

# Experimental Results Obtained in Decolorizing and Desalting Dilute Molasses Solutions With Permasep<sup>1</sup> Ultra Filtration Modules

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## Introduction

This paper is concerned with ultra filtration (or reverse osmosis), purification of dilute molasses solutions. Experimental work conducted by Zanto et al. (9)<sup>3</sup> utilizing ultra filtration purification of various process juices with cellulose acetate membranes indicated that it was possible to effectively separate low molecular weight nonsugar impurities and water from higher molecular weight sucrose. Conversely, it was possible to separate relatively low molecular weight sucrose from high molecular weight colorants. During the initial study employing cellulose acetate membranes it was noted that hydrolysis (8) of the membrane under alkaline process conditions limited the effective lifetime of the membrane to approximately one week of service.

It was concluded from the initial research investigation (9) that successful adaptation of ultra filtration to process juice purification was dependent upon the following membrane and module characteristics:

- 1 - Chemical and physical resistance to hot (65-85°C) weakly alkaline (7.0-8.5 pII) process juices.
- 2 - Membrane immunity to organic fouling of the pore structure.
- 3 - Economically feasible membrane permeate flow rates as described in terms of weight units of nonsugars eliminated in the membrane permeate stream/unit time/module.
- 4 - Feasible chemical or mechanical cleaning of membrane surface area.

Contacts with major organizations involved in membrane development and module production revealed that only DuPont Permasep nylon hollow fiber membranes satisfied the important consideration of resistance to alkaline feed solutions. A joint project was organized with DuPont involving the use of their Permasep ultra filtration modules. The objective of the project was to make ultra filtration of process juices an economically

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<sup>3</sup> Numbers in parentheses refer to literature cited.

profitable venture on the basis of increased white sugar extraction.

### Theory

Ultra filtration membrane performance may be described in terms of product flow through the membrane. Figures 1 and 2 indicate desalting and decolorization of dilute molasses solutions, respectively. The models represented show a longitudinal cross section of a nylon hollow fiber capillary with a critical diameter pore as described by Sourirajan (7). In the case of desalting the vendor terminology of permeate is actually the low purity relatively salty discard. The reject is the partially purified higher purity dilute molasses product. When decolorization is discussed the permeate becomes the decolorized product and the highly-colored reject is the discard. The models in Figures 1 and 2 demonstrate the selectivity of the membrane in terms of the critical pore diameter. In terms of molecular dimensions water and salts may permeate the desalting membrane in Figure 1, sucrose however is rejected on the basis of molecular size. Applying this model to decolorizing in Figure 2, sucrose may permeate the membrane but the long chain high molecular weight colorant of the melanoidin type are rejected on the basis of molecular size.

In reality all the membrane pores are not the same diameter. This fact allows a significant amount of sucrose to permeate the membrane during desalting and conversely, a significant amount of color bodies to permeate the membrane during decolorization.

The basic equations describing membrane performance have been described by several investigators (1,2,5).

Permeate flows through the membrane

$$F_1 = A (\Delta P - \Delta \pi) \quad \text{Equation - 1}$$

Salt permeation through the membrane

$$F_2 = B (C_1 - C_2) \quad \text{Equation - 2}$$

Where A = Membrane water permeation constant.

$\Delta P$  = Applied pressure differential.

$\Delta \pi$  = Osmotic pressure differential.

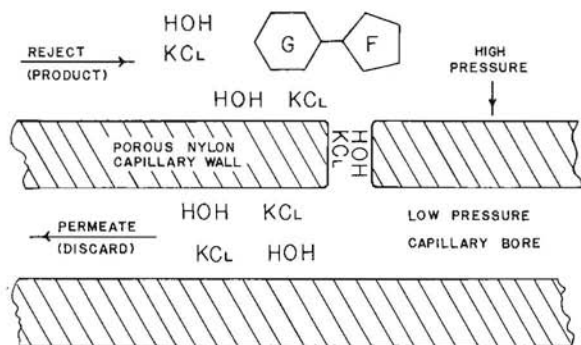


Figure 1.

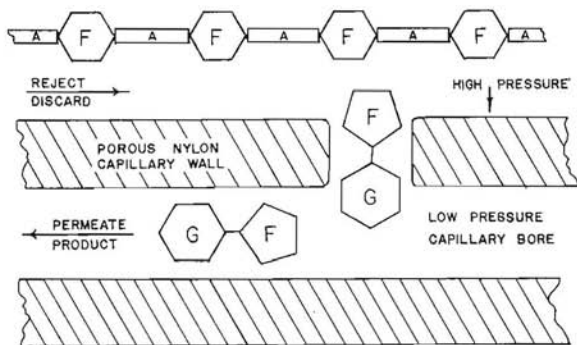


Figure 2.

B = Membrane salt permeation constant.

$C_1$  = Salt concentration in reject.

$C_2$  = Salt concentration in permeate.

$C_1/C_2$  = Membrane selectivity.

Equation - 1 indicates that at a constant osmotic pressure dependent on solute concentration the volume of the salt or sucrose containing permeate produced per unit area of membrane will increase directly as a function of applied pressure. The salt flux equation - 2 indicates that the quantity of salts passing through the membrane is not dependent on applied pressure. The pronounced influence of temperature on permeate flow was noted by Zanto (9) and also Mattson and Tomsic (4). Feed temperature increased from 20 to 40°C increased permeate flow from 2.5% to 3.0% per degree increase relative to the permeate flow rate at 20°C. Membrane selectivity was not affected at the higher temperatures.

### Description of Equipment and Process Flows

Experimental equipment consisted of several 4-inch diameter  $\times$  7 ft high Permasep Permeators with membrane selectivities ranging from 5% SPE (salt passage) to 19% SPE. The data herein concerns only 3, 7, 8 and 19% SPE modules. Modules having high salt passage values were utilized as decolorizing modules and those having low salt passage were used as desalting modules. Figure - 3 shows a 4-inch diameter Permasep module with a cutaway section showing the permeable nylon capillary bundle. A standard 4-inch diameter  $\times$  7 ft Permasep Permeator has  $2.3 \times 10^6$  hollow fibers with outside diameters of .45 microns and inside capillary bore diameter of 24 microns. The bundle of hollow nylon fibers has a void fraction of 28.5% and a packing density of 50%. Total permeation area approximates 84,000 sq ft. The typical 4-inch diameter Permasep Permeator has a rated capacity of .5 gpm at 30°C and a feed pressure of 600 psig. Each nylon hollow fiber capillary is packed in a U-

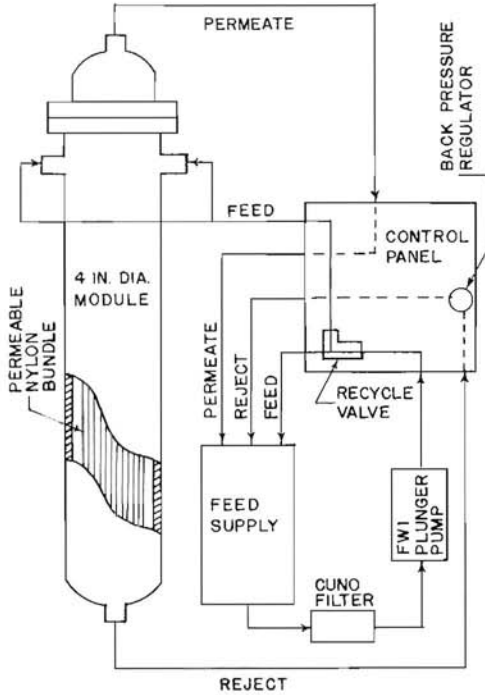


Figure 3.

shaped loop. The hollow fiber ends of the capillary are encapsulated in a proprietary epoxy resin which forms the tube sheet. The tube sheet is incorporated in the top, high pressure flange design. The epoxy resin tube sheet is subject to thermal creep under pressure over  $40^{\circ}\text{C}$ . This consideration limits the permeator operating temperature to  $40^{\circ}\text{C}$ .

Use of hollow fiber nylon capillaries has the advantage of high surface area, elimination of membrane support, and high membrane strength. In contrast to cellulose acetate the use of nylon membranes does not preclude the use of mild chemical cleaning agents. The tightly-packed hollow fiber bundle does have the following disadvantages - they function as a very efficient filter, and promote poor circulation with subsequent small dead volumes of juice. The stagnant volumes of sugar-containing juice within the capillary bundle can contribute to eventual bacterial infection of the permeator. It is impossible to mechanically clean the bundle. Visual inspection of the permeator bundle may only be accomplished by pulling the entire bundle from the high-pressure casing.

Support equipment noted in Figure 3 includes a high pressure variable rate feed pump, a control panel complete with pressure gauges flow meters and control valves. The dilute molasses feed

tank is temperature controlled. All feed to the permeator was polished with a .5 micron polish filter. Figure 4 shows a flow sheet for series flow one-stage decolorizing and desalting of a dilute molasses solution. The initial feed solution is first decolorized with a 19% salt passage permeator. The permeate from the decolorizer module is then desalted as feed to the 8% salt passage module. The reject from the desalting module represents the finished product from the one-stage decolorizing-desalting process scheme.

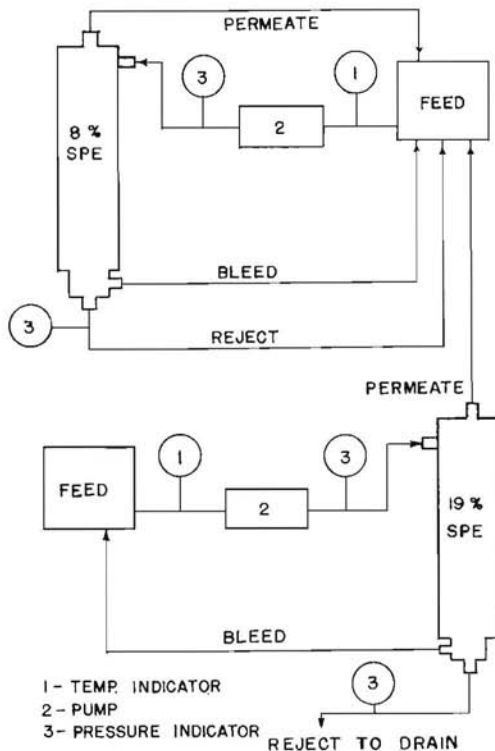


Figure 4.

The experimental flow scheme recycles the permeate, reject and bleed to the feed supply tank for remixing to insure a feed of constant composition for steady state operating conditions. The module bleed is used to promote uniform circulation within the module. The percent conversion, or the percent of the feed which was allowed to permeate the membrane, is controlled by the back pressure regulator on the module reject line. Performance runs ranged from 16 to 24 hours in duration. During the run, grab samples of module permeate and reject were taken for analysis and purity determinations. In all cases steady state

operating conditions were established before sampling of process streams began. This usually required 2 or 3 hours.

### Experimental Results and Discussion

In order to reclaim additional sugar from molasses it is necessary to decolorize and desalt the molasses solution. Impurity removal from molasses should elevate the molasses purity to at least the approximate purity of the low raw pan feed No-2 green purity. Tabular data in Table 1 shows typical results as obtained from six runs employing a 19% salt passage Permasep decolorizing module.

Table 1.—Decolorization of diluted molasses with 14-inch DuPont<sup>1</sup> 19% SPE Permasep modules. +\*

	Feed	Permeate (product)	Reject
Pressure (psig)	600	-----	-----
Temperature °C	39	Ambient	Ambient
pH	6.7	6.6	6.7
R.D.S.	11.25	4.12	20.95
Purity	59.68	56.98	59.95
Flow rate GPM	2.50	1.41	1.09
Color**	11,145	3,206	12,742

<sup>1</sup> All data in Tables 1 and 2 are calculations based on the results of experimental observation of two (19 and 7% SPE) four-inch modules. This is also the case for the data presented in Table 2 concerning stages 2 and 3.

+ Values calculated from computer data No. 35 - 40.

\* One-stage decolorization treatment.

\*\* Color determined at 560  $\mu$  as color units on sugar in solution.

In this case the initial one-stage treatment represents only one stage of several stages necessary to decolorize an optimum amount of sugar in solution. The first stage of permeators would reduce the color on 19.7% of the total sugar by 70%. The module reject stream containing 80.3% of the sugar in the feed must be treated with additional permeators to reduce molasses color prior to desalting and recycle of the partially purified molasses to the low raw pan.

Table 2 indicates performance data obtained from 10 typical runs using a 7% salt passage Permasep desalting module operated independently. During the course of the investigation on 8% SPE module was also used, as previously stated, as the desalting module during tandem operation. Slight differences do occur between the 2, 7 and 8% SPE, but for the purposes of this paper the results of both have been integrated and should be considered as equal.

Performance data obtained from the first stage desalting treatment has been extended to encompass three-stage treatment. Total accumulative sugar loss after three-stage desalting treatment would approximate 23%, total accumulative nonsugar

Table 2.—Three-stage purification of diluted molasses with 14-inch DuPont 7% SPE Permasep modules †

Stage	Feed			Permeate			Reject		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
R.D.S.	10.66	10.66	10.66	2.73	2.73	2.73	20.81	20.81	20.81
A.P.	63.68	67.26	71.26	38.27	42.30	47.62	67.26	71.26	71.66
Lbs. Tds/Min*	2.24	1.93	1.67	.31	.26	.21	1.93	1.67	1.46
Lbs. Sug/Min	1.42	1.30	1.19	.12	.11	.10	1.30	1.19	1.09
Lbs. N.S./Min	.82	.63	.48	.19	.15	.11	.63	.48	.37
% N.S. Elim.**	----	----	----	23.2	41.5	54.9	----	----	----
% Sug. Loss*	----	----	----	8.5	16.2	23.2	----	----	----
Flow Rate (GPM)	2.42	2.42	2.42	1.36	1.36	1.36	1.06	1.06	1.06

\* Tds/Min = Total Dry Substance (Recovered + lost)

\*\* Accumulative % elimination and loss

Average % conversion 56.2

† Values calculated from computer data No. 14, 15, 18, 19, 20, 21, 22, 28, 29, 30

All rate values are/14-inch permeator.

Feed pressure - 592 PSIG

elimination would equal 54.9%. Purity of the final combined first, second and third stream permeate would approximate 42.7. The combined permeate, with an R.D.S. of 2.73 could be considered for concentration and subsequent addition to dried pulp. The reject of the first stage is the feed for the second stage. In order to maintain flow it is necessary to dilute the relatively concentrated 20.81 R.D.S. reject to approximately the initial feed concentration of 10.66 R.D.S. As the concentration of salts increase the pressure necessary to overcome the osmotic pressure increases (Equation - 1). In order not to exceed the critical design pressure of the permeator and the pumping system, dilution of feed between stages is advisable.

As the percent conversion is increased it was found that nonsugar impurity elimination and sugar loss in permeate increased to a maximum of about 50% conversion. Expressed as the volume of permeate flow per one hundred volume of feed flow, percent conversion is that portion of the feed which is allowed to permeate the membrane. Above this point decreased circulation of reject through the packed hollow fiber bundle becomes a limiting factor because of high salt concentration around the hollow fiber capillaries. The adverse effect of polarization on membrane performance has been described by several investigators (3,6).

In terms of individual nonsugar impurities the first stage of the desalting module eliminated a total of 22.0% total N, 11.9% amino + pyrrolidonecarboxylic acid N, 13.8% betaine, 46.2% nitrate, 39% chloride, 15.8% calcium, 29.6% sodium, 20.1% potassium, and 17.4% invert, respectively, from the permeator feed stream. Total nonsugars eliminated were 23.2%. Referring again to the critical pore diameter in Figure 2, it is probable that an elimination of the trisaccharides raffinose and kestose would be accomplished during decolorization. Eliminations of raffinose and kestose ranged between 40 and 50% - the raffinose and kestose being retained in the reject stream with the higher molecular weight colorants.

During each experimental run, extreme care was taken to polish filter permeator feed and maintain reasonably sterile conditions within the permeator. The feed was polished with a 0.5 micron filter and formalin was added to the dilute molasses feed to a concentration of 0.5%. In spite of these efforts the low salt passage permeators experienced a 30 to 40% permeate flow decrease operating during a ten-day continuous operating period. The high salt passage permeator showed a capacity decrease of 50 to 80% over an equal length of time. Various types of chemical cleaners were used to flush the permeator bundles in an attempt to restore initial capacity. Among these were oxidizing agents, reducing agents, strong and weak acids, and enzyme

containing detergents. A strong base chemical cleaning agent was also used in conjunction with reverse flush of the hollow fiber capillaries. All of these attempts at restoring permeator capacity were partially effective on a daily basis, however, the long range capacity decrease trend was still observed. The exact cause of the permeator capacity decrease has yet to be defined. There is some reason to believe that one or more of the following may be affecting permeator capacity:

- 1 - The hollow fibers have been plugged with residue (dextran) due to microorganism growth in stagnant juice zones within the permeator bundle.
- 2 - Molecular plugging of the porous hollow fiber surface.
- 3 - Compaction of the hollow fiber permeator bundle.

### Summary

Performance data obtained employing high and low salt passage modules operating in the decolorizing and desalting modes on dilute molasses has been discussed. Consideration of approximate initial permeator cost and effective permeator service lifetime indicate that ultra filtration purification of dilute molasses solutions is not economically competitive with other proven purification processes at this time. Improvements must be made in permeator capacity to eliminate nonsugars. An obvious approach to the capacity problem is permeators designed to accommodate high temperature 90 to 100°C feed juices. In addition, permeator capacity decrease must be defined as to cause and prevented by improved permeator design or effective pretreatment of the feed juice.

### Acknowledgment

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