Review Article

Alternative Thermal Processing Technique for Liquid Foods- Membrane processing

Abstract

Liquid foods are sensitive to temperature and concentration by conventional methods results in product deterioration. Alternative processes, such as freeze concentration, have the drawback with respect to the maximum achievable concentration (only up to 40 to 45°Brix). In recent years membrane processes such as Microfiltration, Ultrafiltration and reverse osmosis are gaining importance for the concentration of liquid foods. Since heat is not involved in this process, it is also called Alternate thermal processing technique. This process can be employed as a pre-concentration step to reduce water load on subsequent processing steps and can be easily scaled up. Liquid foods such as fruit juices are of high nutritive value as they are naturally enriched with minerals, vitamins and other beneficial components required for human health. When extracted from their sources fruit juices have low solid content, color strength and high-water load. Recent advances and developments in this membrane processing used for the concentration of liquid foods are discussed here.

Key words: Liquid foods, membrane processing, Types, Modules

Introduction

Membrane processing is a technique that permits concentration and separation of macro and micro molecules based on molecular size and shape. It is the fast emerging among various unit operations available for separation processes, especially in the field of food processing. Better process economy, higher yield, improved product quality, utilization of byproducts and a solution to some environmental problems, can all be achieved by using membrane processing.

Separation science is essential to manufacturing food and beverage products. Evaporation, centrifugation, media filtration, distillation, and solvent extraction are just a few of the traditional processes used in solid/liquid and liquid/liquid separations needed

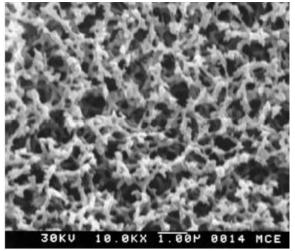
in the sector. Since their debut in the food industry about 30 years ago, membranes have found both large-volume and niche applications across a range of food and beverage industries, including fluid milk, cheese, and other dairy products; grain and oilseed products; beer, wine, and soft drinks; frozen, canned, preserved, and juiced fruit and vegetables; sugar and other sweeteners; meat, poultry, and seafood products; and various miscellaneous foods and food additives.

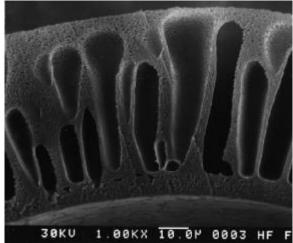
Reasons for concentration

- 1. To increase the solid concentration.
- 2. Removal of large amount of water reduces storage and transportation costs.
- 3. Removal of water helps to reduce the microbial load, thereby favoring an increase in the shelf-life of the liquid foods.
- 4. In the sugar industry, concentration is used as a pretreatment in to crystallization of sugar.
- 5. In the wine industry, concentration is sometimes used to raise the alcohol content to a prescribed level.

Membranes

Membranes are of either isotropic or anisotropic. An isotropic membrane has uniform pores all the way across the membrane thickness, while anisotropic membrane consists of a thin layer of selective material on the surface of a porous backing. Microfiltration membranes are isotropic, while the selective, high flux membranes are used in Ultrafiltration and Reverse Osmosis which are often anisotropic. The manufacturing processes result is a number of different membrane structures such as, microporous, asymmetric, composite, etc. Figure 1.1 illustrates some of these structures through photomicrographs.





Symmetric microporous membrane (Cross Section); mixed cellulose ester with a 2 μm nominal pore size. (courtesy of Poretics)

Hollow fiber membrane (Cross-Section) polysulfone with 500,000 nominal molecular weight cutoff (courtesy of Romicon).

Fig. 1.1. Different membrane structures (Jatal D. Mannapperuma, 1997)

How pores are formed

Membranes are formed by casting the sheets using a polymer solution in a volatile solvent followed by evaporation of the solvent. Removal of solvent leaves a porous structure in the membrane. Large pore membranes are produced by subjecting a non porous polymeric membrane to high energy radiation.

Membrane Characteristics

- a. Mean pore size
- b. Range of pore size distribution
- c. Membrane thickness
- d. Pore configuration.

Commercially available membranes

- **Cellulose** acetate
- Real Polyvinyl chloride
- R Polycarbonate
- R Polyamide
- **Reserve** Polysulphone
- R Polyacrilonitrile
- Alumina

™ Zirconium oxide

Membrane Separation Process

A form of filtration which employs selective membranes as the filter medium is used to separate solute, macro molecules, and small suspended particles in liquids. A thin membrane having small pore size and with selectivity for passing solute or solvent is used. The solvent and small molecules pass through the membrane and other solutes, macro molecules or suspended solids are retained. There are two types of filtration. They are Dead end filtration and Cross flow filtration.

In conventional **dead-end filtration**, particles retained by the filter build up with time as a cake layer which results in increased resistance to filtration. This requires frequent cleaning or replacement of filters.

In **cross-flow filtration** the bulk phase under pressure is forced to flow along the surface of the membrane, sweeping the retained particles so that the cake layer remains relatively thin and the resistance to filtration remains low. This allows relatively high fluxes to be maintained over long periods of time. Figure 1.2 illustrates the difference between these two modes of filtration.



Fig. 1.2. Dead-end and cross-flow filtration.

Cross flow filtration is the most efficient method used to obtain high solids concentration in the product. The liquid passing through the membrane is called Permeate and the fraction retained is called retentate (concentrate). The fluid entering the membrane is the feed.

Principle of separation and forces involved

In all the three processes hydraulic pressure (through a pump) is used to provide the force for permeation. The process is simple, involving only the pumping of the liquid mixture across the appropriate membrane. This is depicted in the fig.1.3. The difference in the thermodynamic activity on either side of the membrane is the driving force for the permeation of solutes and solvent. Pure solvent is withdrawn as permeate, leaving a concentrated solution (retentate) on the high pressure side of the membrane.

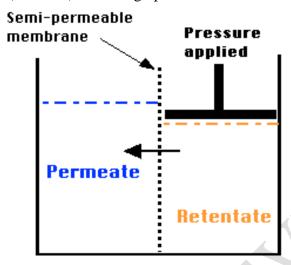


Fig. 1.3. Principle of membrane separation process

Membranes used for different Separation Process

Plyproylene Microfiltration (MF)

Polysulfone Ultrafiltration (UF), Gas Separation (GS)

Polyimide Gas Separation

Polyamide Reverse Osmosis (RO)

Polyacrylonitrile Ultrafiltration

Cellulose Microfiltration, Ultrafiltration, Reverse Osmosis

Different types of separation process

The different types of membrane separation processes in practice are

- 1. Microfiltration (MF)
- 2. Ultrafiltration (UF)
- 3. Reverse Osmosis
- 4. Electrodialysis

In recent years, above processes is gaining importance for processing liquid foods. These processes normally operate at ambient temperature, thereby reducing the thermal damage to the product and retaining the color, flavor/aroma and nutritive components of the product. Studies have shown that membrane applications can be less energy intensive than evaporation and freeze concentration.

1. Microfiltration

In this process, large molecules (e.g. fat globules) and suspended particles are held by the membrane while the remaining components of the solution pass through the membrane. MF resembles conventional coarse filtration and can selectively separate particles with molecular weights greater than 200 kDa. The pore sizes of microfiltration membranes are in the range of 0.05 to 10 μ m and the porosity of the membrane is about 70 per cent. Membrane thickness is in the range of 10 to 150 μ m. In microfiltration the applied pressure is in the range of 0.1 to 2 bar. Microfiltration finds application in cell harvesting, clarification of fruit juice, wastewater treatment, separation of casein and whey protein and separation of oil—water emulsions.

2. Ultrafiltration

This process is mainly used for clarification, concentration and purification of fruit juices, natural colors etc. The membranes are made up of polysulphone, polyvinyldene fluoride and cellulose acetate of pore size 1–100 nm. The applied pressure is in the range of 1–10 bar. Ultrafiltration is also used for the separation of high molecular components from low molecular components having applications in the food, dairy, pharmaceutical, textile, chemical, paper and leather industries. The various applications in the food and dairy industry are concentration of milk, recovery of whey proteins, recovery of potato starch and proteins, concentration of egg products and clarification of fruit juices and alcoholic beverages.

Diafiltration is a specialized type of ultrafiltration process in which the retentate is diluted with water and re-ultrafiltered, to reduce the concentration of soluble permeate components and increase further the concentration of retained components.

3. Reverse Osmosis

In this process the concentration of solute in the solution (feed) will increase by the flow of water (or solvent) across the membrane to a dilute solution. This can be accomplished by applying the pressure in excess of the osmotic pressure (10 to 100 bar) of the solution. RO removes most of the organic compounds and up to 99 per cent of all ions. This process achieves rejection of 99.9 per cent of viruses and bacteria and was the first cross flow membrane separation process to be widely commercialized. The RO involves dense membranes having pore size of <2 nm. The porosity of the membrane is

about 50 per cent. The separation mechanism is based on solution diffusion across the membrane. Membranes are made up of cellulose triacetate, polyether urea and polyamide. RO finds application in the concentration of liquid foods such as fruit juices, milk, etc. and desalination of brackish and seawater. Hyperfiltration is the same as RO.

The separation through three processes can be shown by means of fig.1.4.

4. Electrodialysis

Electrodialysis is used for demineralization of milk products and whey for infant formula and special dietary products. Also used for desalination of water.

Principles of operation:

Under the influence of an electric field, ions move in an aqueous solution. The ionic mobility is directly proportioned to specific conductivity and inversely proportioned to number of molecules in solution.

Charged ions can be removed from a solution by synthetic polymer membranes containing ion exchange groups. Anion exchange membranes carry cationic groups which repel cations and are permeable to anions, and cation exchange membranes contain anionic groups and are permeable only to cations. Electrodialysis membranes are comprised of polymer chains - styrene-divinyl benzene made anionic with quaternary ammonium groups and made cationic with sulphonic groups. 1-2V is then applied across each pair of membranes.

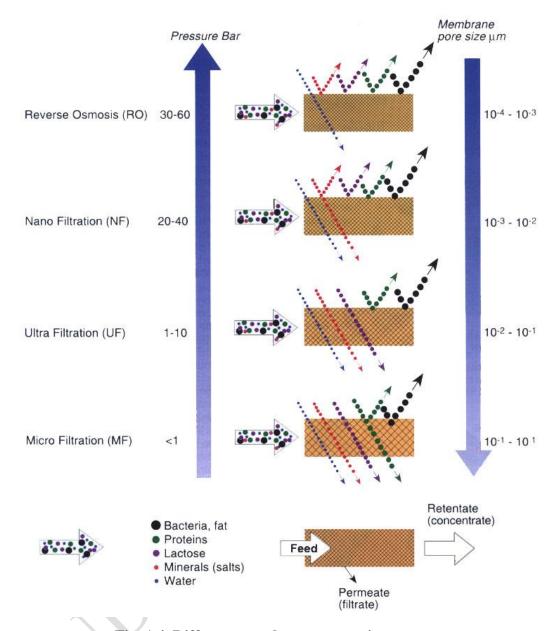


Fig. 1.4. Different membrane separation processes

Process:

Amion and cation exchange membranes are arranged alternately in parallel between an anode and a cathode. The distance between the membranes is 1mm or less. A plate and frame arrangement similar to a plate heat exchanger or a plate filter is used. The solution to be demineralized flows through gaps between the two types of membranes. Each type of membrane is permeable to only one type of ion. Thus, the anions leave the

gap in the direction of the anode and cations leave in the direction of the cathode. Both are then taken up by a concentrating stream.

Membrane Modules

Membranes are assembled as modules that are easily integrated into systems containing hydraulic components. Primary objectives of module design are to accommodate large membrane areas in a small volume, to withstand the pressures required in filtration, and cross-flow velocities required to maintain a clean membrane surface. Plate & Frame, tubular, hollow fiber and spiral-wound are common module configurations.

a) Plate and Frame Module

In flat plate modules two flat sheets of membranes are separated by a support plate which also contains the permeate channels. These membrane sandwiches are separated by a spacer plate which also has the feed-flow channels. Alternate layers of membrane sandwiches and spacer plates are assembled and held together by bolts. This module can withstand high pressures but is susceptible to fouling by suspended particles.

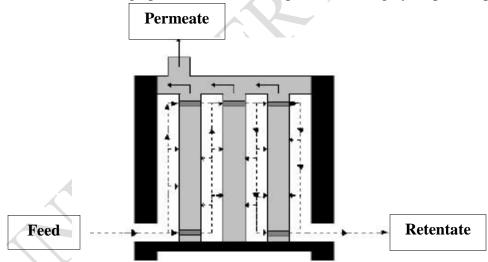


Fig. 1.5. Schematic view of Plate and Frame module

In Fig. 1.5. the arrows show the upstream and permeate paths. The upstream leaves as the retentate and is enriched in non-permeate. Permeates is collected from channels in support plates and leaves enriched in the most permeable component.

Advantages: Easy to clean and replace membranes.

Disadvantages: Low membrane area per volume

b) Tubular Module

A schematic diagram of tubular membrane is shown in Fig. 1.6. Tubular modules consist of membranes formed inside tubes, typically 6 to 25 mm in diameter, and are of three basic types.

- > Self supporting tubular modules
- > Externally supported tubular modules
- ➤ Monolithic tubular modules

A self supporting tubular module consists of several membrane tubes held together as a pack and connected to common headers and permeate vessels. Typical modules have 1, 7, or 19 tubes. This type is limited by its structural strength to low-pressure applications.

Externally supported tubular membrane modules consist of tubular membranes held inside individual porous support tubes. Several such tubes are assembled to common headers and permeate vessels to form a module. This type can withstand high pressures and is therefore used in reverse-osmosis applications.

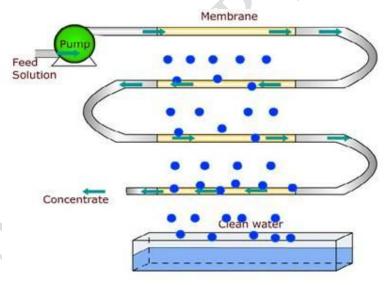


Fig. 1.6. Schematic view of Tubular module (courtesy of Paulsingh)

In monolithic tubular modules several tubular channels are formed in a porous block of material and the membrane layer is formed inside the tubes. All types of tubular modules can accommodate suspended particles.

c) Hollow fiber:

Hollow fiber modules consist of bundles of hollow fibers typically 0.5 to 3 mm in diameter sealed into plastic headers and assembled in permeate casings. The feed passes through the central bore and permeate collects in the outer casing. Hollow fibers are self supporting hence these modules are for use in low-pressure applications only. These can accommodate moderate levels of suspended particles. The illustration of hollow fiber membrane and its flow patterns are shown in Fig. 1.7 & 1.8.

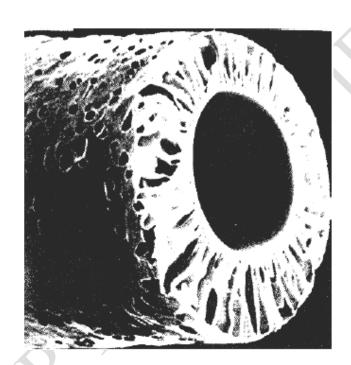
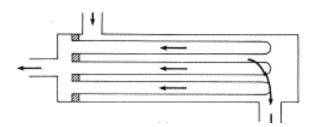
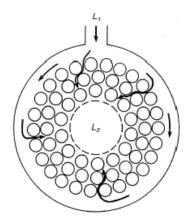


Fig. 1.7. Magnification of hollow fiber membrane
(Outer diameter between 50 to 200 microns)



Flow pattern inside the bundles (side view) show hollow fiber with left end sealed and right end open to exit manifold.



Flow pattern inside the bundles

Fig. 1.8. Flow pattern of hollow fiber

d) Spiral-Wound Module

Spiral modules are made by placing a plastic mesh which acts as the permeate channel between two membrane layers and sealing three sides. Fourth side of this sandwich is attached to the permeate tube, another plastic mesh which acts as the feed channel is laid over it and the assembly is wrapped around the central permeate tube. This module also can withstand high pressures but is susceptible to fouling by suspended particles. Spiral membranes are only used for nano filtration and Reverse Osmosis (RO) applications. Fig. 1.9 shows the spiral - wound module

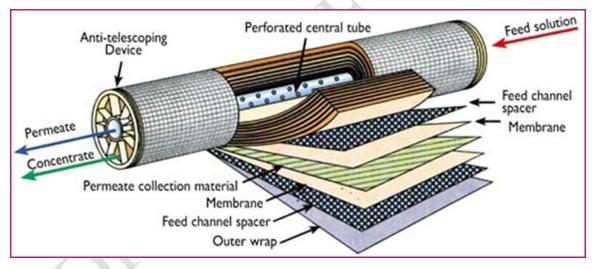


Fig. 1.9. Spiral - Wound Module

Applications of different types of membrane processing technique in food industries

The various application of membrane processing in dairy, juice and sugar is shown in Table. 1.1. Some of the other applications of membrane processing are wine, brewery, waste water treatment etc.

Industry	Application	Process	Module	Membrane
Dairy	Milk Concentration	RO	Spiral	CA, TFC
	Whey Concentration	RO	Spiral	CA, TFC

	Whey Fractionation	UF	Spiral	PS, PVDF, PES
	Lactose Concentration	RO	Spiral	CA, TFC
	Milk Pasteurization	MF	Tubular	Ceramic
	Desalting	NF	Spiral	TFC
Juice	Clarification	MF	Tubular	Ceramic
		MF	Hollow fiber	PS, PE
		UF	Hollow fiber	PS
		MF/UF	Tubular	PVDF, PS
	Concentration	RO/NF	Spiral	TFC
		RO/NF	Tubular	TFC
		RO/NF	Hollow fine fiber	TFC
	Caustic recovery	MF	Tubular	Ceramic
Gelatin	Concentration	UF	Spiral	PS
Corn Sweetener	Dextrose clarification	MF	Spiral	PS/PES
Sugar	Clarification	MF/UF	Tubular	Ceramic
	Pre concentration	RO	Spiral	TFC

Note: UF RO reverse osmosis; ultrafiltration; MF microfiltration; NF nanofiltration; CA = cellulose acetate; TFC film composite; thin polyvinylidine PS polysulfone; **PVDF** difluoride; PES = polyethersulfone; PE = polyester.

Table.1.1. Application of membrane processing in dairy, juice and sugar industry

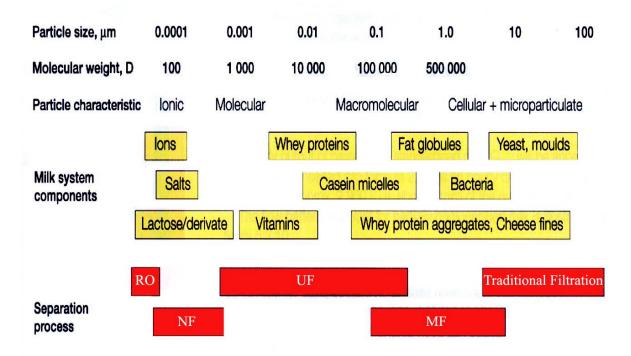


Fig. 1.10. Spectrum of application of membrane separation processes in the Dairy Industry

Wine and Brewery

In wine making, diatomaceous earth filters and pad filters are being replaced by tubular and hollow fiber microfiltration membranes in the clarification process. Ultrafiltration has been effective in replacing fining to a limited scale. Concentration of wines using reverse osmosis accelerates the tartrate precipitation process in cold stabilization. Reverse osmosis is used to produce low alcohol wine.

Microfiltration through ceramic membranes is used to produce cold sterilized beer. Reverse osmosis is used to produce low alcohol beer. Vapors leaving beer stills are condensed and treated by reverse osmosis membranes to reduce air pollution and to recover thermal energy.

Animal Products

Blood is a high-volume waste product of abattoirs. Byproduct recovery from waste blood using membranes includes separation and purification of blood cells by ultrafiltration, concentration of plasma by ultrafiltration, and concentration of homogenized blood. These applications employ tubular, spiral, and flat plate modules.

Gelatin is an animal byproduct containing colloidal proteins formed by hydrolysis of collagen. The hydrolysate containing 3 to 15% solids is concentrated and dried to produce gelatin powder. The traditional method involved steam evaporation and drum drying. Ultrafiltration was found to be superior to steam evaporation due to less thermal damage and lower cost. Ultrafiltration also allows leakage of salts thus producing a superior product. In clarification of gelatin, diatomaceous earth filters have been replaced by tubular microfiltration systems.

Process Effluents

Food processing plants discharge large volumes of water containing suspended and dissolved solids. Increasing effluent disposal costs in urban areas have forced food processors to look for advanced effluent treatment technology. When the effluents disposal problem is related to dissolve organic matter or salts, reverse osmosis becomes the technology of choice. The brining and pickling industry has employed microfiltration to clarify brines for reuse and reverse osmosis for concentration of brining waste for alternative disposal. Effluent containing dissolved organic matter is treated biologically. Aerobic treatment is the best choice for dilute effluents while anaerobic treatment is better suited for more concentrated effluents. Membrane treatment can be used to concentrate the dilute effluents for anaerobic treatment with the added benefit of water recovery.

Advantages of membrane processing

- Simple in operation. It involves only a bulk fluids using mechanical energy.
- Does not involve phase change.
- **A** Can be done at ambient temperate.
- * Requires low energy compared to other dewatering method.

Limitations of membrane processing

- Cannot be dried
- Cost of the membrane
- Concentration polarization
- Constraints on the maximum attainable concentration (only up to 25 to 30°Brix).

Economic feasibility

In general, membrane applications cannot be justified on savings on disposal costs alone. Recovery of byproducts, chemicals, and heat can complement the benefits and make the application cost effective. Recovery of sugars from rinse waters and recovery of chemicals from cleaning water are some examples where membrane systems have found to be economically feasible.

Conclusion

The use of membrane technology in the food and beverage industries was dominated for many years, and to a large extent still is, by applications in the treatment of milk and whey. Other application such as juice and wine clarification, and protein processing are also increasing. Wastewater treatment will continue to be the primary pollution prevention focus for food and beverage processors. But, another industry trend for minimizing waste and improving the bottom line is converting food byproducts to value-added products. Many conversion activities offer opportunities for membranes: transforming salts in waste to useful acids and bases, recovering blood proteins from slaughterhouse wastes, or fermenting corn starch to ethanol, corn oil and other corn co-products.

In addition to the common food and beverage processing applications, recent developments in membrane filtration technology are being used to concentrate nutraceuticals and functional food ingredients to enhance the quality of food products. Examples include the concentration of soy isoflavones from water extracts of soybeans and concentration of green tea leaf extracts. The advantage of membrane-based processing is that flavors and functional food components are preserved because the separation is achieved without thermal processing.

Reference:

 Arthanareeswaran, G., Thanikaivelan, P., Srinivasn, K., Mohan, D., & Rajendran, M. (2004). Synthesis, characterization and thermal studies on cellulose acetate membranes with additive. European Polymer Journal, 40(9), 2153-2159.

- 2) Bhattacharjee, C., Saxena, V. K., & Dutta, S. (2017). Fruit juice processing using membrane technology: A review. Innovative food science & emerging technologies, 43, 136-153.
- 3) Daufin, G., Escudier, J. P., Carrère, H., Bérot, S., Fillaudeau, L., & Decloux, M. (2001). Recent and emerging applications of membrane processes in the food and dairy industry. Food and Bioproducts Processing, 79(2), 89-102.
- 4) Girard, B., & Fukumoto, L. R. (2000). Membrane processing of fruit juices and beverages: a review. Critical Reviews in Food Science Nutrition, 40(2), 91-157.
- 5) Mannapperuma, J. D., & Santos, M. R. (2004). Reconditioning of poultry chiller overflow by ultrafiltration. Journal of food process engineering, 27(6), 497-516.
- 6) Paraskeva, C. A., Papadakis, V. G., Tsarouchi, E., Kanellopoulou, D. G., & Koutsoukos, P. G. (2007). Membrane processing for olive mill wastewater fractionation. Desalination, 213(1-3), 218-229.
- 7) Tamime, A. Y. (Ed.). (2012). Membrane processing: dairy and beverage applications. John Wiley & Sons.
- 8) Ulbricht, M. (2006). Advanced functional polymer membranes. Polymer, 47(7), 2217-2262.
- 9) Valentas, K. J., Rotstein, E., & Singh, R. P. (1997). Handbook of food engineering practice. CRC press.