THE POTENTIAL APPLICATION OF MEMBRANE PROCESSES IN THE CANE SUGAR INDUSTRY

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Abstract

The potential uses of membrane processes, such as cross-flow microfiltration, ultrafiltration and reverse osmosis in the sugar industry are described. Emphasis is placed on the commercially available membrane modules and configurations with their performance parameters and limitations. The application of membrane technology in cane sugar processing has been inhibited by a number of special problems which are discussed, together with some possible ways of overcoming them. A review of investigative work from the literature, including some experimental work undertaken by the Sugar Milling Research Institute (SMRI), is given.

Introduction

Membrane filtration is gaining popularity as an alternative to conventional industrial separation methods. It became popular in the early 1960s when asymmetric membranes were developed. Before this, membrane processes were hardly used in industry because of low fluxes, low selectivities, difficulties in fabrication and because conventional separation methods were cheaper.

Since the first asymmetric reverse osmosis membranes became available in the early 1960s, membrane technology has developed markedly resulting in the present day commercialisation of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), which is also called hyperfiltration.

The membrane processes discussed in this paper are pressure driven. These should not be confused with membrane processes such as dialysis or electrodialysis, which use driving forces such as concentration differences and electrical gradients.

Microfiltration, ultrafiltration, nanofiltration and reverse osmosis

The most useful definition (Schweitzer, 1979) of separation processes is based on the smallest particles or molecules which can be retained by the various membranes (see Figure 1). A composite membrane that was able to separate organic substances from monovalent anions was developed in the early 1980s. The properties of this membrane prevented it from being easily characterised as either RO or UF, and it was therefore classed as a nanofiltration membrane.

The separation of the constituents of sugar process streams in a raw house or refinery (or in a distillery) are summarised for the UF and RO filtration processes in Figure 2.

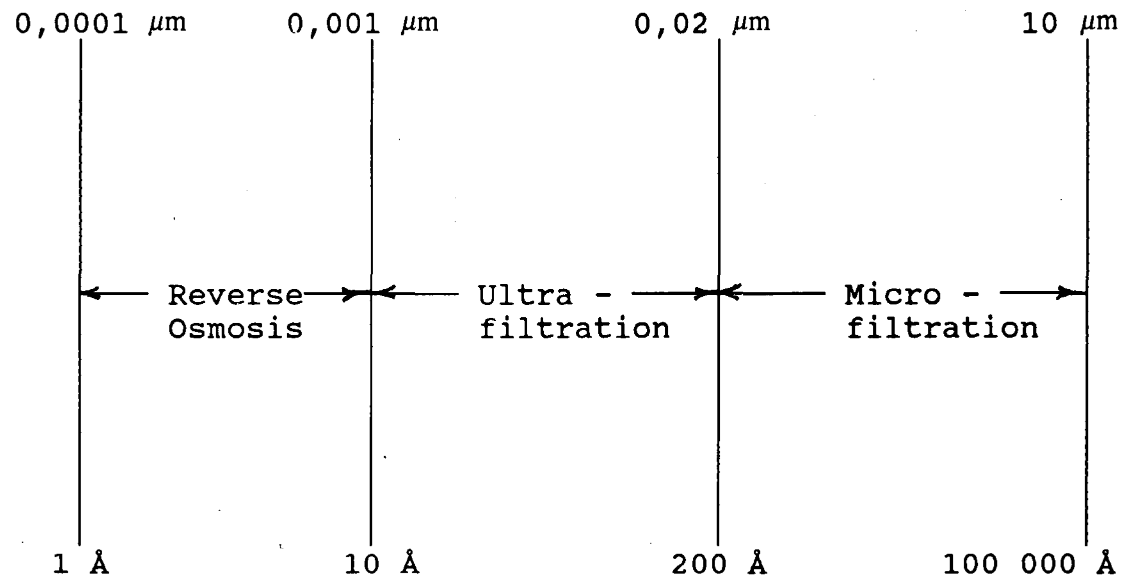

FIGURE 1 Definition of pressure driven membrane processes based on the smallest particle retained

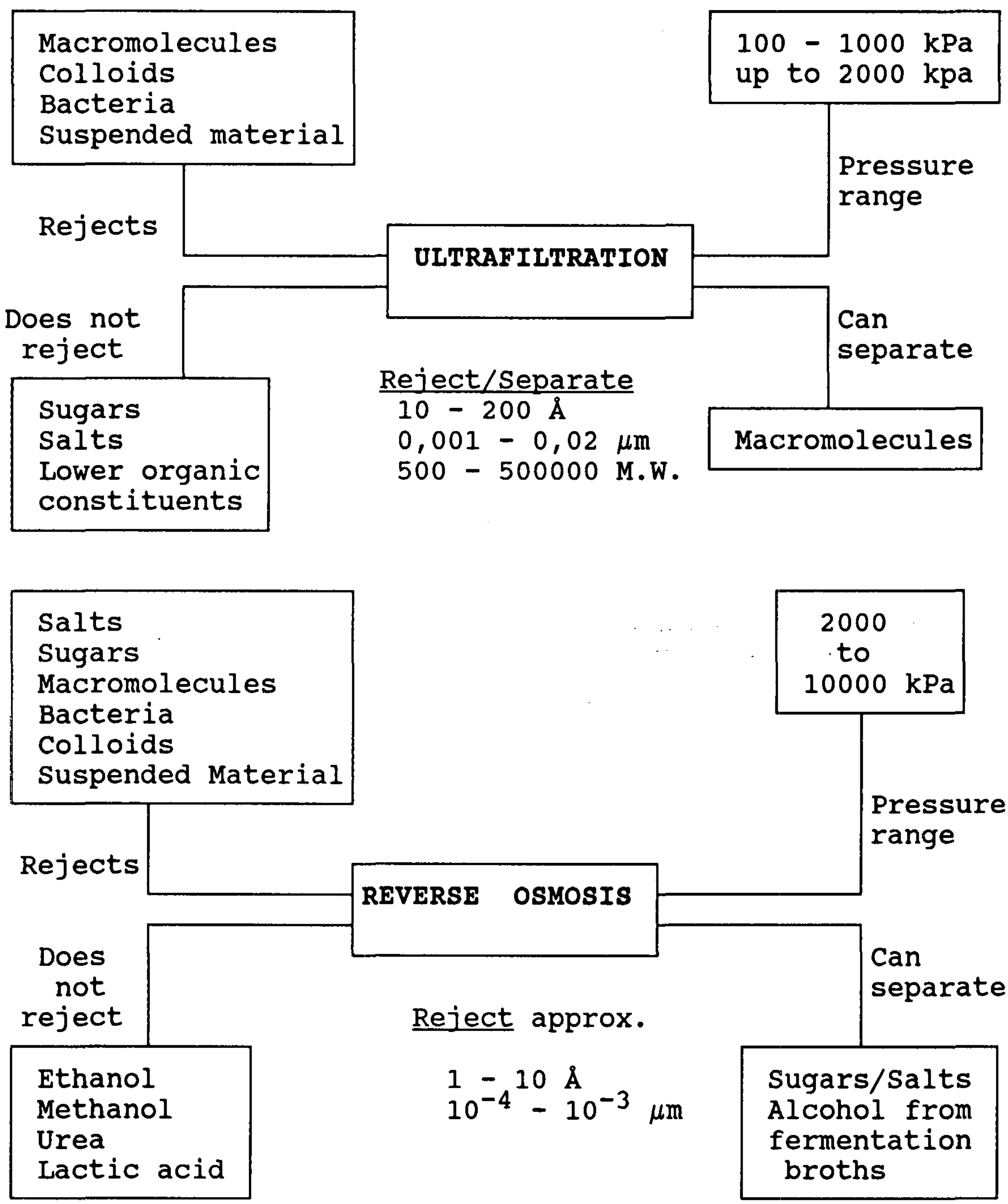

FIGURE 2 UF and RO separation characteristics for sugar mill process streams

Flow configuration, modules and materials

Flow configuration

The term 'crossflow filtration' (CF) appears frequently in the literature along with 'membrane filtration' and 'microfiltration'. The CFMF competes with the traditional 'dead end' technique. CF uses the shearing effect of the feed stream flowing parallel (or tangentially) to the filtration medium to prevent the formation of filtercake, to maintain relatively high fluxes, as compared with 'dead end' filtration (see Figure 3). In dead end filtration the feed stream flows at right angles to the filter medium, and this results in a rapid flux decline due to blocking of the membrane pores by the solute and a build up of filtercake.

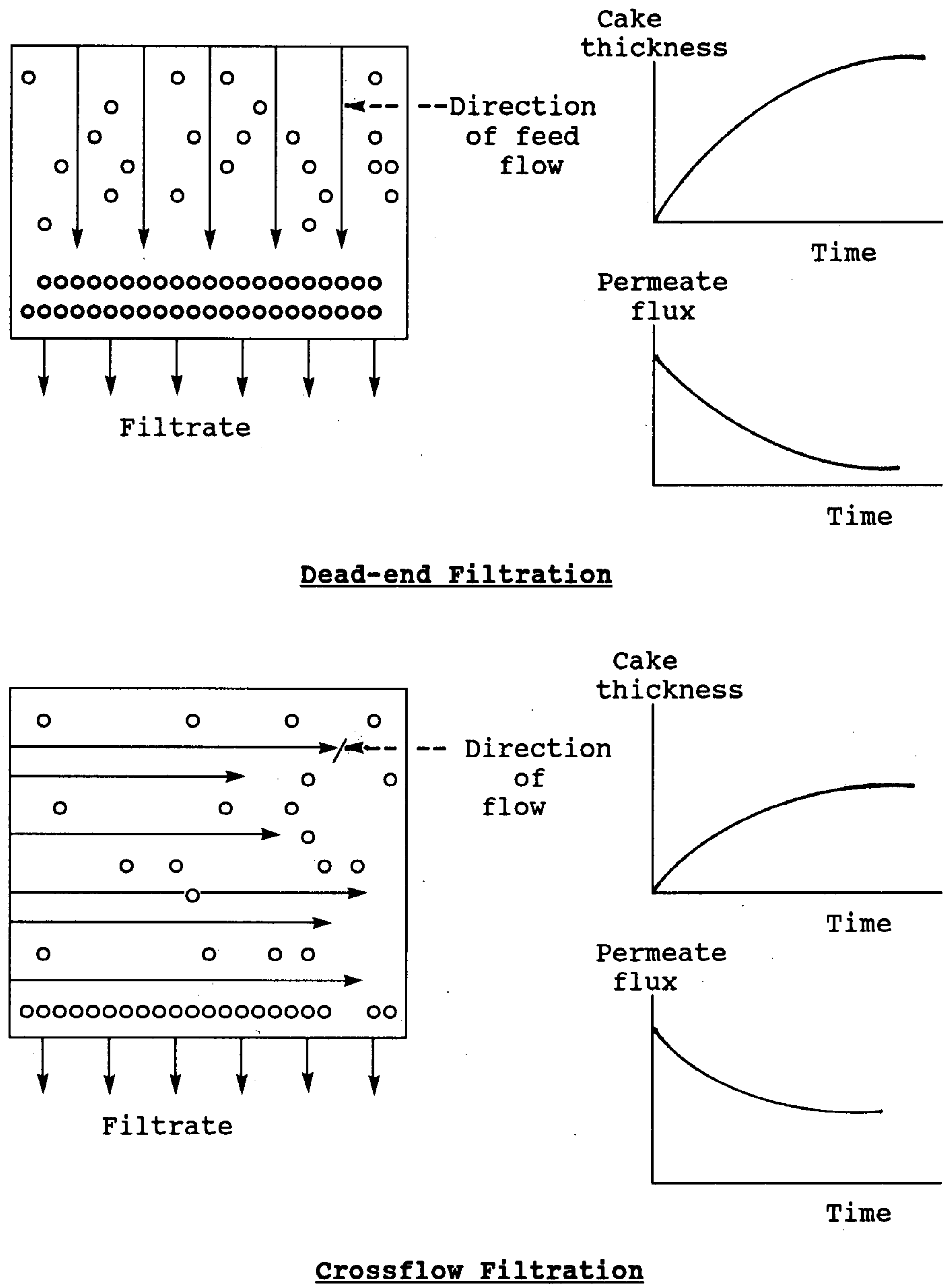

FIGURE 3 Flow configurations

Module types

Tubular: All tubular modules are used in the crossflow mode.
Membrane area per unit volume is small compared with the spiral wound and hollow fibre systems, but this arrangement is less susceptible to fouling. When fouling occurs, the tubular membranes offer the advantage of possible mechanical as well as chemical cleaning.

Spiral wound: A spiral wound module consists of sandwiched layers of supporting material, membrane layer, and spacer material to facilitate permeate flow. All these layers are spirally wound around a permeate collection pipe. This type of configuration offers more membrane area per volume than tubular systems but is more vulnerable to fouling. Packing density is around 1 000 m2/m3.

Hollow fibre: These are made with membrane on both the inside and the outside of the fibre. The fibres have inside diameters of 500-1 000 microns and are formed into bundles with epoxy adhesive applied at both ends. Fibres are encapsulated in a low pressure vessel. Feed enters the device at one end and leaves the fibre bores at the other. Permeate flows through the substructure and is removed through the product port. These types of membranes have the highest packing densities.

Flat membranes: These consist of plates with membranes on both sides covering a drain grid in which the permeate is to be collected. Flat membranes are used in dead end filtration as well as in crossflow filtration. Packing density is about 500 m2/m3 for the plate and frame modules.

Materials for construction of membranes

The materials used for membrane fabrication include a range of modified natural, (e.g. cellulose acetate) products and synthetics which use various polymers. These polymers can operate at relatively high temperatures (up to 130°C) and are tolerant of extremes of pH. Dynamic membranes normally involve the use of metallic oxide (e.g. ZrO2, Al2O3 etc.) on a polyelectrolyte, such as polyacrylic acid.

Flux decline in membrane processes

A major reason why membrane processes are not more extensively used is the flux decline during filtration. This is caused by several phenomena, on and near the membrane.

Resistances which can occur during filtration are shown in Figure 4. Except for the resistance of the membrane (Rm), which is always present, resistance increases during filtration. Pores can become blocked by the solute (Rp) and adsorption of the solute on the walls of the membrane pores results in lower permeability (Rs).

Another very important phenomenon is the so-called 'concentration polarisation', which is due to the solute being retained by the membrane and the solvent passing through it. The solute therefore accumulates at the membrane interface to form a layer with a relatively high concentration. This is expressed by the additional resistance Rcp. This phenomenon also results in a higher osmotic pressure 'π' at the membrane interface (even when macromolecular solutions are used) which leads to a decrease in the driving force, 'applied pressure π'. Finally the concentration at the membrane interface can reach such high values that the concentrated solution will change to a gel, with a resistance Rg.

The flux decline phenomenon (van den Berg and Smolders, 1988) can be divided generally into two main categories - concentration polarisation, which is reversible and takes place immediately, and fouling which is irreversible and a long term phenomenon.

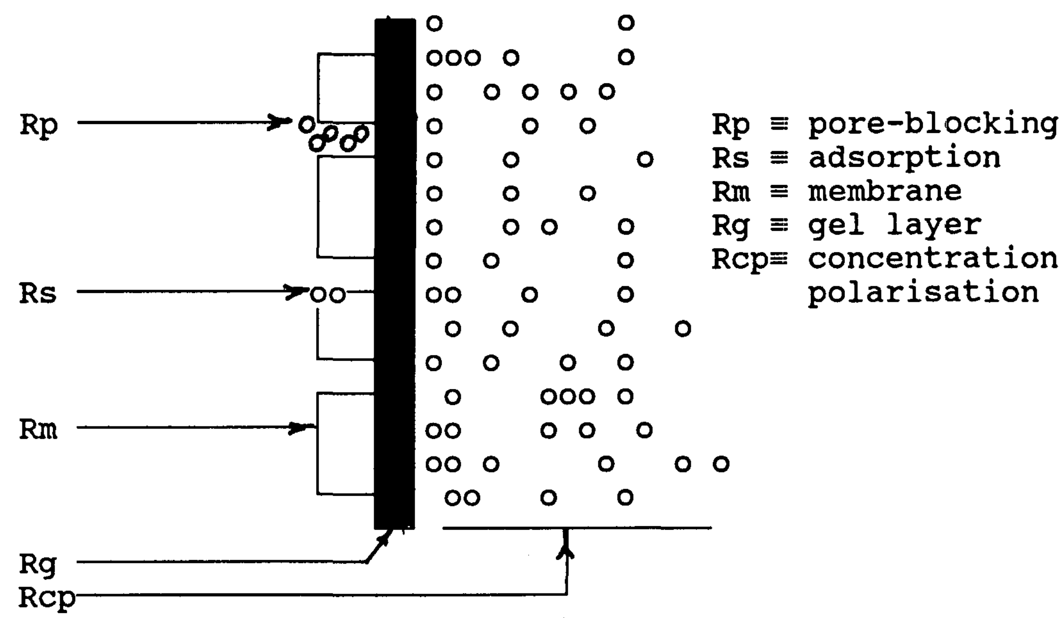

FIGURE 4 Possible resistances to solvent transport

Concentration polarisation may be controlled (Forbes, 1972) in several ways, some of which are given below:

- By reducing the flow rate, the small particles will follow the flow stream lines more easily and pass through without capture
- High crossflow velocity will sweep away part of the accumulated layer
- Pre-filtration will reduce the number of particles retained on the membrane surface or in the pores
- Backwashing depends on the morphology and the size of the particles, e.g. it does not work on gummy or gelatinous deposits
- Ultrasonic vibrations will tend to prevent accumulation of particles by dispersing them back into the bulk of the solution.

Fouling can be caused by precipitation or through an interaction between the membrane and the foulant due to polarity or charge effects built into the membrane. The techniques used to reduce fouling involve either minimising the formation of deposits on the membrane or removing the deposits already formed. The following effects are used to reduce or prevent fouling (Milisic and Bersilion, 1986):

- Pre-treatment such as filtering, dissolving and adding dispersants
- Fluid shear rate and pressure control
- Hardware configuration and channel geometry
- Mechanical or chemical cleaning
- The use of electric fields
- The use of abrasives, filtration aids, backwashing and pulsations.

Experimental work and pilot plant studies on the use of membranes in the sugar industry

Crossflow microfiltration

Decloux and Punidadas (1990) carried out crossflow microfiltration (CFMF) using ceramic membranes of different pore diameters, viz. 0,1, 0,2, 0,5, 0,8 and 1,4 microns. From their tests on beet juice they found that colour and turbidity of the filtrate generally increased with pore diameter but the effects were different for each pore diameter:

- A 0,1 m membrane removed practically all the hazy material, but colour was never lower than 2 950 ICUMSA units which corresponded to 47% colour elimination
- Between pore diameters of 0,1 and 0,5 m turbidity and colour elimination did not vary much
- With the membrane of 1,4 m pore size, there was an 80% turbidity removal and a 20% colour elimination.

Complete studies on the influence of operational parameters were limited to the dependence between trans-membrane pressure and crossflow velocity. The following conclusions were drawn from results obtained in these experiments:

- Crossflow velocity improved filtrate flux without modifying quality
- Pressure increase was only envisaged for membranes with small pore diameters. However the flux gain was very low
- In the start up method for small pore membranes the velocity should be high from the begining to reduce the thickness of the layer which forms on the surface. For large diameter pore mebranes, the velocity should be low at the begining to increase the porosity of the deposited particle layer
- Temperatures up to 90°C significantly improved the filtrate flux
- Backflush did not give the expected increase in the flux.

Under the tested operational parameters, flux stabilised at about 38 l/m2/h.

Rhoten & Groves (1989) tested the CFMF concept on the processing of raw beet juice. They used patented equipment consisting of a commercial arrangement of 30 parallel tubes 12,5 mm in diameter. Pilot scale operation of the CFMF unit on raw juice showed consistent purity improvement over a broad range of raw juice qualities. The effectiveness of this separation did not seem to be influenced appreciably by pH or operating pressure. The flux rate was in the range of 35-45 l/m^2/h. This flux rate was sustainable over long operating periods. They concluded that CFMF of raw juice coupled with certain secondary treatment processes was technically feasible for the partial or complete replacement of the lime/CO^2 juice purification.

Ultrafiltration

The Danish Sugar Corporation (DDS) started research on the use of membranes in 1964 (Madsen, 1973). Traditional cane juice purification does not completely eliminate substances such as dextrans, starches, fat, waxes and colourants, whereas UF could remove these high molecular weight compounds. It is difficult to judge what the improvement in juice quality would mean to sugar quality, but Madsen (1973) states that it is not unlikely that a good quality mill white sugar could be obtained directly in a raw sugar factory if UF membranes were included in juice purification. UF membranes with at least a 5 000 molecular weight cutoff have to be used to obtain colour removal of about 80%. Madsen (1971) reports a flux of 50 to 130 l/m^2/h for UF of clarified juice, which corresponds to 50-120 t/day in a 42 m^2 production module.

In 1985 Crees (1986) set up an UF plant, using Patterson Candy International's (PCI) BX1, BX6 and FP10 membranes. The membrane characteristics are presented in Table 1.

Table 1

PCI ultrafiltration membranes used for clarified juice

Membrane	Mol.wt. cutoff	Water flux* l m^2/h	Operating conditions		
			Pressure (kPa)	Temp. (°C)	pH
BX1	20 000	> 40	1 500	70	2-12
BX6	25 000	> 45	1 500	70	2-12
FP10	100 000	>200	1 000	70	2-12

* at 100 KPa, 20°C

It was expected that the BX1 and BX6 membranes would retain some colour, but the FP10 with its high cutoff was not expected to affect colour at all. The fact that all three membranes give similar results, as shown in Table 2, suggests that the separation process is controlled primarily by the formation of a gel layer at the surface, rather than by the membrane itself. This phenomenon is referred to as concentration polarisation.

Allowing for a two hour cleaning cycle twice a day and an average flux of 45 l/m^2/h, a factory processing 500 t/h of clarified juice would require a total membrane area of 13 500 m^2. The installed cost of such an operation in 1985 was approximately 20 000 000 Australian dollars.

Table 2

Rejection characteristics of membranes processing clarified juice

Membrane Type	Nominal cutoff	Rejection %			
		Starch	Dextran	Colour	Turbidity
BX1	20 000	>98	100	52	100
BX6	25 000	>98	100	50	100
FP10	100 000	>98	100	50	100

No attempt was made to assess the benefits of ultrafiltration to subsequent processing. However, the complete removal of high molecular weight polymers from juice should result in lower viscosities on the pan stage, paticularly the low grade station. This in turn should lead to some improvements in boiling, crystallization and centrifuging rates, which may partly offset the other operating costs. Crees concluded that the capital and operating costs were too high for the process to be economically viable.

The effects of several kinds of pre-treatments on the ultrafiltration flux of cane juice were studied by Kishihara *et al.* (1981). It was thought that the wax from the cane stalk and suspended materials in the juice could unfavourably affect the flux during ultrafiltration. The objective of the investigations was to optimise the flux by various pre- treatments of the sugarcane stalk and of the expressed raw juice. Colouring matter, starch and substances insoluble in acidified ethanol, which are not easy to eliminate by conventional juice purification, were examined in the ultrafiltrate and compared with those in the juice clarified by lime defecation.

The results showed that:

- Flux was not improved by removal of wax from sugarcane stalks
- Liming was the most effective pre-treatment to improve the flux
- Liming the juice to pH 7,5 gave the highest flux and was safer to counter any chemical degradation of the juice
- Increasing the temperature of the juice from 30 to 60°C almost doubled the flux
- Membranes with molecular weight cutoff levels of 10 000-3020000 were more suitable for purification of the juice.
- Clarification by ultrafiltration was superior to ordinary lime defecation because it gave juices of higher purity and lower colour, free from starch and substances insoluble in acidified ethanol.

Reverse osmosis

Madsen (1971) and Baloh (1976) have investigated the use of RO as a partial replacement for evaporation. Currently this does not seem to be an attractive area for membrane application, for the following reasons:

- For RO, high pressures and expensive high pressure equipment are necessary
- Capital investment costs for RO membranes are high
- In most RO membrane types the filter surface area is very small in comparision with the equipment volume
- The membrane is susceptible to plugging, compaction and bacterial degradation and therefore needs good operational control and skilled labour
- In most cases pre-filtration of the solution is necessary
- Baloh reports an energy saving of 29% which is offset by greater use of electrical energy for pumping equipment.

Work in Hawaii (Anon, 1988) involved the use of PCI's ZF99 reverse osmosis membrane for the concentration of mixed juice. A steady decline in flux was reported and repeated cleaning could not restore the flux to the original levels. The study on juice concentration has been stopped until a membrane with better fouling resistance is developed.

Naito *et al.* (1986) dealt with the concentration of sweet water by reverse osmosis. They used a ROGA 4100 hollow fibre RO module, with a maximium operating pressure of 42 300 kPa. The results and conclusions were:

- The highest concentration of sweet water reached by reverse osmosis was about 30° brix in a laboratory test. In the factory, due to lower fluxes, concentrations in the range of only 10 to 20° brix were achieved
- The sugar rejection was 99,8% with solutions of 3 to 20° brix
- To use reverse osmosis in the refinery the following problems should first be overcome:
  (a) thermal stability of membranes
  (b) sterilisation of membranes
  (c) life of membranes.

Nanofiltration

Modern manufacturing techniques enable semi-permeable membranes with a more uniform pore size to be made. As a result, membranes for the separation of salts from sucrose are now commercially available. Generally referred to as nanofiltration membranes, they have a sucrose rejection rate of from 95 to over 99% and a monovalent ion rejection rate of less than 70%. Since the ash in sugar juice is predominantly composed of monovalent ions ($K+$ and $Cl-$), simultaneous removal of water and ash from juice is possible. Some of these membranes can withstand temperatures of 100°C (Anon, 1988) or higher and could be used for processing clarified juice. In a factory the process could be applied to partially remove ash and water from clarified juice, thereby making it possible to achieve the dual purposes. Naito *et al.* (1986) investigated the use of RO membranes to concentrate sweet water. They found limitations with respect to the thermal stability, bacterial resistance and life of the membrane. The nanofiltration membrane MPW SELRO MPT 30 overcomes these limitations. It has a 99% sucrose rejection rate with the additional benefit of ash removal. Komoto and Kishihara, (1978) investigated the use of UF and RO membranes for separation and re-use of regeneration effluent from decolourising ion exchange resin. They found UF membranes unsuitable due to insufficient elimination of colour. However, if the 'regeneration effluent' is to be recycled, then perhaps the organic foulants in the effluent could be removed by the use of an appropriate microfilter, followed by the use of a nanofilter such as FilmTec NF40 or NF70 (rejection rates for NaCl of 45 and 80% respectively) or by the use of MPW SELRO MPT30P, which has a higher maximum operating temperature of 80°C.

Tests conducted by SMRI

Ultrafiltration

UF tests were carried out using a Rhone Poulenc-Carbosep 2S37 pilot plant, which has a zirconium oxide membrane on a sintered carbon support medium. The filtration module is tubular, the 1,2 m long tubes having an internal diameter of 6 mm. The unit has 37 tubes per bundle and two bundles in series. The membrane area per bundle is 0,9 m^2, giving a total of 1,8 m^2. This unit has a maximum operating temperature of 121°C, an operational pH range of 0 to 14, an operating pressure of 10 MPa and a bursting pressure of 60 MPa. The average crossflow velocity is 4 m/s and the nominal molecular weight cutoff is 20 000 Daltons.

Ultrafiltration tests were carried out on diluted raw syrup at 14, 43 and 52° brix and diluted A molasses at 25° brix. The average test period was three hours. The clean water flux, which should be in the 170 to 190 l/m^2/h range, was checked at the start of each run. The average delivery pressure was controlled at 410 kPa. The temperature ranged from 61 to 80°C during the tests, a better temperature control being impossible due to the heat exchanger not being connected to the system. With the higher brix material there is an increase in temperature with recirculation due to the higher viscosity. After each test the system was rinsed and cleaned with a germicidal detergent. The results are presented in Table 3.

Table 3

Ultrafiltration of syrup and diluted A molasses at 400 kPa

Brix	Temperature °C	Flux l m^2/h	Colour elimin. %	Turbidity removal %
Syrup 14	68	170	17	88
Syrup 43	72	80	38	91
Syrup 52	74	80	40	86
A mol.25	70	140	17	88

Temperature was found to have an important effect on the flux. With 52° brix syrup at temperatures of 61, 74 and 100°C the respective fluxes were 60, 80 and 100 l/m^2/h. Crees (1986) reports an average flux of 45 l/m^2/h for clarified juice. With the Carbosep unit, for syrup diluted to 14° brix, a flux of 170 l/m^2/h at 74°C was attained. The purity rise as a result of the ultrafiltration of 14, 43 and 52° brix syrup was 0,9, 0,2 and 0,2% respectively.

An UF membrane with at least a 5 000 molecular weight cutoff has to be used to eliminate more than 80% of the colour. The lower cutoff membranes have a gel layer formed on them which act as secondary membranes, resulting in a greater colour elimination. Syrup treatment by UF has the advantage that the volume is smaller (20-25% on clear juice) and polymerised products formed during evaporation will be removed. The inorganic membrane systems, which can cope with high temperatures and viscosities, would enable these UF units to be installed after, for example, the second or third effect in a bank of evaporators.

Crossflow microfiltration

During the 1990 milling season, a pilot CFMF unit was used to conduct tests on various streams in a mill. The CFMF unit consists of 30 parallel tubes, 1,77 m in length and 12,5 mm in diameter. The unit has a total filtration area of 2 m^2. At each end of the tubular array a manifold is fitted. This directs the flow and allows a recirculation path to and from the pump. The nylon filter tubes have a bursting pressure of 600 kPa and an operating temperature of up to 90°C.

A pump with a 10 m^3/h volumetric throughput at 220 kPa and operating with a 220 V motor was recommended by the supplier. The unit can be operated with 30 tubes in parallel or with 10 tubes in series in three passes. The transmembrane pressure is controlled by a valve on the retentate line to the feed tank. The unit is robust, compact and simple to operate.

Some typical results on the fluxes and permeate quality attained after 30 minutes of filtration are presented in Table 4.

Table 4

CFMF of various streams in the mill

Stream	Average tube pressure kPa	Crossflow velocity ms	Flux l m^2/h	Colour elimin. %	Turbidity removal %
Clear juice	170	1,3	28	10	90
Presswater	180	1,9	32	11	98
filtrate*	195	1,8	initial 43 final 10	18	94
Anaerobic effluent**	195	1,9	initial 93 final 61	–	98

* Suspended solids 5 360 ppm. Flocculant addition of 50 ppm.
** Suspended solids 120 ppm. 50 ppm addition of $AlCl_3$.

The quality of the permeate with clear juice and presswater treatment can be improved, in terms of colour elimination and turbidity removal, by pre-coating the filtration tubes with material such as kaolin. Higher fluxes can be obtained by increasing the crossflow velocity.

From the tests on filtrate it was observed that the flux declines rapidly to a low level and then shows a continuous slight drop. This behaviour is due to the rapid formation of resistance on the surface of the membrane, mainly exerted by the retained macromolecules. The macromolecular layer formed on the surface causes the effective cutoff size to be smaller than the pore diameter on the membrane. An increase in the crossflow velocity reduces the boundary layer thickness and this results in lower resistance to mass transfer, causing the flux to increase. Buckley *et al.* (1990) have shown the importance of high crossflow velocity being attained as rapidly as possible. Progressive increase in the crossflow velocity may result in the formation of a thick polarisation layer, which cannot be removed or reduced by high crossflow velocity attained later. Operating the CFMF test unit in the configuration with 10 tubes in three passes results in higher crossflow velocities due to a higher volumetric flow through a smaller cross-sectional area.

Higher transmembrane pressure could be obtained by throttling the valve on the return line but the flux gain is very small. The throttling action also leads to a turbulent flow, which offers some scouring action. Gain in flux by these two mechanisms is offset by the compaction and consolidation of the fine particles in the cake, corresponding to an increase in resistance. In addition, the throttling action leads to a reduction in the crossflow velocity.

Flocculants have an agglomerating effect, which leads to the increase of the particle dimension, limiting the deposition and infiltration of the cake by the smaller particles. The use of flocculants therefore reduces the specific cake resistance and leads to higher fluxes. This is observed for mud filtrate and anaerobic effluent.

CFMF has a potential for treating anaerobic effluent. It removes suspended and colloidal material as a concentrated sludge in the tube, which can be returned to the anaerobic dam. The permeate stream has an improved clarity and a reduced chemical oxygen demand (COD) on average of about 8%.

Conclusions

Crossflow velocity is the most important parameter when trying to optimise fluxes. Higher crossflow velocities have been reported for the ceramic micro- and ultrafiltration units and they lead to larger fluxes. This has been confirmed by the high fluxes obtained with the Carbosep UF unit, for tests conducted on syrup and diluted molasses. The flux was found to be much higher than that reported in the literature for tests on the same streams where organic UF membranes were used. The ability of inorganic membranes to withstand higher operating temperatures and pressures, to operate in a wider pH range and to cope with higher cleaning frequencies leads to longer service lives when compared with organic membrane systems. Although they have a higher initial capital investment cost, this is offset by the reduced membrane area required due to higher fluxes, and by a longer amortisation period. Further test work is therefore planned, using ceramic MF and UF membranes, on the various factory process streams.

In spite of the specific advantages of crossflow filtration its current limitations should be noted. In many instances this technique is insufficient or inadequate for the following reasons:

- The filtrate flux at equilibrium is too low
- The backflushing frequency for membrane cleaning is prohibitive
- Streams where suspended solids are too high cannot be treated
- The degree of dewatering is insufficient
- Membrane pores become plugged.

The CFMF test unit exhibited the above mentioned limitations. However it has potential for treatment of streams such as sweet water and anaerobic effluent, especially where the level of suspended solids and the particles smaller than one micron are not high. CFMF could also serve as a pretreatment stage to other separation techniques such as UF, RO, nanofiltration or ion-exchange. Test work will therefore continue in these areas.

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