit suitable for specific desired single (**Mistry and Maubois, 1993**) or multipleapplications.Water industry (drinking water + wastewater processing + water desalination)has the largest commercial market formembranes worldwide. In last 20-25 years, the market volume of different membranes has increased aboutú800ï850 million in food industries and the same is now stands as thesecond largest commercial market for membrane on global basis(**Lipinzki, 2010**).Moreover, about 20-30 % of the total membrane production is used in food industries, annually increasing at the rate of 7.5% in this sector on global basis (**Kotsanopoulos and Arvanitoyannis, 2013).** Membrane separation is performed above the atmospheric pressure (that varies with particularmembrane process) in a closed systemso,these processes are known as pressure-driven membrane processes. Four membrane processes(in theirascending pore diameter) are Reverse osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF) and Microfiltration (MF) are mainly used in food processing. UF systems as well as UF membranes have the maximumshare (35%) in global membranes market followed by the share of MF systems and membranes (33%) and NF/RO systems and membranes (30%). Membrane contactors (MC), Electrodialysis (ED) and Pervaporation (PV) are the other membrane processes but contribute only for 2% share in total membranes market(**Lipinzki, 2010**).

34.2 *Classical Membranes, Their Types and Design:*Membranes are semi-permeable barriers, used to separate two phases, which restrict the transport of various substances in permeate and retentate streams in a specific way i.e. on the basis of particle size, shape, electric charge etc. (**Cheryan, 1998**). The separation efficiency of a particular membrane is usually affected by different processing factors like feed composition, pH, temperature, pressure, feed flow as well as interactions between feed component and membrane surface (**Lin *et al*., 1997**). During membrane processing, a particular membrane material is fixed in a particular membrane module (Plate & frame, Spiral wound, Hollow fiber, Tubular) and operated within pre-fixed operating conditions to perform assigned tasks.Membrane processes were initially operated in dead end filtration mode (Figure 1, a)in which feed (single stream) was subjected to membrane that retains the bigger size molecules in retentate and allowed the smaller molecules to pass in permeate (single stream). The main problem of such systems is the rapid cake layer formation overthe membrane surfacewhich is directly responsible for membrane flux decline (Figure 1, b). This problem was overcome in cross flow designin which single feed stream is subjected to membrane, parallel to its surface in closed system at higher pressure with turbulent flow that divide the feed in to two streams namely permeate (molecules that passed through membrane) and retentate (containing rejected molecules).The turbulent flow helps in reduction of cake layer formation throughcontinuous sweepingaction of suspended particles over the membrane surface that results in better flux than dead end filtration over the higher length of time.

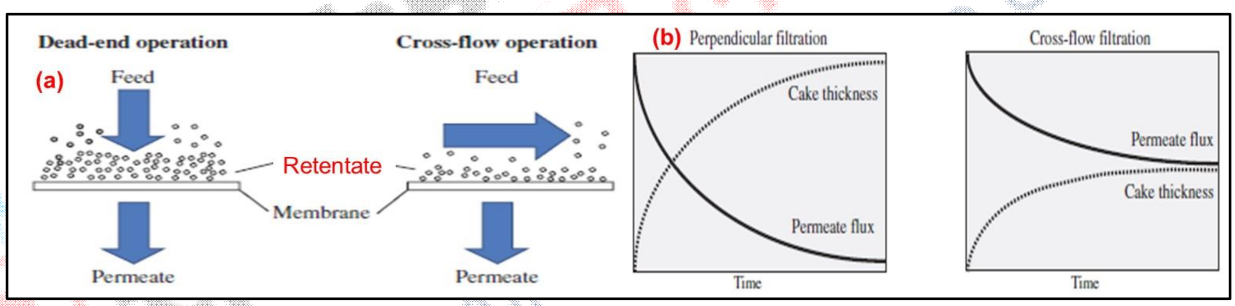

Figure 1. (a) Schematic of a dead-end filtration and cross-flow filtration Source: adapted from Hausmann*et al*., (2013), (b)Effect of perpendicular and cross-flow filtration on flux and cake thickness. Source: adapted from Smith, (2013).

34.3. Membrane Generations: As per the technical development carried out till date, membrane materials can be classified in four generations (**Couthino*et al.*, 2009**).

First generation: Cellulose acetate derived membranes, which were developed to desalinate seawater. They were susceptible to microorganisms and disinfectants as well as sensitive to (3-8) pH and(maximum 50 ^{o}C) temperature (**Cheryan, 1998**).

Second generation: Developed from synthetic polymers like polysulfone or polyolefin derivatives), these are better than first generation as having better resistant towards hydrolysis, pH and temperatures, but have lower resistance to mechanical compacting (**Porter, 1990**).

Third generation: Mineral membranes consisting ceramic material based on zirconium or alumina oxide are usually deposited on a graphite surface. These membranes have great mechanical strength, are chemically inert and can be operated on high pressures, wide pH range (0-14) and temperatures > 400 ^{o}C. Their main demerit of these membranes is their cost(expensive than other membrane materials), but the same is compensated by their long operational life (**Cuperus and Nijhuis, 1993**).

Fourthgeneration: Hybrid process i.e. combination of conventional Electrodialysis& different pore sizes membranes (E.D.+MF/UF/NF) (**Aider *et al.,* 2008**). The continuous electrophoresis with porous membranes (CEPM) is defined as an electrochemical process to separate charged organic molecules utilizing electric field as a driving force. Under the effect of an electric current, ions are transported from one solution to another through one or more semipermeable porous membranes (**Bazinet*et al.*,1998; Tanaka, 2006**).

34.4. Membrane Processing in Food Processing

Availability of few food materials in naturally pure form underlines the importance of different separation and purification processes in transforming food or food substances into safe and direct consumable form.For selected applications, membrane processing is superior to other conventional methods owing to its inherent advances such as low energy consumption, fewer and mild processing steps, greater separation efficiency, improved final product quality, eco-friendly and ócleanerô processing i.e. better quality products at lowest cost with highest environment protection through minimum/low waste generation.Now a days, these processes have been become an integral part of different industries like functional food and nutraceuticals industry, agricultural, dairy and food and bio-product industries (**Strathmann, 1990**).

34.4.1 Membrane application in Beer, wine and vinegar production

Currently, membranes are being used in this area for clarification of beer, wine and vinegar as well as dealcoholization of beer. In the classical beer production process (for details seeLipinzki, 2010), as an alternate, reverse osmosis is used for beer dealcoholization prior to its clarification by microfiltration before pasteurization and bottling.Cross-flow MF is used to recover beer from the yeast-beer mixture (settled on fermentation tank bottom) and also to concentrate yeasts. The membrane system investment is usually compensated by the beer recovery.Moreover, MF now successfully employed for beer clarification i.e. for removal of yeasts, microorganisms and hazewithout adversely affecting its sensorial attributes.RO is used to tailor the alcohol content in beer to produce alcohol free or reduced alcohol (8-10 times less alcohol content) beer without affecting its flavour. It is carried out in four steps i.e. beer is pre-concentrated in permeate (water + alcohol) and retentate (concentrated beer + flavour) followed by diafiltration of the permeate and tailoring of alcohol content as per the desired tasteusing desalted and deoxygenized water; post treatment which includes the addition of hops and syrups in alcohol tailored beer to compensate the taste losses arises from the loss of taste carrier alcohols. These steps are performed Ò7°C that results in the production of improved quality beer rather than conventional process.

Reverse osmosis is used for the must correction, rejuvenation and dealcoholization of wine, while MF/UF is used for the wine clarification during wine manufacture (for details see Lipinzki, 2010). Must composition is balanced with the help of RO, which increase sugar content in wine through concentration and at the same time enhances tannins and organoleptic components by 5-20%. It is an efficient method to maintain the quality of must obtained from the grapes harvested during rain (i.e. with moisture content) but the same is less effective in maintaining the quality of must made from the grapes of stalled maturity due to cold weather. The use of thisparticular method is depends on theregulationof various countries. During wine clarification,MF and UF providesan alternative to the classical fining substances, filters and also reduces the number of processing steps. Lipinzki, (2010), reported that 0.20-0.50 εm and 0.45-0.65 εm pore size MF membranes are usually used during the filtration of white and red wines, respectively.Rejuvenation of older wines is accomplished through RO process which removes the water, alcohol and other substances responsible for adverse aroma followed by the addition of mineral free water during diafiltration. Alcohol content of the wines is also tailored in the same manner as discussed above for beer.

Clarification of vinegar employing UF not only provides wider vinegar range with same sensorial attributes without turbidity,but also reduces number of operations and reduces storage time.

34.4.2 Membrane Application in Fruit Juice and Beverages Production

MF and UF are the economic and efficient alternatives to the classical filtration methods available for clarification of different juices. The use of membrane processing in beverage industry have severalinherent advantages likeimproved product quality, reduced cost of production, better working environment, cleaner production with less waste generation and improved product safety (**Koseoglu et al., 1990; Hagg, 1998**). **Cassano, (2010**) reported several merits of membrane processes over classical beverages or fruit juice fining agents such as reduced energy consumption and cost, eradication of different filtration aids, mild thermal treatments that safeguard the product against thermal degradation, easier process and compact equipment design, fewer wastes, reduced chemicals requirement andenhanced productivity (96ï 98%, juice recovery). Moreover, fruit juice clarification with MF and UF have substantial potential of cost saving. Annual production costs of a UF plant (capacity- 250 m^3 of juice / day) was estimated 79% lesser than a conventional plant (**Mondor and Brodeur, 2002**).Different characteristics of conventional processes and MF filtration is compared and shown in Table 1.

Table 34.1 Clarification of fruit juices-comparison of traditional processes with microfiltration (Adapted from Cassano, 2010**)**.

Processing method	Operating time	Fibres	Sensory and nutritional quality	Operating cost
Decanting	Very long	Poor	Poor	Intermediate
Dead-end filtration	Long	High	Intermediate	Intermediate
Centrifugation	Very short	Poor	High	High
Microfiltration	Short	High	High	Low

MF (pore sizes, 0.05ï 10 εm) is resembles classical coarse filtration, employed to filter juicesin fibrous enrichedpulp (in retentate)as well as microbes free clarified fraction (in permeate). Moreover, it is known as cold - sterilizationprocess. UF process is the alternate of the fining step used in classical method. It is wider membrane pores than MF yet retails the bacteria, fats, proteins and colloids but allow to pass the smaller molecules like vitamin, minerals and sugars (Cassano, 2010). Prior to UF process, both pre and enzyme treatment of the juice is essential for better yield, high capacity and excellent product quality.Juices are first concentrated in RO, which decreases the moisture content to its half value but retains major amount of sugar (98ï 99%) and volatile flavours (80-90%) in the retentate (having 20-25 ŬBrix) and same then concentrated > 75 ŬBrix in classical evaporation. This combination results in 60-75% saving of energy than traditional evaporation (Lipinzki, 2010). A detailed review on membrane processing of fruit juices and beverages has been already published by Girard and Fukumoto, (2000).

34.4.3 Membrane Applications in Functional Foods and Nutraceuticals

Global market of functional foods and nutraceuticals is rising rapidly. The future of recently evolved bio-activemolecules and nutraceutical ingredients is usually decided by theseparation ability and efficiency with the retention of the desired characteristics/biological activity of these ingredients by the employed separation process with minimum inputs (i.e. energy + capital + labor cost). Separation as well as purification of such ingredients is highly expensive. Although, a number of challenges have to overcome to raise the concentration of a target substance in the end product from its raw material yet, several methods are accomplishing such tasks successfully. On commercial scale, membrane processing is now considered as low cost and effective tool to concentrate and purify several bioactive substances from different feed streams (Akin *et al*., 2012).

Table 34.2 Established markets and applications in nutraceutical and bioactive separation industries (Adopted from Akin *et al*., 2012)

Process	System	Remarks
Ultrapure water, Water softening	RO/UF	Classical
Effluents	RO/NF/UF	Classical
Fine chemical processes	NF/UF	Developing rapidly
Milk/whey/milk bioactives	RO/NF/UF	Almost classical/Developing
Extract concentration	RO/NF	Restricted due to thecomplexity of processes
Emulsion separation	UF/MF	Classical but also expensive
Caustic recovery	Ceramic	Good technology for causticrecovery for all industries
Fruit juice clarification	MF	Established market
Oil/Water separation	UF/RO	Works well for non-emulsifiedmixtures
Alcohol purification	PV	Efficient inwater content <20% - developing, but goodpotential
Enzyme recovery	UF/NF	Pharmaceutical industries ï established but growingmarket
Protein concentration and purification	UF/NF	Protein isolate fractions-Specialized applications
Waste water recovery	NF/RO	Commercial. Still developing
Wine clarification, Beer recovery	MF	Commercial
Wine sugar concentration	RO	Commercial
Color removal	NF	Commercial
Phospholipid removal fromcrude oils	NF/UF	Developing- Good Potential
Bio-active recovery from fruit and vegetable juices and herbs and botanicals	NF/RO	Good potential
Improve beverage stability	MF	Good application-eliminates heat treatment better flavor

Various membrane processes alone or in combination are used to produce numerous nutraceuticals and bioactive substances from lipids, carbohydrates and proteins protein based sources. Moreover, this technology offers many key advantages during processing of such ingredients which includes elimination of classical evaporation (that reduces their activity and highly energy consuming); reduces overall water needs by re-utilizing waste water; enhances profit by formation of new products and needs lesser floor space and investments. Table 2, represents the various application of membrane processing in different classical processes and in separation bio-actives.

34.4.4Membrane Application in Vegetable Oil Processing

Traditional oil refining methods have several demerits like nutrient loss, needs higher amount of energy, water and chemicals; greater losses of neutral oil as well as the generation of more effluent. Vegetable oil refining employing membranes has been not only reported as an easier/simpler process but also the same offers different advantages like better nutrient retention, reduced demand of energy and added chemicals, milder process parameters and cleaner production (Subramanian et al., 2001). Several researchers have been used membrane processes for the recovery of solvents from the micelle, degumming, bleaching, deacidification as well as hydrolysis of fats and oils**Couthino*et al.,* 2009**).For detailed information on membrane applications in vegetable oil processing, the review published by Couthino*et al.,* (2009) must be refereed.

34.4.5 Membrane Application in Dairy Processing

Dairy industry is one of the early adaptor of the membrane processes.It has greatly benefited by membranes as a number of applications like removal of water/concentration, liquid-liquid as well as solid-liquid separations are routinely performed. From 1960, the major milestones in membrane development and their application in dairy processing is presented in Table 34.3; different filtration spectrums available for the separation of milk constituents is shown in Table 34.4.

Table 34.3 Milestones in the development of membrane technology and its applications in dairy processes since 1960s (adopted from Pouliot, 2008)

	Advances in membrane technology	**Applications of membranes in dairy processing**
1960s	• Development of reproducible membranes by manufacturers	-
1970s	• Materials with improved chemical resistance (from CA to PS) • First design of sanitary modules	• Design of whey pre-treatments to prevent membrane fouling • Development of processes for the UF of acid whey • Development of the first UF-based cheese manufacture processes
1980s	• Improvement of membrane system hardware (module designs, spacers, anti-telescoping devices) • Development of commercial inorganic (ceramic) membranes	• Using UF or RO membranes to concentrate milk on farm • Defatting of whey (WPI manufacture, recovery of minor compounds) • Separation of б-lactoglobulin& Ŭ-lactalbumin • Desalting whey with loose-RO (NF) membranes
1990s	• Improvement of hydrodynamics of MF membranes (UTP) • Porosity gradient membranes • Control of particleôs deposition (vibration, rotating disk, Deanôs vortices, static mixer) • Functionalized membranes (ion exchange)	• Removing spores from cheese milk and whey • Defatting whey • Separating casein micelles from milk (ideal whey) • Extending milkôs shelf life (ESL milk) • Fractionating hydrolysates using UF/NF membranes

Table 34.4 Filtration spectrum available for the separation of milk constituents (adopted from Pouliot, 2008)

Pore size	Separation mechanism	Operating pressure (MPa)	Membrane materials	Module config-uration	Separation domain	Membrane-based commercial dairy ingredient
MF >0.1 µm	Sieving	0.01-0.2	Inorganic Polymeric	T, MC	Somatic cells, bacteria, spores Fat globules Casein micelles	Micellar casein, Native whey proteins
UF 1-500nm	Sieving & charge	0.1-1		T, HF, SW, PF	Soluble proteins Caseino-macropeptide	WPC, WPI, MPC, ϐ-Lg, Ǚ-La
NF0.1-1nm	Sieving & charge	1.5-3		T, HF, SW, PF	Indigenous peptides Salts (divalentcations)	Bioactive Milk & whey proteins hydrolysates, Glycomacropeptide
RO<0.1 nm	Sieving & Diffusion	3-5		SW, PF	Salts, Water removal	Lactose, Concentration of Whey permeate Delactosed, deproteinized whey

Polymeric: cellulosic, polysulfone, polyamide; inorganic: ceramic, carbon-supported zirconium oxide, stainless; T, tubular; MC, multichannel; HF, hollow fiber; SW, spiral wound; PF, plate and frame ;WPC, whey protein concentrate; WPI, whey protein isolate; MPC, milk protein concentrate.

The key membrane applications in dairy industry is categorized in three main classes which are shown in Figure 2. Moreover, the use of different classical membrane processes particularly in milk and whey processing is shown in Figures 6 and 7, respectively. For detailed information, recently published handbook on ñMembrane Processing: Dairy and Beverages Applicationsò edited by A.Y. Tammie, (2013) must be referred.

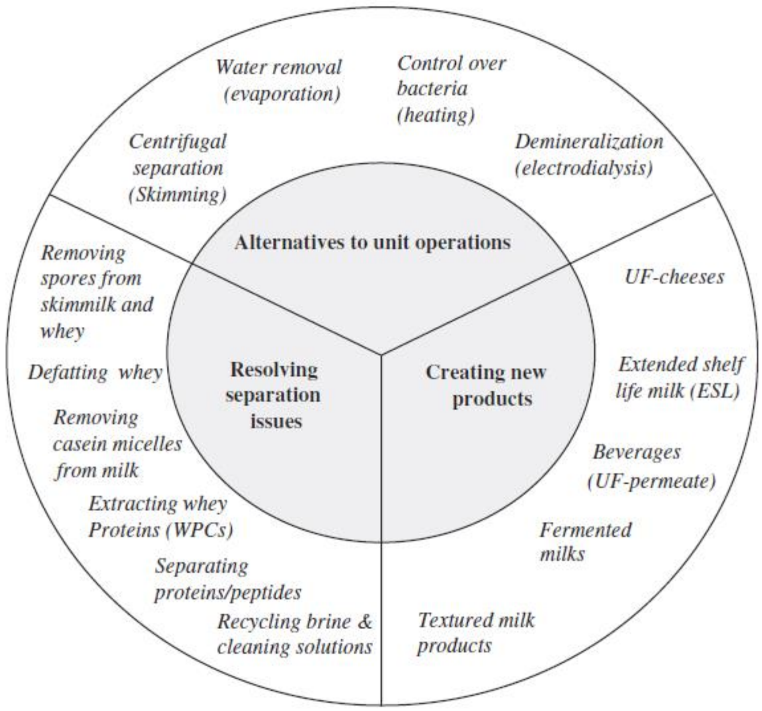

Figure34.2 Membrane processes in the dairy industry: a look at the applications. Source: adapted fromPouliot, (2008).

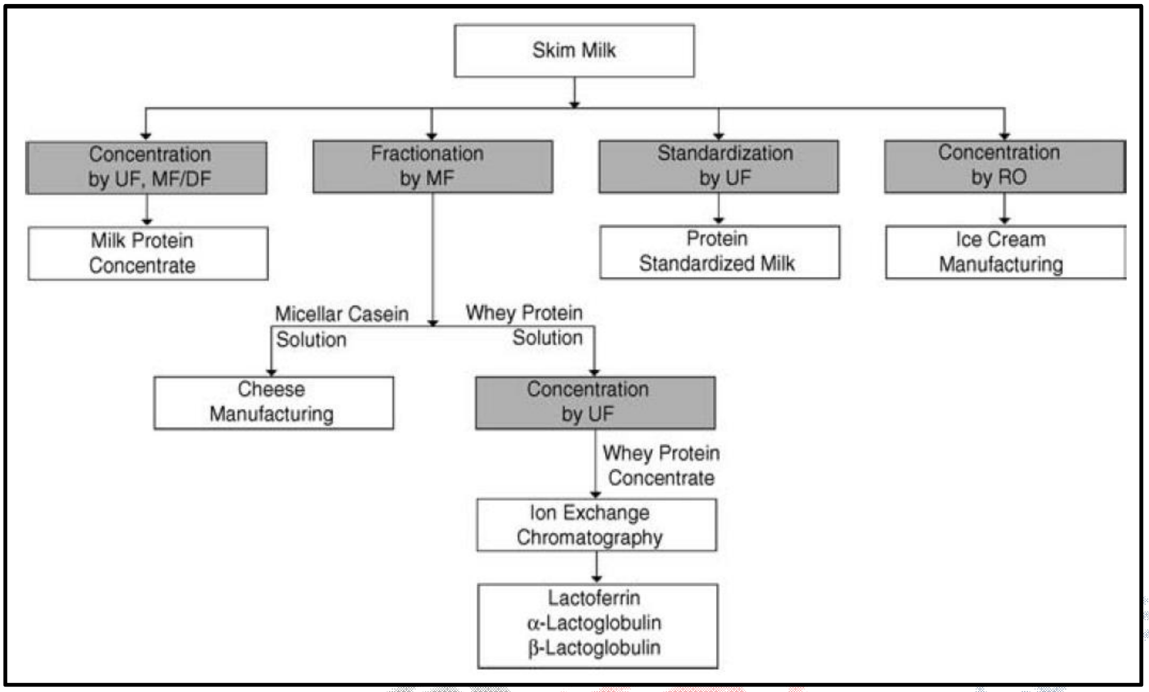

Figure 34.3 Applications of membrane technology in milk processing. Source: adapted fromLipinzki, (2010).

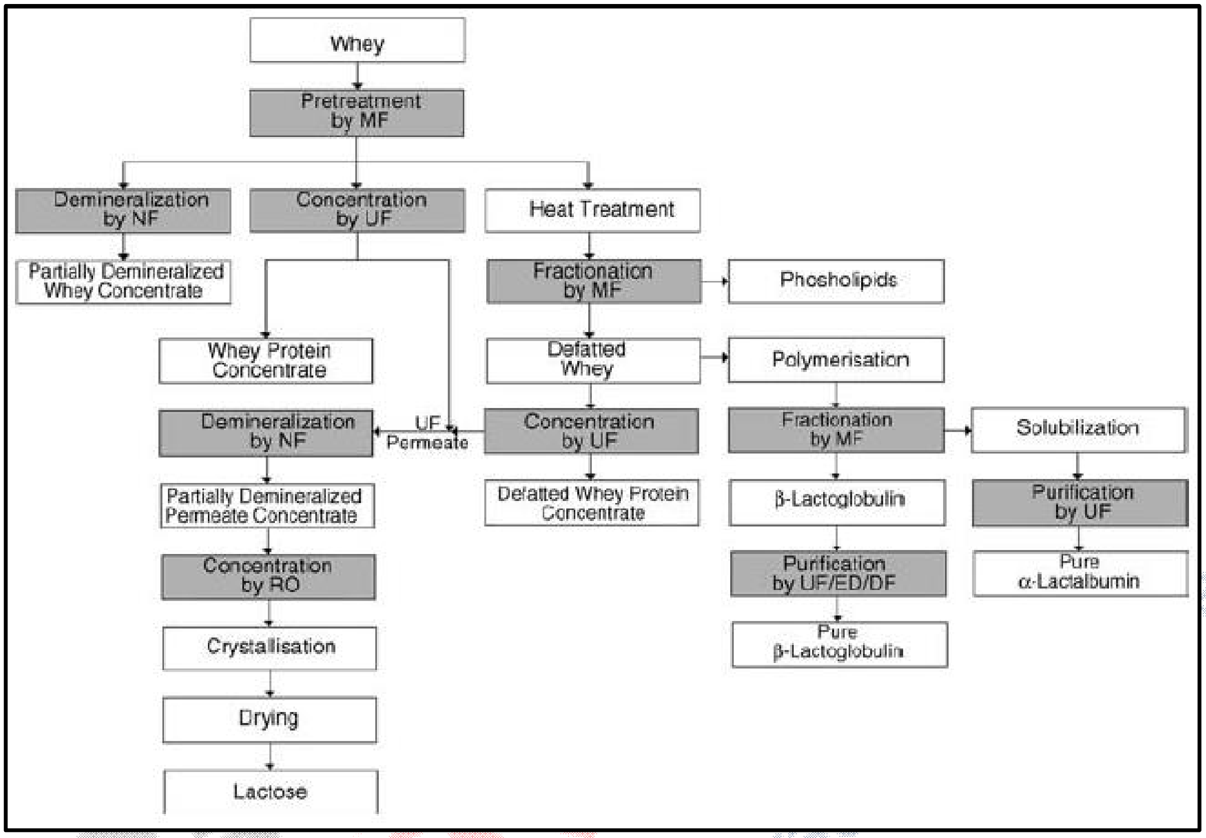

Figure 34.4 Applications of membrane technology in whey processing. Source: adapted fromLipinzki, (2010).

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