AN ABSTRACT OF THE THESIS OF

Zeferino H. Garcia-Quintero for the degree of Master of Science

in Food Science and Technology presented on August 29, 1983

Title: Ultrafiltration of Grape Juice by Hollow Fiber Membranes

Abstract approved: _____
Dr. Arthur F. Badenhop

The feasibility of using hollow fiber ultrafiltration for clarification, stabilization and preservation of white grape juice was evaluated. Flux and process parameters of a hollow fiber membrane ultrafiltration unit (Romicon pilot scale, model FXS-MXII), were studied using white Riesling grape juice. Optimum processing conditions were determined for different nominal membrane molecular weight cut-off values. The effect of cut-off value changes on viscosity, pectin retention, pH, sugar content, titratable acidity, haze reduction and color were evaluated.

Optimum conditions for processing were nominal membrane molecular weight cut-off = 50,000, temperature = 50°C, inlet pressure = 1.75 Kg/cm^2, outlet pressure = 1.40 Kg/cm^2, permeate flux = 72.57 L/M^2-H. Concentration polarization

and fouling of the membrane increased with feed juice viscosity and were limiting factors in permeation rate. A 93% retention of pectins was achieved and haze reduction was in the range of 91-93%. Sugar content, pH, titratable acidity, and color were not affected for any of the nominal membrane molecular weight cut-off values.

Ultrafiltration of Grape Juice by Hollow Fiber Membranes

by

Zeferino Heberto Garcia-Quintero

A THESIS
submitted to
Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed August 29, 1983
Commencement June 1984

APPROVED:

Associate Professor of Food Science and Technology
in charge of major

Head of Department of Food Science and Technology

Dean of Graduate School

Date thesis is presented August 29, 1983

Typed by Zeferino H. Garcia-Q. for Zeferino H. Garcia-Quintero

ACKNOWLEDGMENTS

It is hard to express with words my gratitude for all those persons who made my stay here enjoyable.

I express sincere appreccciation to Dr. David L. Griffith for his advises and support at the beginning of my studies, and to Dr. Arthur F. Badenhop for his support at the end of my program.

Special thanks go to Dr. David A. Heatherbell for his assistance and encouragement through my research; to Dr. Paul E. Kifer for his kindness and for providing me with a departmental tuition during those hard times.

I also thanks to the Department of Food Science and Technology, especially Dr. Morris W. Montgomery. Dr. Dale E. Kirk, Dr. Allen F. Anglemier, Mr. Darrell V. Beavers, and Mr. George W. Varseveld for their help.

I wish to thank to CONACYT and CIADE that made me possible to study here providing a full scholarship. My thanks also go to the Oregon Table Wine Research Advisory Board, and the O. S. U. Agricultural Research Foundation for their financial support to achieve his research.

Finally, I want to dedicate this work to my parents Heberto and Josefina Esperanza, my brother Marte Jaime Jorge, and my sisters Fatima Dulce Maria y Aurelia Josefina for their love and encouragement through my life and

especially now that I am away from home; to my aunt Amalia for her love; to Robert and Brenda Clark who opened their hearts to me being my family here in Oregon; lastly, to those persons that I love and to those who gave me their smiles in those rainy days.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ULTRAFILTRATION OF GRAPE JUICE BY HOLLOW FIBER MEMBRANES

INTRODUCTION

The Pacific Northwest is a major producer of fruits and vegetables and a large processing industry has developed to preserve these products. Fruit juices and wines are two of the fastest growing products processed in the Northwest. Grape juice is one of the most attractive products due to its composition and nutritional value. Hence particular technological attention to procedures used in production is necessary (Niketić-Aleksić and Jaksić, 1980).

In the processing of the fruit for juice, fractionation, clarification and concentration of components are unit operations that form an integral part of the processing scheme. The clarification process treats a particularly important quality problem in juice production. Different conventional and chemical clarification methods involve several batch operations. These include enzymatic hydrolysis of cloud-stabilizing polysaccharides such as pectin and starch; addition of chemical coagulants and fining agents such as gelatin, silica sols and bentonite; centrifugation; and filtration. However, they are labor intensive, time and energy consuming and do not always fully

achieve the intended purpose (Heatherbell et al., 1977). Application of ultrafiltration (UF) as new technology in juice processing offers the following potential advantages:

(1) Elimination of clarification problems by removing cloud stabilizing polysaccharides such as pectins and starch, proteins and phenolics, resulting in improved product quality.

(2) UF processes are highly energy efficient and may also reduce the number of processing stages required, or eliminate current expensive processing techniques such as those described as labor intensive above.

(3) UF allows the simultaneous separation and purification of valuable by-products.

(4) Improved quality resulting from application of a physical process permitting "cold-sterilization." (Heatherbell, et al., 1977: Paterson Candy International, Ltd., 1982).

Objectives of this pilot scale study were: (1) to evaluate the feasibility of utilizing hollow fiber membranes for clarification, stabilization and preservation of white grape juice; (2) to optimize the process parameters expected to have the greatest influence on permeate flux; (3) to determine the effects of nominal membrane molecular weight cut-off (MWCOFF) and volume concentration ratio (VCR) on viscosity, titratable acidity (TA), pectin

retention, pH, sugar content, haze and color measurements of ultrafiltered grape juice.

The effects of UF on grape juice composition, quality and preservation were reported in a separate study (Fombin, 1983).

REVIEW OF LITERATURE

In 1906, Bechold coined the term UF, and since then until the middle of the century, nearly all research studies were done with cellodion membranes and cellophane films. Asymmetric membranes were manufactured at the start of the second half of the century, making membrane filtration on an industrial scale feasible (Friedrich, 1981).

UF refers to efficient selective rejection of solutes by convective solvent flow through the lumen of an anisotropic "skinned" membrane. In UF, solutes, colloids or particles with dimensions larger than the specified membrane cut-off are quantitatively retained in solution, while solutes smaller than the uniform minute skin pores pass unhindered with solvent, under the driving force of pressure through the supportive membrane structure (Amicon, Corp., 1980).

UF is often confused or equated with reverse osmosis (RO), another pressure activated membrane filtration process, but important differences do exist between these two processes. The key to understanding these differences is to recognize, at least from a physical point of view, the different method by which each membrane functions (Michaels, 1968; Griffith, 1981; Breslau, 1982).

Membranes are said to be asymmetric. Such a membrane is non-uniform with a tight, extremely thin "skin" of 0.1 to 1 μm thickness on its surface (Figure 1). This "skin" is the active membrane surface with the remaining substructure that ideally consists of an open cell foam with the pore size increasing from the top to the bottom side, serving primarily as a spongy support. Both the skin and the spongy support form rigid and highly voided structure (Porter, 1975; Strathmann, 1980).

The pore network of the rejecting "skin" is randomly distributed with the pores passing through the membrane in a tortuous, or straight-trough path. Pore size ratings are generally reported in the 10 to 200 Å range (0.001 to 0.020 μm) (Breslau, 1982).

To obtain maximum filtration rates, porosity of the substructure should be as high as possible and the polymer film should be as thin as possible. However, this limits the pore size of the support structure. To prevent the film from collapsing into the pore under the applied pressure, the pore radius should not be significantly larger than the thickness of the supported polymer film. The ideal substructure should have a high porosity but a small pore size (Strathmann, 1980).

Noticeable progress in the manufacture of polymeric membranes made of materials other than cellulose acetate have been produced in more recent years, and the application

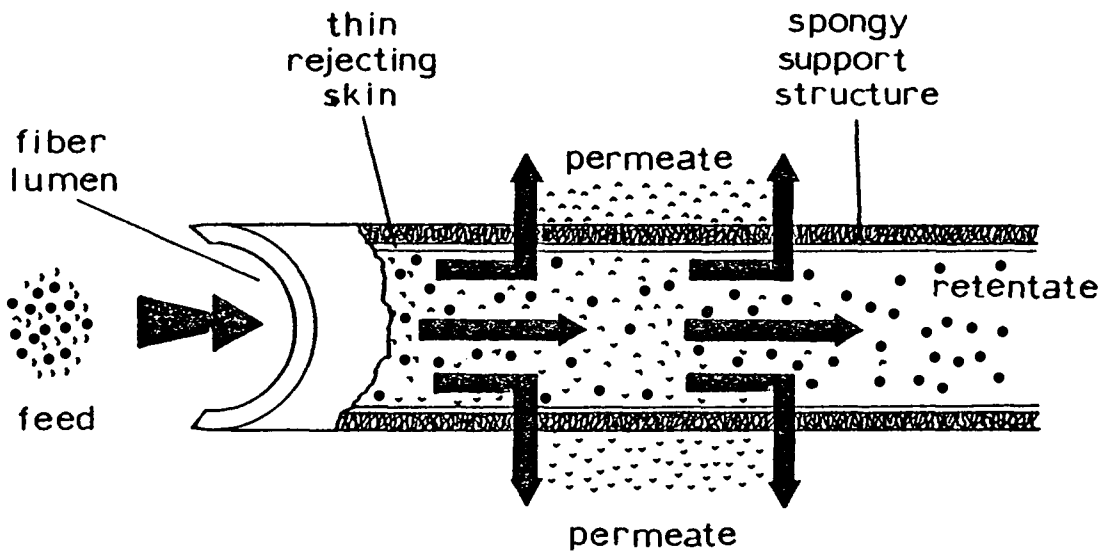


Figure 1. Schematic diagram of a hollow fiber membrane

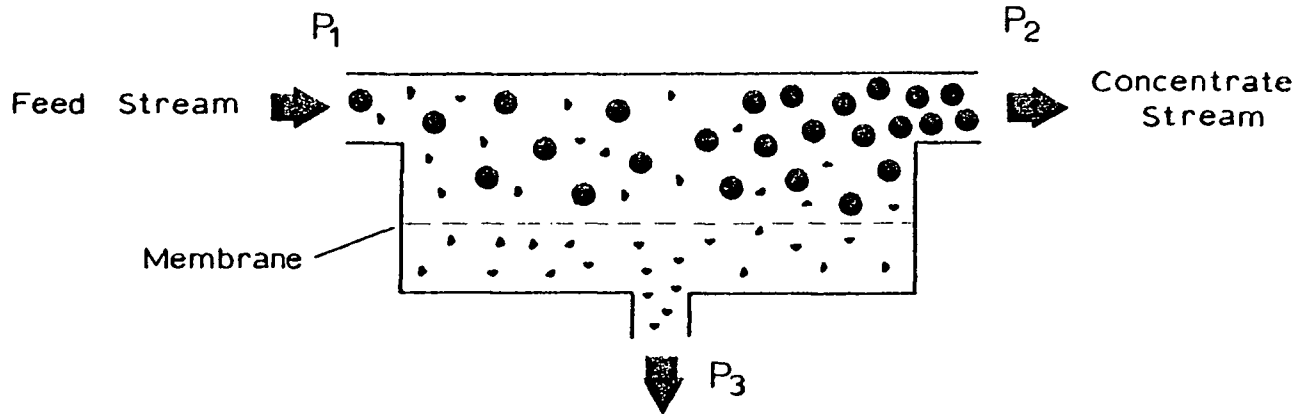
of these for specific purdposes have been examined to a great extent.

There are different membrane compositions, a wide variety of configurations and operating modes of the hollow fiber UF system.

The operation of a hollow fiber is analogous to that of permeable tubes with the feed stream flowing through the center of the fiber and the permeate stream passing through the walls (Figure 2).

As in tube flow, the conventional laws of hydrodynamics apply and the flow regime may be either laminar or turbulent depending on the flow characteristics of the fluid and the pressure drop along the fiber length. Furthermore, just as moving fluid exerts a shear force along the tube wall in tube flow, the process fluid exerts a similar force along the active membrane surface. This continuous movement of fluid across the membrane surface at a velocity determined by the "feed side" pressure gradient shown as $(P_1 - P_2)$ in Figure 2, is referred to as "cross flow" and is used in all UF systems as a means of "sweeping" the membrane surface thereby minimizing fouling, an accumulation of material on the surface of the membranes that decreases the permeate flux (Breslau, et al., 1980).

The pressure gradient $(P_1 - P_2)$ responsible for cross flow is often referred to as the hydrodynamic pressure



Cross Flow $\Delta PHYD = P_1 - P_2$

Driving Force = Transmembrane Pressure ΔP_T

$$\frac{P_1 + P_2}{2} - P_3 \approx \frac{P_1 + P_2}{2}$$

Figure 2. A schematic representation of the ultrafiltration process showing the driving force for cross flow and permeation

ΔPHYD. The solvent and smaller solute molecules passing through the membrane is termed the ultrafiltrate or permeate, and exits at pressure P_3, while the larger solute species and colloids retained on the high-pressure side of the filter is called the retentate or concentrate. The rate of permeate flow is generally reported as a "flux" or as flow rate per unit area of membrane (i.e., L/M^2 - H). The driving force for permeate flow is also a pressure gradient but it is not the hydrodynamic pressure gradient, ΔPHYD; it is instead the pressure gradient that exists through the membrane, from feed side to permeate side, at each point along the membrane surface. This pressure gradient is referred to as the membrane pressure gradient, or transmembrane pressure, ΔP_T, and clearly this pressure gradient varies along the membrane surface, being a maximum at the inlet and a minimum at the outlet.

$$(\Delta P_T)_{inlet} = P_1 - P_3 \qquad (1)$$

$$(\Delta P_T)_{outlet} = P_2 - P_3 \qquad (2)$$

$$(\Delta P_T)_{inlet} > (\Delta P_T)_{outlet} \qquad (3)$$

Although truly a variable along the membrane surface, the transmembrane pressure gradient is generally reported as an average with the average said to be the average driving force for ultrafiltration.

$$\Delta P_T = \frac{(P_1 + P_2)}{2} - P_3 \approx \frac{(P_1 + P_2)}{2} \qquad (4)$$

It should be noted that the average transmembrane pressure gradient can be related to the hydrodynamic pressure gradient by

$$\Delta P_T = P_1 - P_3 - \frac{\Delta PHYD}{2} \qquad (5)$$

which shows that if the inlet and permeate pressures are fixed (P_1 and P_3, respectively) changes associated with $\Delta PHYD$ to control fouling will also affect ΔP_T (Breslau, 1982).

There are several factors affecting flux in hollow fiber membranes, which includes process parameters such as temperature (T), ΔP_T, MWCOFF, and chemical and physical properties of feed composition, such as protein composition and viscosity, which can be "controlled" by the operator. However, there are other factors beyond the scope of the operator that are an intrinsic part of this unit operation. Mainly, these phenomena are concentration-polarization and fouling. Some of the components in the solution are rejected by the membrane due to the characteristics of the membrane filtration process. These rejected components accumulate at the membrane surface. Prior to reaching the steady state, the convective flow of these components to the membrane surface is greater than that of the diffusion backflow to the bulk solution. This pheno-

menon is called concentration-polarization (Blatt et al., 1970). The first gel-polarization model (model based on concentration gradient) was presented by Michaels (1968). The existence of a pressure independent gel-polarized region was confirmed by Blatt et al., (1970). Later, Porter (1972) pointed out the differences that exist between the gel-polarization theory and experimental data. Probstein et al., (1978) found out by means of an integral method that the appropriate diffusivity defining the flux in the gel-polarized region was found to be that at the gelling concentration, rather than at the bulk concentration. The best description of flux behavior in macroporous membranes (UF membranes) is given in terms of the Hagen-Poiseville law for flow through a channel including a correction known as the tortuosity factor to account for the variation in pore size distribution, shape and tortuosity found in real UF membranes (Merin and Cheryan, 1980; Nichols and Cheryan, 1981).

It is not always possible to explain flux behavior only as a consequence of concentration-polarization since fouling is said to occur as well. This takes place when some element in the feed stream plugs or coats the membrane in such a way that flux is reduced, therefore the foulant is not in dynamic equilibrium with the feed stream. So fouling is a condition that must be considered in all membrane applications. Moreover, it is easy to recognize

when a system is not fouled, the behavior of the permeate is pressure and time dependent (Eykamp, 1978).

This work will not deal extensively with the discussion of UF theory and the mathematical models for understanding transport phenomena at the membrane-solute interface. For this topic, excellent references are the investigations made by Blatt et al., (1970), and the review of concentration-polarization and fouling by Matthiason and Sivik (1980).

Membrane compaction also affects flux. It is normally a minor effect and is seen as a change in the pure water flux of a membrane system with time (Eykamp, 1978; Pepper, 1981). Finally, the effect of cleaning with conventional detergents or with dilute bases is to erode the membrane surface (Howell and Velicangil, 1980).

Over the last several years, use of UF has grown enormously and a variety of membranes and associated equipment is presently available. UF has been used for several years in non-food related applications (Smith and Di Gregorio, 1970; de Filippi, 1970; Breslau, 1980; Michaels, 1980).

The potential of pressure driven membrane processes for use in food aplication is confirmed by an average annual increase in industrial use rate of about 37% (Drioli, 1980). Presently, the major area for UF and RO is mainly for dairy products (Glover et al., 1978; Harper, 1980). It has also been used for concentration and frac-

tionation of protein solutions (Cheryan, 1977; Eskin and Singh, 1978; Nichols and Cheryan, 1981). Application to fruit and vegetable products has been limited and mainly done in Europe and Japan, examples include purification of raw beet and cane juices, tartrate removal from wines and musts, treatment of anthocyanic extracts (Griffith, 1980).

New promises applications are appearing in other areas such as juice technology. Application of this filtration technique as an efective alternative to conventional methods for clarification and sterilization of apple juice was first demonstrated by Heatherbell et al., (1977). Hollow fiber membranes were used for clarification of pear juice (Kortekaas, 1980; Hodgson, 1981), for kiwifruit juice (Wilson and Burns, 1983), and for clarification of lemon juice on an industrial scale (Mans, 1981). The effect of T and MWCOFF on ultrafiltered white grape juice composition and quality and preservation of SO_2 treated and untreated grape juice was reported by Fombin (1983). Finally, the effects of mold contamination and UF on the color stability of strawberry juice and juice concentrate was studied by Rwabahizi (1983).

MATERIALS AND METHODS

Source of grapes

White Riesling grape juice from Washington State (OSU lot 81-03) was used in this study. The juice was processed at the Sokol Blosser winery in Oregon and had a sugar content of 19.7 °Brix, pH 3.03, TA of 0.872 g of tartaric acid/100 ml, free SO_2 of 11 ppm and total SO_2 of 33 ppm. Fifteen ppm of SO_2 was added to the grape juice at the Oregon State University winery. It was stored frozen in glass jugs at -7.8 °C. Individual batches were thawed overnight at room temperature and prefiltered through cheese cloth (folded to 4 ply) grade 40 fine weave 24X20 threats/in^2 prior to UF for each trial.

Ultrafiltration

A Romicon model HFXS-MXII pilot scale hollow fiber UF unit was used in all experiments. Four membranes were evaluated: PM-10, PM-30, PM-50 and PM-100, with a MWCOFF of 10,000, 30,000, 50,000 and 100,000 daltons respectively. They were in the form of 50 noncellulosic hollow fibers made of polysulfone of 63.5 cm length, with an internal diameter of 0.109 cm, giving a total surface area of 0.1 m^2.

To reduce variation during data collection, conditioning, cleaning and operating procedures were standardized. All the cartridges were conditioned before the experiments by flushing with: (1) tap water for 5 min, (2) 0.5% phosphoric acid solution for 30 min, (3) tap water for 5 min,

(4) 1% sodium hydroxide solution for 30 min, (5) tap water for 5 min, (6) 200 ppm sodium hypochlorite solution for 30 min, and (7) tap water for 5 min. All solutions were at 50 °C, and the cartridge pressure profile was 1.75 Kg/cm^2 and 0.70 Kg/cm^2 outlet pressures.

Cartridges were cleaned and sanitized by flushing with (1) Terg-A-Zyme (Alconox, Inc.) detergent solution (7.5 g/4L) for 15 min, (2) tap water for at least 15 min, (3) bleach solution (Master-X-bleach, Master Chem. Co.) (15ml/4L) for 15 min, then (4) tap water for at least 15 min. Operating conditions were the same as described for conditioning cartridges.

The circular batch system (concentration mode) employed in this experiment is shown in Figure 3. Prefiltered juice (12L) was poured into the feed tank and heated to the required temperature in a steam kettle. The permeate stream was returned to the feed tank during the first 10 min of each operation to allow the system to reach a pseudo steady state, defined as a slow decline of permeate flux over time (Cheryan, 1977). When this state was reached, flow was measured in the permeate stream using the stopwatch and cylinder method (Kortekaas, 1980; Doshi, 1980).

Process parameters evaluated in this experiment were: (1) temperatures of 20°, 30°, 40° and 50°C controlled to ± 2°C by adjusting the hot or cold water flow rates into the jacket of the feed tank, (2) transmembrane pressures

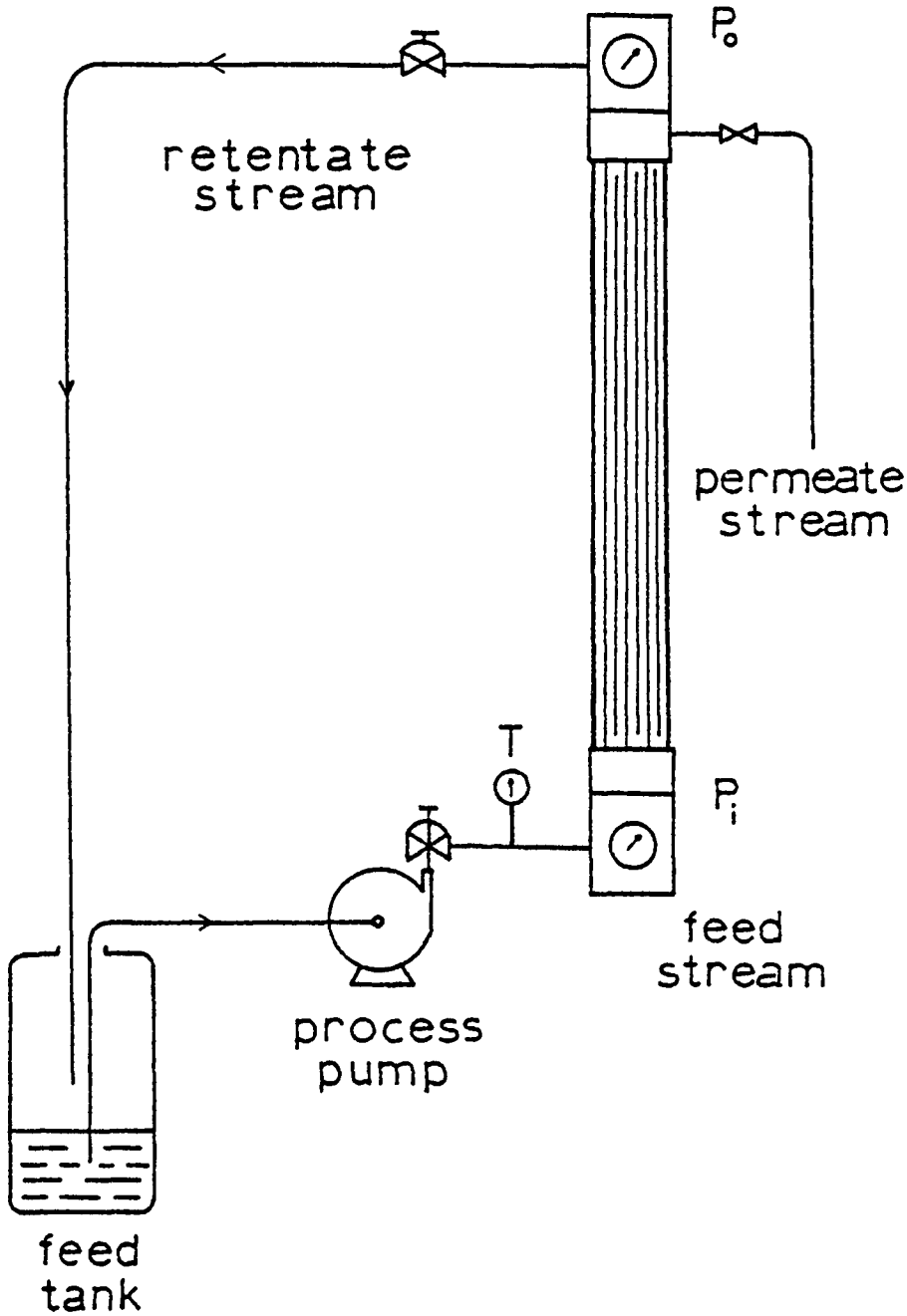


Figure 3. Flow diagram of a hollow fiber ultrafiltration system

of 0.88, 1.05, 1.23, 1.40 and 1.58 Kg/cm^2, and (3) permeate flux.

The effects of VCR's of 1, 2, 4, 6, 8, 10 and 12 and different MWCOFF's were studied on TA, sugar content (°Brix), pH, viscosity, haze, pectin retention, and color of grape juice. To evaluate these effects, the system was operated at the optimum T and ΔP_T.

After each experiment, the cartridge was immersed in 20% ethanol solution until further use.

Samples were taken from the original juice before UF and from the permeate and retentate streams during the process.

Analysis on the juice samples

Sugar content, titratable acidity, pH, viscosity, haze, pectin retention were determined on the original, permeate and retentate samples. Otherwise, analyses were as specified.

Sugar content

Soluble sugar was determined using an Abbe refractometer at 20°C. Results were expressed in °Brix.

Titratable acidity

Total titratable acidity in permeate and original samples were determined by titrating 10 ml of juice with

0.067N NaOH to reach pH 8.3. Results were expressed as g of tartaric acid/100 ml of juice.

pH

pH measurements were made at 20°C using a Corning pH meter 125.

Viscosity

Viscosity was measured in retentate samples with an Ostwald viscometer calibrated at process temperatures using 10 ml of samples. Results were expressed in centipoise.

Haze and color

Color specification parameters such as Hunter "L," "a," "b" were measured in a 1 cm pathlength cell using a Hunter model D25 P-2 Color Difference Meter, which was standardized against a white tile (No. DC 122 L = +94.02, a = -0.9, b = +1.2). All measurements were made in the transmission mode with the light source in the normal aligned position (arrangement I) for the diffuse transmittance only excluding the specular component.

Haze measurements were calculated as the ratio of Y in arrangement I over Y in arrangement III (Y_I/Y_{III}).

Pectin retention

Pectins were extracted and quantitatively determined using methods described by Robertson (1979) and Blumenkrantz and Asboe-Hansen (1973).

A 5 ml aliquot of juice was weighed into 50 ml centrifuge tubes. Ethyl alcohol (95%) was added to a volume of 30 ml and the mixture heated for 5 min in a water bath at 85°C, with occasional stirring with a glass rod. The tubes were centrifuged at 10,000 rpm for 20 min in an RC-5 automatic superspeed centrifuge (Du-Pont Instruments/ Sorvall). The supernatant was decanted and discarded. The pellet was dispersed in approximately 5 ml of distilled water and stirred vigorously in a vortex mixer.

0.2 ml extract was added to each of three tubes (20 X 150 mm). To each tube, 1.2 ml of 0.0125M sulfuric acid/sodium tetraborate solution was also added and immediately cooled again in ice water. To two of the three tubes, 20 µl of m-hydroxydiphenyl reagent (0.015 g of m-hydroxydiphenyl in 10 ml of 0.5% NaOH) was added, while 20 µl of 0.5% NaOH was added to the third tube. This tube acted as a blank to correct for the slight pink-yellowish color produced when neutral sugar containing materials are heated in sulfuric acid/sodium tetraborate. After mixing the sample, the absorbance at 525 nm was read using a Beckman 550 double beam spectrophotometer, using 0.2 cm pathlength cuvettes.

A standard curve was prepared using polygalacturonic acid (Sigma Chemical Co.). The polygalacturonic acid standards were prepared as suggested by Blumenkrantz and Asboe-Hansen (1973). Results were reported as µg of uronic acid/ml of juice.

RESULTS AND DISCUSSION

Optimum operating conditions, such as process T and ΔP_T for four different hollow fiber UF membranes, PM-10, PM-30, PM-50 and PM-100, with a MWCOFF of 10,000, 30,000 50,000 and 100,000 daltons, respectively, were determined. After the process conditions were optimized, the four different membranes were used to study the effects of MWCOFF on permeate flux, pH, sugar content, TA, color, pectin retention, viscosity, haze reduction and VCR.

Effect of process T, MWCOFF, and of SO_2 on ultrafiltered juice composition and quality were reported by Fombin (1983). Components and attributes, such as proteins, phenolics, browning, haze, polyphenoloxidase and microorganisms as well as sensory quality and storage stability were discussed.

Effect of transmembrane pressure

Effect of transmembrane pressure on permeate flux for each MWCOFF used is shown in Figure 4. PM-10 and PM-30 membranes showed similar trends for the effect of ΔP_T, being closer at 1.4 and 1.6 Kg/cm^2. The PM-50 membrane had the same behavior but higher permeate fluxes.

Behavior of the flux was typical of food and other biological systems containing macromolecules rejected by the membrane in that flux (J) initially increases linearly with applied ΔP_T as described by Equation (6) and then

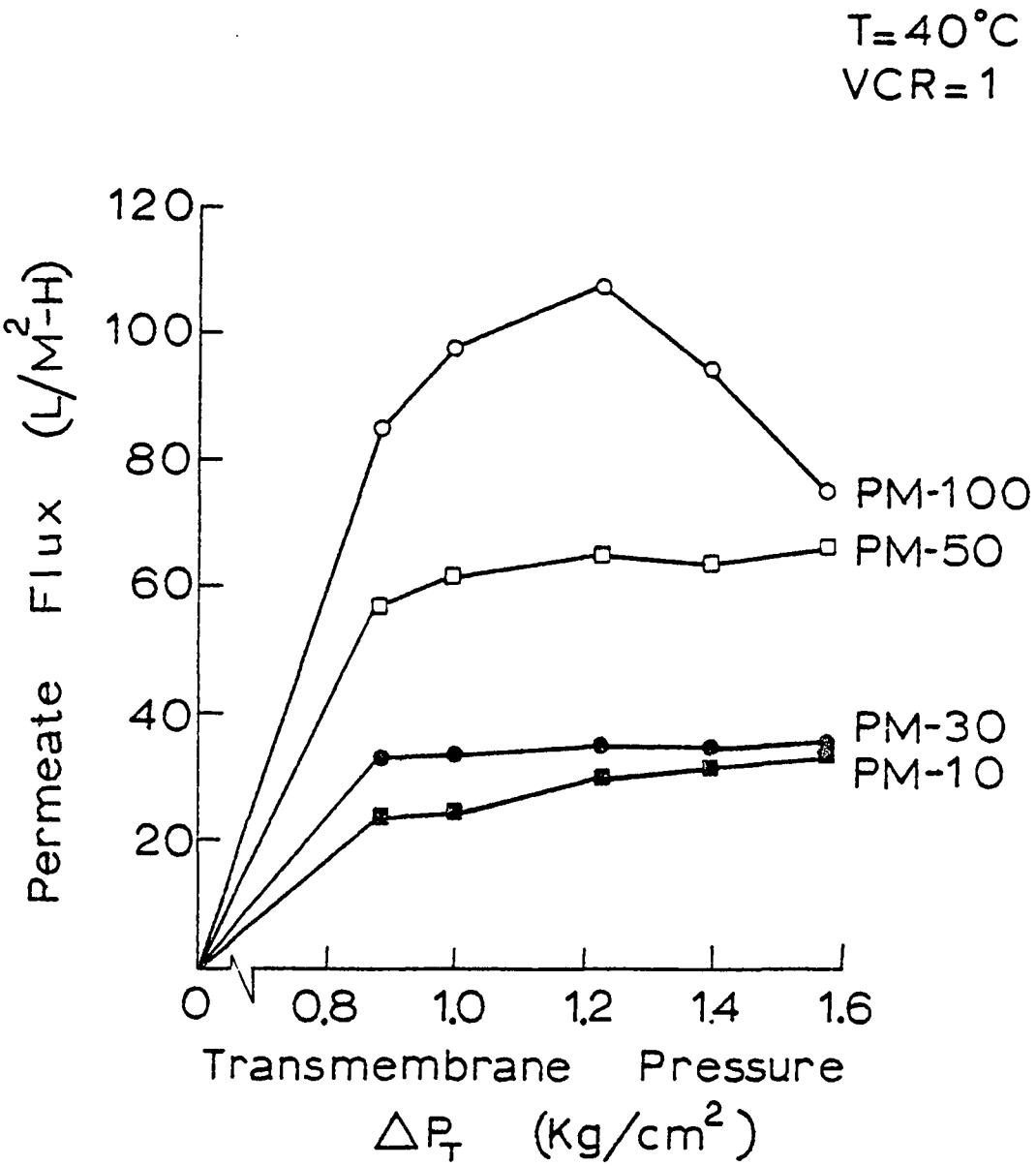


Figure 4. Effect of transmembrane pressure on permeate flux

come nearer to an asymptotic value, indicating the beginning of the mass-transfer controlled region, as expressed in Equation (7).

$$J = \frac{A(\Delta P_T - \Delta \P)}{\mu} \qquad (6)$$

$$J = K \ln \frac{C_g}{C_b} \qquad (7)$$

Where A is a membrane permeability coefficient characteristic of a particular membrane, μ is the viscosity of the feed, $\Delta \P$ is the transmembrane osmotic pressure of the solute, K is a mass transfer coefficient, C_g is the concentration of macromolecules at the membrane surface and C_b is macromolecules concentration in the bulk of the solution (Blatt et al., 1970; Cheryan and Schessler, 1978). The findings of Fombin (1983) for protein retention and browning polymeric complexes on the UF of grape juices, together with the pectin retention, agree with the assumptions of the above investigators and appears to be a direct consequence of this flux-transmembrane pressure behavior. This may be influenced by temperature having larger fluxes when the system is operated at 50°C.

These experiments were done returning the permeate stream to the feed tank so that good approximation for maintaining the feed stream constant (VCR=1) was reached.

Therefore, the system was operated at the maximal permitted inlet pressure (P_i= 1.75 Kg/cm^2), varying only the outlet pressure to get the desired pressure drop along the hollow fiber.

The criteria for evaluating the optimal ΔP_T is to maximize the permeate flux. For the PM-10, PM-30 and PM-50 cases the optimal ΔP_T was determined to be 1.58 Kg/cm^2. If this result is compared with those findings by Blatt et al., (1970), Setti (1976), and Cheryan and Schessler (1978) for protein solutions, the optimal ΔP_T would be 0.8-1.0 Kg/cm^2. For PM-100 membrane, the optimum was 1.23 Kg/cm^2 due to the bell-shaped permeate flux pressure behavior.

In addition, statistical analyses were used to determine the effect of MWCOFF and ΔP_T which have effects on permeate flux (J) and to fit a polynomial regression equation is expressed as follows:

$$J = 39.729 - 1.635\ MWCOFF + 17.048\ \Delta P_T + 0.035\ MWCOFF^2 \qquad (8)$$

The equation indicates that permeate flux-transmembrane pressure behavior was significantly dependent on MWCOFF, while ΔP_T has a slight influence on the system in the polarized region. This suggests that concentration-polarization effects were significant because this phenomenon initiated the formation of a gel layer related to the rejection characteristics of the membrane, and directly rated by the MWCOFF.

Formation of the protein layer can have two effects: (i) localized increase in osmotic pressure, thereby reducing the driving force in Equation (6), and (ii) and additional hydrodynamic resistance for transport of solvent and permeable solute. Either mechanism will reduce flux and cause pressure independence when ΔP_T is greater than the optimal ΔP_T, as illustrated in Figure 4 (Cheryan and Schessler, 1978).

Since PM-100 membrane showed a bell-shaped permeate flux-transmembrane pressure behavior, data for this membrane were not considered for the analysis of the above model, Equation (8).

The bell-shaped permeate flux-transmembrane pressure behavior agree with those findings by Kortekaas (1980) for UF of pear juice. This bell-shaped behavior may have been the consequence of the formation of a gel layer of retained macromolecules on the membrane surface initiated by concentration-polarization. This build-up may be due to the effect of protein-phenolic-pectic complexes.

Pectic substances have physical characteristics different from proteins. Protein can be visualized as having a spherical shape. When a gel layer of proteins forms, the spherical shape leaves spaces for passage of permeate. Upon applying transmembrane pressure, these spaces never totally close off, explaining the asymptotic behavior.

Pectic substances are chain-like polymers of galacturonic acid units aggregated by hydrogen bond bridges and Ca^{++}. When the gel layer is compressed, these bridges can collapse and the network of chains can clog up the membrane pores (Kortekaas, 1980), as well as the opened channel pathways in the gel layer. This will explain the decrease in permeate flux as transmembrane pressure was increased above the optimum.

The influence of temperature on denaturation of proteins and pore size distribution also account for these effects. There is less uniformity and more roughness on the gel layer causing possible differential increments in turbulence in the permeate stream increasing the permeate flux before the collapse of the membrane with an increase in ΔP_T.

In the UF process an analysis of the concentration-polarization phenomenon is rather complex. It involves knowledge of the rheology of concentrated polymeric solutions, and diffusion coefficient variation with concentration. In addition a deep particle trajectory analysis is required to determine the axial migration of colloids and other macrosolutes in the feed stream. Consequently, the permeation flux will not be influenced by the build up of the deposited layer of particles but will itself affect the net rate of deposition (Green and Belfort, 1980).

To partially restore the permeate flux and also reduce concentration-polarization during UF of grape juice is it important to start working at the optimal transmembrane pressure for protein solutions, ΔP_T = 0.8-1.0 Kg/cm^2. Later during the process, it is important to increase to the maximal permissible transmembrane pressure ΔP_T = 1.58 Kg/cm^2, for short periods of time, to have a possible sweeping away of the outer layers of the gel formation. One strategy to reduce concentration-polarization is increasing the mass tranfer of dissolved solids from the membrane surface back to the bulk liquid. This can be achieved by applying high velocity gradients along the membrane, short flow length along the membrane and by increasing the solids diffusivity by working at higher temperatures (Bruin et al., 1980). The citations of Matthiason and Sivik (1980), state the flux decline due to fouling depends on the initial flux, showing a more severe decline with high initial flux than with low initial flux. However, the benefits of increasing permeate flux must be balanced against a large increase in pressure drop and a consequent increase in pumping costs (Breslau and Kilcullen, 1977; Cheryan and Schlesser, 1978).

Effect of temperature

Temperature has an important role during UF processing. It has been established that flux in the polarized region

is a function of temperature, mixing, and the nature and concentration of the solution being ultrafiltered (Blatt et al., 1970; Porter and Michael, 1971; Goldsmith, 1971; Pace et al., 1976). The effect of temperature on flux in the polarized region has usually been described by demonstrating that flux is a linear function of temperature (Fenton-May et al., 1971; Payne et al., 1973; Pace et al., 1976). In the UF of grape juice this linear relationship (R^2 = 0.996) exists as shown in Figure 5. For PM-50 membrane at the maximal permissible transmembrane pressure of 1.58 Kg/cm^2, an increase of 0.57 L/M^2 - H/°C of permeate flux was obtained.

For maximum permeate flux, temperature should be increased as much as possible. The membrane cartridge used in this experiment has a maximum temperature rating of 75°C (Romicon, Inc.). However, temperatures greater than 50°C ± 2°C were not used because there is a limiting factor, which is the nature of solution being ultrafiltered (Blatt et al., 1970; Goldsmith, 1971; Porter and Michaels, 1971). Quality deterioration like browning and haze retention increases at higher temperature for ultrafiltered juices (Heatherbell et al., 1977; Hodgson, 1981; Fombin, 1983).

For this experiment, due to the limited number of samples, it was not possible to prove any statistical significance on the effect of temperature on permeate

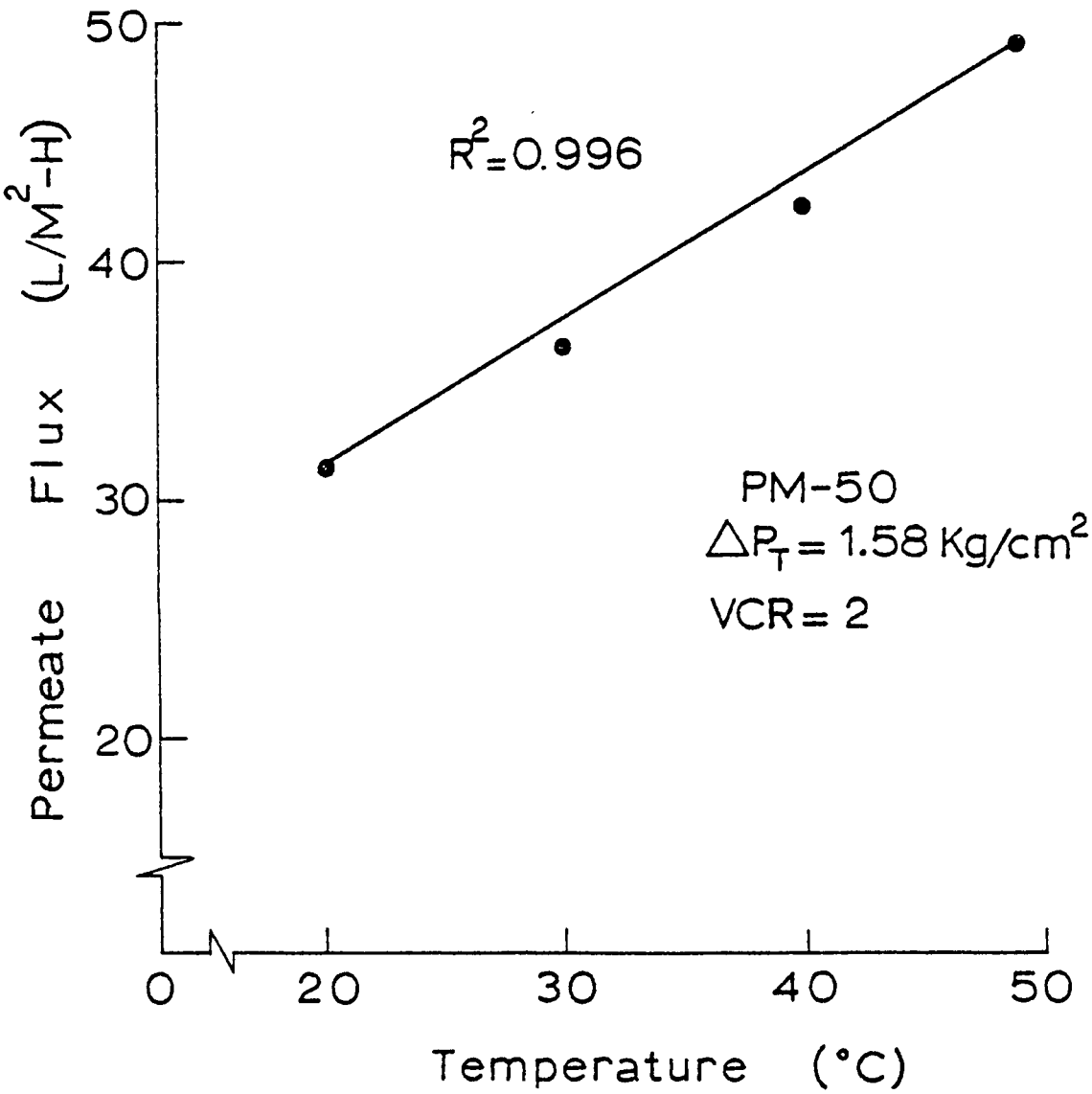


Figure 5. Relationship between processing temperature and permeate flux

flux to find the optimal temperature. However, from the reasons above mentioned and also from the higher permeate fluxes, illustrated in Figure 6, the optimal temperature can be determined.

The flux in the polarized region is a function of temperature and the nature and concentration of solution being ultrafiltered (Blatt et al., 1970; Fenton-May et al., 1971; Goldsmith, 1971; Porter and Michaels, 1971; Pace et al., 1976). The asymptotic behavior of the permeate flux leads to an exponential decay relationship between VCR and temperature (Figure 6).

When ΔP_T was set at 1.58 Kg/cm^2 and a PM-50 membrane cartridge was used, the decay of the flux was more noticeable at the highest temperature (50°C), than the rest of the evaluated temperatures. This behavior may be attributed to protein denaturation, perhaps aggravated by the high shear rates occuring in hollow fiber systems, which results in fouling of the membranes (Nichols and Cheryan, 1970).

When the feed stream becomes more concentrated (VCR 4), using a processing temperature of 50°C, the decay of permeate flux is significant and similar in magnitude to that found for VCR 1 at 30°C. Fouling of the membrane pores, changes in the viscoelastic properties of the gel layer due to high shear forces, and the applied ΔP_T at

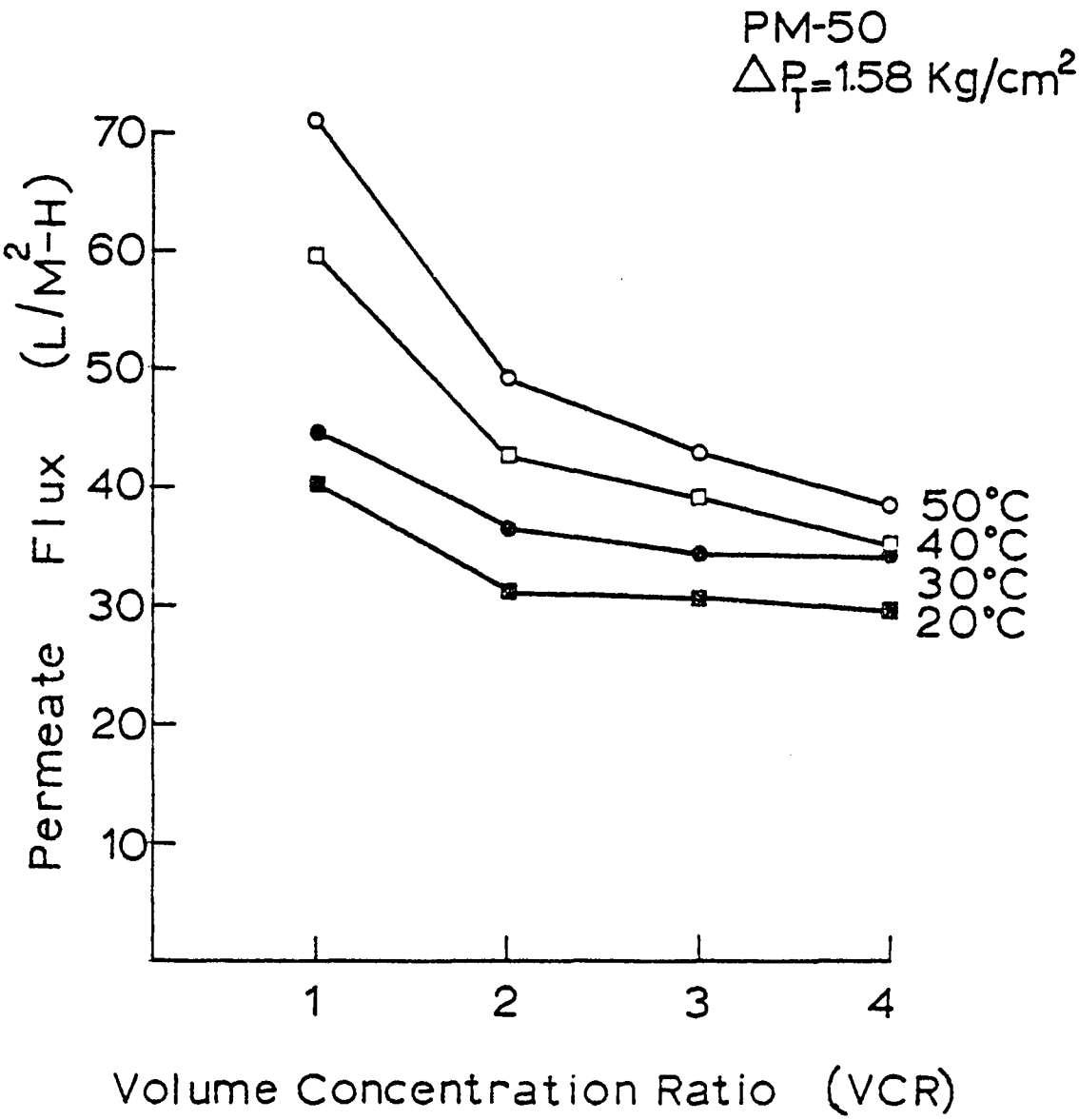


Figure 6. Effect of processing temperature on permeate flux as a function of volume concentration ratio

50°C could account for the reduction of the permeate flux at this temperature.

Effect of volume concentration ratio

The permeate flux of UF unit usually decrease as the material being processed is concentrated (Breslau and Kilcullen, 1977). The relationship of permeate flux with nominal membrane molecular weight cut-off as a function of volume concentration ratio is illustrated in Figure 7. The permeate flux behavior for the four different membranes showed the typical decrease as the feed stream becomes more concentrated. The constants K_1 and K_2 tend to decrease with decreasing MWCOFF. Since the maximal permissible transmembrane pressure of 1.58 Kg/cm^2 was used in this experiment, no conclusions at lower ΔP_T can be made.

Membranes with larger pores resulted in higher permeate flux. This is in agreement with the data of Cheryan and Schessler (1978) and Kortekaas (1980) for UF of aqueous extract of soybeans and pear juice, respectively.

The exponential decay of the flux at VCR 1 to VCR 9 can be attributed to the concentration of solute at the wall of the membrane, which is lower than the gel concentration, so the concentration-polarization modulus C_w/C_b is lower than the gel concentration (Figure 8). Further, for VCR 10, 11, and 12, C_w/C_b is large enough so that the

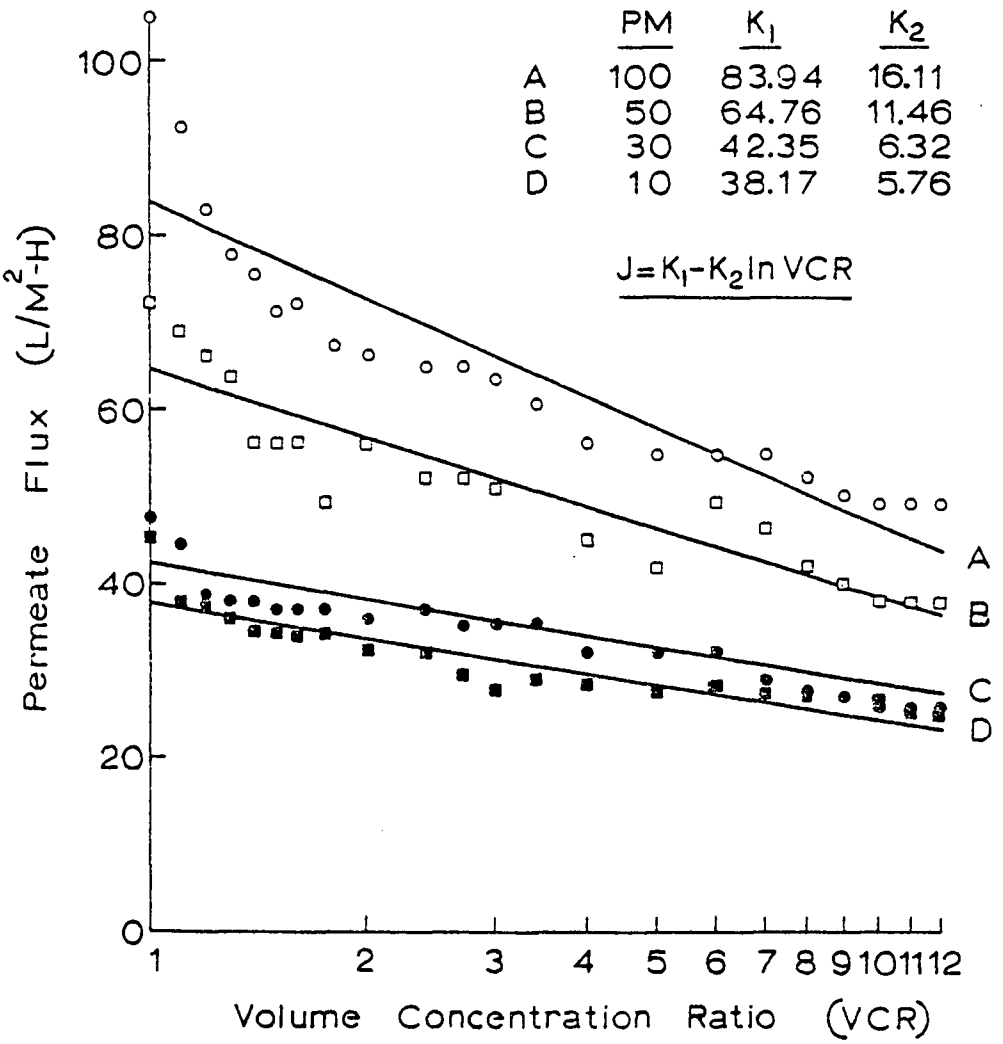


Figure 7. Relationship of permeate flux with nominal membrane molecular weight cut-off as a function of volume concentration ratio

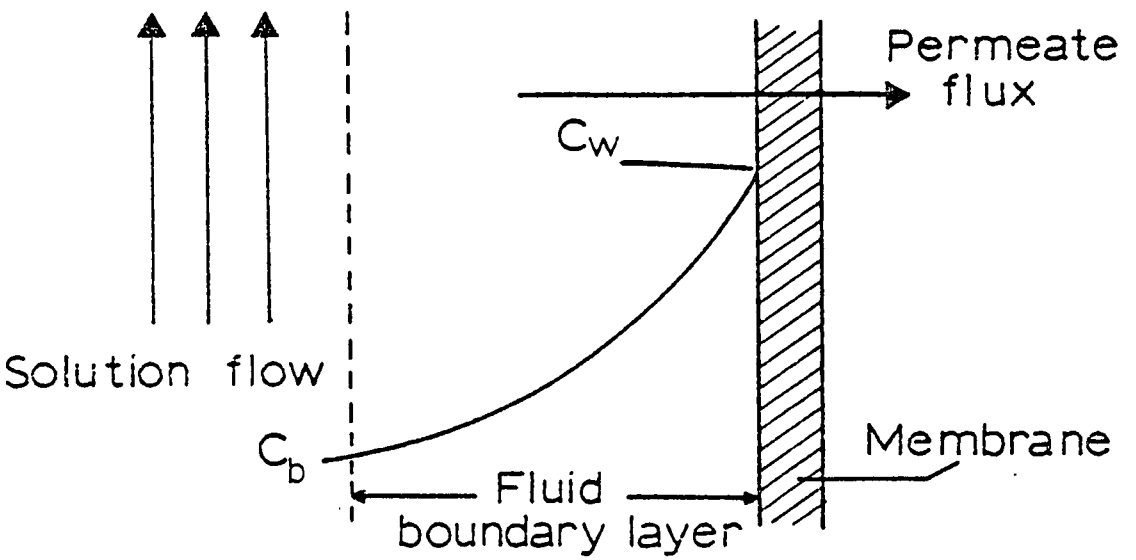


Figure 8. A model of concentration polarization for a macrosolute system.

wall concentration is equal to the gel concentration C_g (Figure 9). In this region, the wall concentration has reached the limiting gel concentration which is the highest concentration possible. All further build up of solute must occur by thickening of the gel layer at the membrane surface. This leads to an increased resistance which reduces the transmembrane flux until the convective mass transfer of macromolecules to the membrane is counterbalanced by the diffusive transport back to the bulk solution. This means that when the wall concentration has reached the gel concentration, the permeate flux at steady state is constant for a given bulk concentration and mass transfer coefficient C_w is substituted by C_g. This can be expressed by the following equations:

$$J = K \ln \frac{C_w}{C_b} \tag{9}$$

$$J = K \ln \frac{C_g}{C_b} \tag{10}$$

In other words, the permeate flux is entirely controlled by rate of back-transport from the surface into the bulk solution. This means that any factor that increases the permeate flux without increasing the back transport has no influence on the transmembrane flux at steady state condition. This explains why the flux, which initially increases linearly

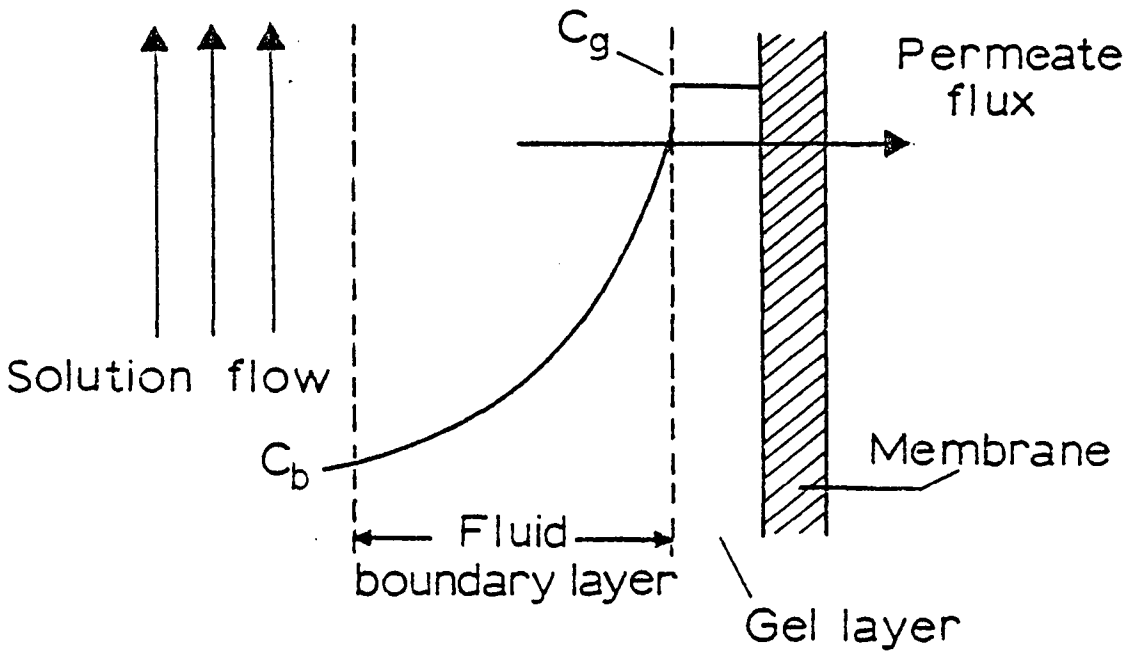


Figure 9. A model of gel polarization for a macrosolute system

with the ΔP_T, becomes independent of pressure as it increases (de Filippi, 1977; Matthiason adn Sivik, 1980). This is shown in Figure 4.

It is possible that a real steady state was reached in this experiment at VCR 10, 11 and 12, which accounts for the steady behavior of the flux at these stages. Further investigations can be made to study the permeate flux behavior at this steady state.

Effect of nominal membrane molecular weight cut-off

The nominal membrane molecular weight cut-off is said to be that molecular weight value which is almost totally rejected by the membrane (Jonsson, 1980). An essential factor affecting the process of separation is the change in flux properties with time at increasing solids content, since this is one of the factors that determines the flux conditions in UF process (Randahn, 1976; Glimenius, 1980; Water and Fane, 1981). The permeate flux decay expressed as a function of time is shown in Figure 10. The four membrane cartridges showed similar trends for the UF process. PM-100 and PM-50 showed greater decreases in permeate flux, while PM-30 and PM-10 showed a slight permeate flux decay with time.

The PM-100 membrane was more susceptible to fouling than the rest of the evaluated membranes. This could be

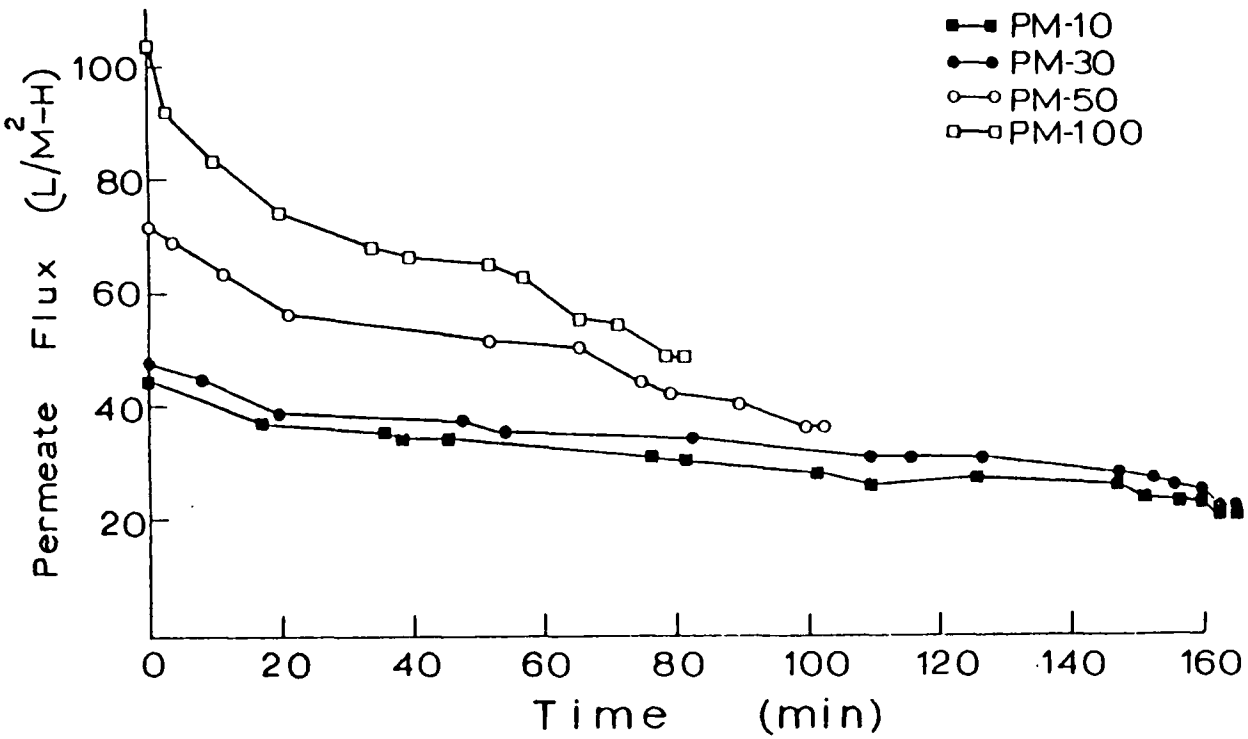


Fig. 10 Permeate flux decay with time for different nominal membrane molecular weight cut-off at a transmembrane pressure of 1.58 kg/cm and temperature of 50°C.

due to the more relatively heterogeneous porous membrane structure because of the pore size distribution and more heterogeneous surface because of gel layer formation which is directly affected by the ΔP_T and operating temperature.

The PM-50 membrane showed the best balance between the operation time (∿100 min) and retention characteristics at ΔP_T= 1.58 Kg/cm^2 and T= 50°C. PM-100 gave the shortest operation time (∿80 min) but showed more susceptibility to fouling. Conversely, PM-30 and PM-10 showed longer operation time (∿160 min) and fouling also occurred when VCR 12 was reached.

Effect of viscosity

The ease with a fluid pours is an indication of its viscosity (Mott, 1972). The effects of VCR on retentate viscosity for all the four membranes tested are plotted in Figure 11. A linear relationship, was observed from VCR 1 to VCR 4, then the behavior changed to an asymptotic curve. This may be due to moderate fouling of the membranes, as a consequence of the rejection characteristics of the UF membranes, determined mainly by the ratio of the hydrodynamic diameter of the solute and the apparent pore diameter.

In general membrane rejection increases with increasing concentration for components normally permeable (Cheryan and Schessler, 1978). However, this increase is probably

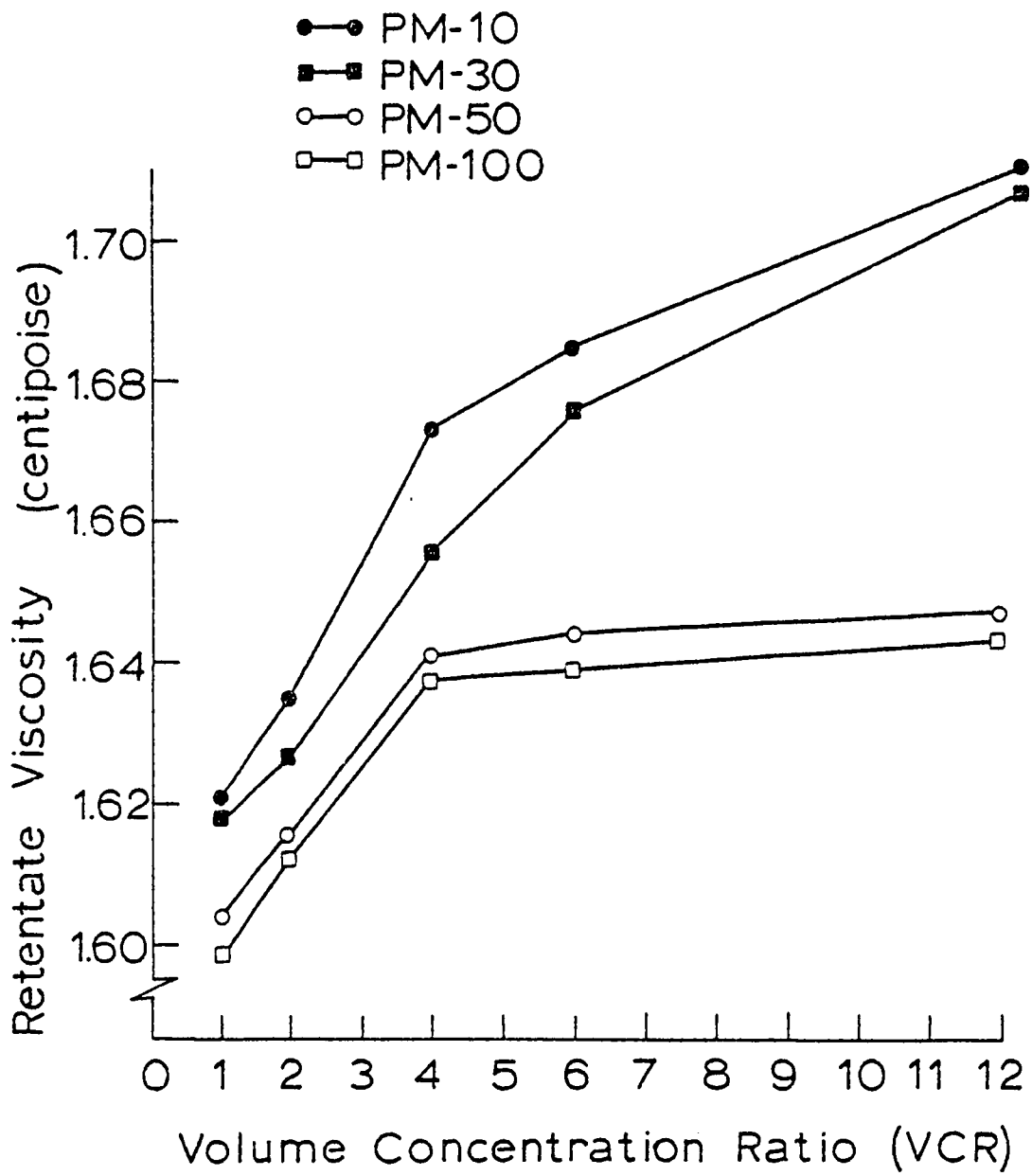


Figure 11. Effect of volume concentration ratio on retentate viscosity

due to increasing amounts of pore plugging by protein-phenolic complexes (Fombin, 1983) and protein-pectin complexes (Kortekaas, 1980).

Influence of the concentration-polarization alone can not be ignored, since it is possible that it may act as a second membrane specifically interacting with and retaining smaller molecules, causing and apparent increased rejection, therefore increasing retentate viscosity. Blatt et al. (1970), have explained it in terms of increasing drag exerted by smaller molecules in large membrane pores, thereby reducing flux while increasing solute rejection or retentate viscosity, as showin in Figure 12. This effect is more noticeable in the PM-100 membrane possibly because the gel is more strongly attached to the membrane surface due to ΔP_T effects.

Pectins

Batches of 12 L of juices of mixed varieties of grapes were used. PM-100 and PM-50 membranes showed partial permeability to pectic substances. Good retention was achieved in the process. The retention of pectic substances gradually increased as VCR increased as tabulated in Tables 1 and 2. This is due to resistance offered by the gel layer formed at the membrane surface, combined with pore size discrimination for permeability of macromolecules,

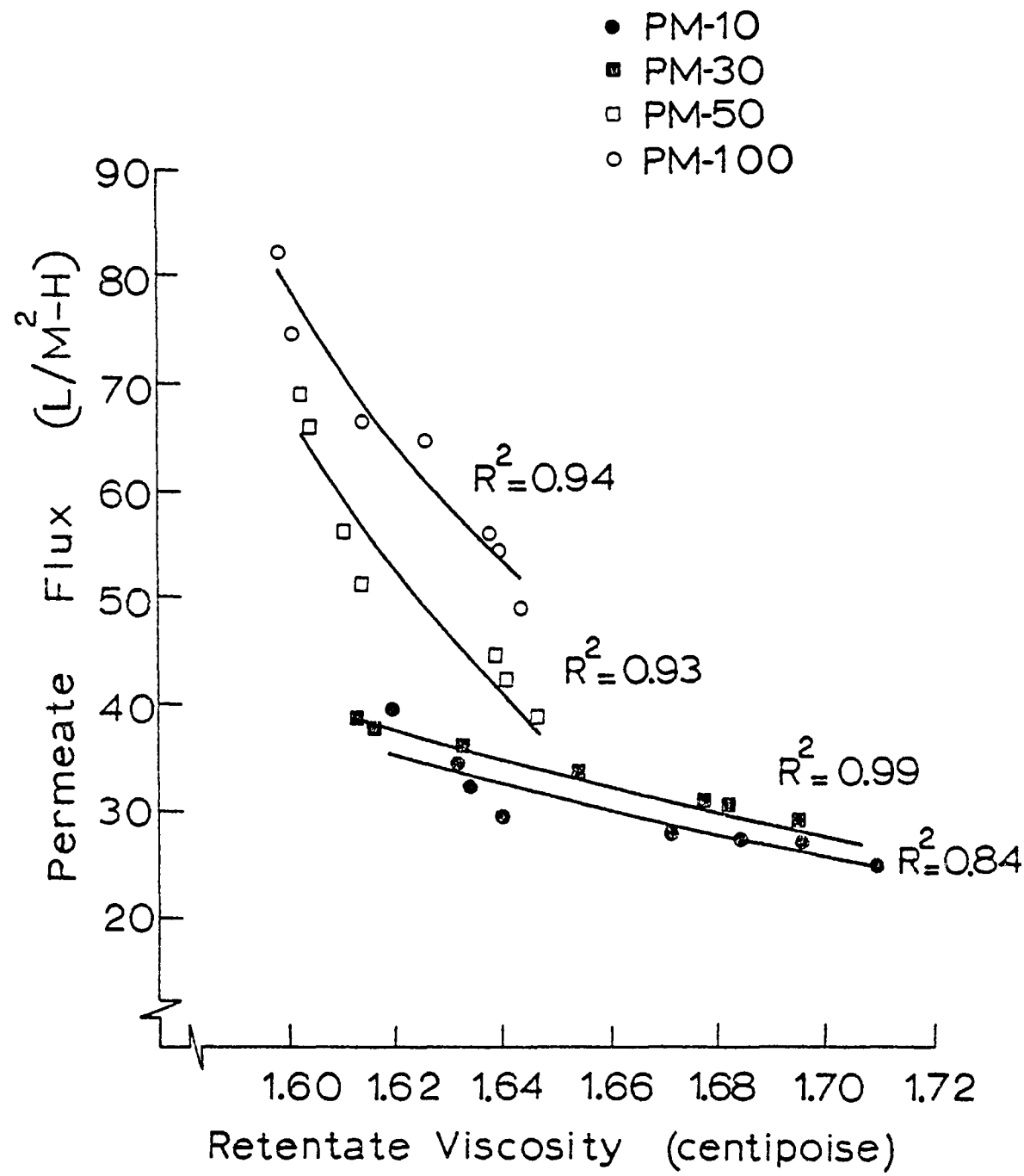


Figure 12. Effect of retentate viscosity on permeate flux

which can be expressed as a back-diffusion concentration gradient of macromolecules from the gel layer to the bulk stream.

The decrease in % retention from VCR 1 to VCR 1.2 in PM-50 could be attributed to formation of the non-homogeneous gel layer at the membrane surface, which accounts for that stable retention (69.1%) until VCR 2 was reached.

At VCR 1, PM-100 and PM-50 membranes showed different percentages of pectin retention, due to possible heterogeneous membrane surface represented by pore size distribution characteristics of each membrane. However, both membranes showed similar % retention at in latter stages of the process. This behavior can be attributed to the gel layer stability as a result of compression of the gel layer by working at maximal permissible ΔP_T. Pectic substances could partially clog the membrane pores, as well as the opened channel pathways in the gel layer. This was confirmed by the decrease of pectin content in permeate stream when the VCR effect was taken into account for calculation of pectin content at the last stages of the process.

Noticeable decrease in permeate flux was observed when pectin content in the retentate stream increased (Figure 13). Both membranes showed similar behavior being greater for the PM-100 membrane. This may be influenced by the stability of the gel layer attached to the membrane

Table 1. Effect of nominal membrane molecular weight cut-off PM-50 on pectin retention in ultrafiltration of grape juice[1]

VCR[2]	Permeate[3]	Retentate[4]	% Retention[5]
Initial juice	349[6]		
1.0	108	278	69.1
1.2	181	335	56.8
1.4	151	328	69.1
1.8	194	336	69.1
2.0	155	362	77.8
3.0	147	369	86.0
4.0	226	509	83.8
6.0	231	682	89.0
8.0	260	924	90.7
10.0	276	1599	92.1
12.0	289	1663	93.1

1 Mixed varieties of grape juice ultrafiltered at P_T = 1.58 Kg/cm , T = 50°C

2 $VCR = \frac{\text{Initial volume}}{\text{Retentate volume}}$

3 µg of polygalacturonic acid/ml of permeate

4 µg of polygalacturonic acid/ml of retentate

5 $\% \text{ Retention} = \frac{C_i - C_r / VCR}{C_i}$

6 µg of polygalacturonic acid/ml of grape juice

Table 2. Effect of nominal membrane molecular weight cut-off PM-100 on pectin retention in ultrafiltration of grape juice [1]

VCR [2]	Permeate [3]	Retentate [4]	% Retention [5]
Initial juice	529 [6]		
1.0	232	259	56.1
1.2	158	310	75.1
1.4	149	284	79.9
1.8	188	299	80.3
2.0	158	334	85.1
3.0	149	445	90.6
4.0	160	414	92.4
6.0	216	449	93.2
8.0	262	504	93.8
10.0	417	732	92.1
12.0	447	767	93.0

1 Mixed varieties of grape juice ultrafiltered at ΔP_T = 1.58 Kg/cm^2 T = 50°C.

2 $VCR = \frac{\text{Initial volume}}{\text{Retentate volume}}$

3 µg of polygalacturonic acid/ml of permeate

4 µg of polygalacturonic acid/ml of retentate

5 $\%\ \text{Retention} = \frac{C_i - C_r/VCR}{C_i}$

6 µg of polygalacturonic acid/ml of grape juice

surface. The change in the behavior of the permeate flux decay for PM-100 was due to a decrease in transmembrane pressure due to pumping problems at this point. When the pumping problem was corrected, an increase of permeate flux was observed, as well as increases in pectin content, in retentate and permeate streams. It is possible that there was a partial removal of the outer layers of the gel, weakening the gel layer resulting in an increase in pectin permeability due to the hydrodynamic equilibrium rupture of the gel layer.

Titratable acidity, pH, sugar content, haze, and Hunter "L," "a," "b" values

All the membranes tested produced a "sparkling clear" pale light colored (whitish to pale yellow golden) ultra-filtered permeates. The effect of the four different MWCOFF tested on pH, °Brix, TA, haze and Hunter "L," "a," "b" values for the permeate at VCR 1.2 obtained by operating the system at ΔP_T= 1.58Kg/cm^2 and T= 50°C are shown in Table 3. Since data for all four cartridges at different VCR showed sufficient similarity not all of the data obtained are presented here.

Sugar content (°Brix) behaved as freely permeable, non-interacting solutes for any MWCOFF. This permeability of the membrane for sugars is also in agreement with Drioli

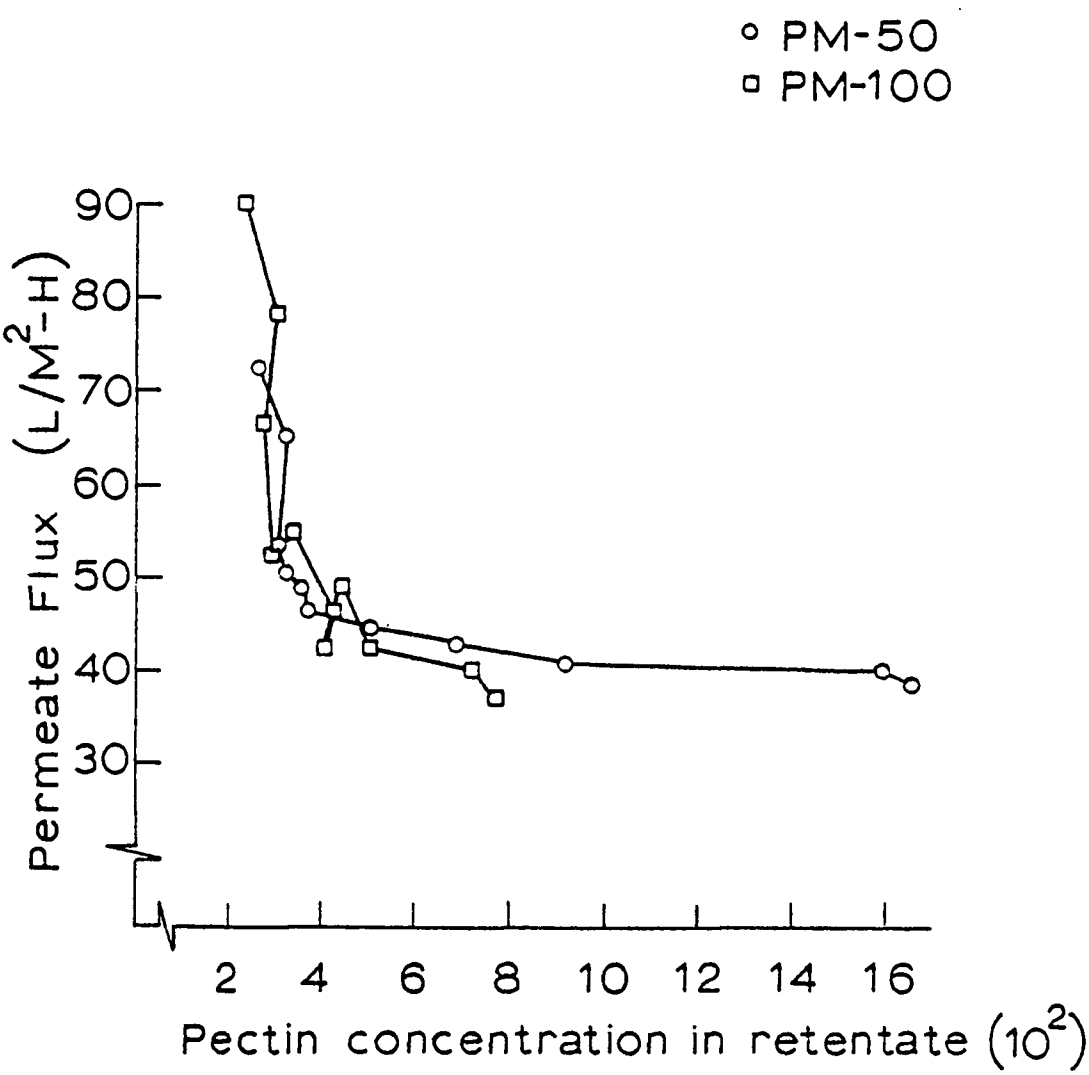


Figure 13. Effect of pectin concentration in retentate on permeate flux

Table 3. Effect of nominal membrane molecular weight cut-off on pH, sugar content, titratable acidity, haze, Hunter "L," "a," "b" values on permeate[1]

MWCOFF	pH	Sugar content[2]	Titratable acidity[3]	L[4]	a[5]	b[6]	% Haze
Initial juice	3.03	19.7	0.87	91.8	-0.9	+5.9	38.96
PM-10	2.89	19.7	0.85	95.6	-1.0	+3.2	2.74
PM-30	2.88	19.9	0.82	95.4	-1.0	+3.5	2.75
PM-50	2.90	19.5	0.81	95.4	-1.1	+3.6	3.30
PM-100	2.90	19.4	0.82	95.3	-1.1	+3.7	3.31

1 Operating conditions, P_T = 1.58Kg/cm , T = 50°C, VCR = 12
2 °Brix
3 mg of tartaric acid/100 ml of juice
4 lightness
5 redness
6 yellowness
7 values reported are means of duplicates readings

(1980) for must treatment with UF and RO and also with the findings of Heatherbell et al. (1977) and Hodgson (1981) for apple and pear juice clarification by UF, respectively.

Titratable acidity and pH of the grape juice were not affected when hollow fiber membranes within 10,000 to 100,000 nominal membrane molecular weight cut-off were evaluated (Table 3).

High reduction (91-93%) of haze was achieved by the membranes, because of the combined effect of MWCOFF an the gel layer formed in the outer side of the thin "skin" of the active membrane surface. Furthermore, Hunter "L," "a," "b" were used to confirm that there were no detectable differences in grape juice color with increasing VCR through the all four membranes tested.

SUMMARY AND CONCLUSIONS

Ultrafiltration using hollow fiber membranes was found to be feasible for clarification, stabilization and preservation of white grape juice. The effect of nominal membrane molecular weight cut-off (MWCOFF) and transmembrane pressure (ΔP_T), on the flux (J) is modeled by the following polynomial regression equation:

$$J = 39.729 - 1.635\ MWCOFF + 17.048\ P_T + 0.035\ MWCOFF^2$$

This equation indicates that permeate flux behavior was significantly dependent on molecular weight cut-off, while transmembrane pressure has a slight influence in the polarized region of the system (Figure 4).

The criteria for evaluating the optimum ΔP_T is to maximize the permeate flux. For the PM-10, PM-30, and PM-50 membranes the optimum ΔP_T was determined to be 1.58 Kg/cm^2. While the optimum ΔP_T was 1.23 Kg/cm^2 for PM-100 due to the bell-shaped permeate flux behavior.

Temperature showed a linear relationship with permeate flux (Figure 5), but this parameter is a limiting factor for the quality of the juice. A temperature of 50°C was chosen as the optimum, due to increase in rate of filtration, as well as no significant quality deterioration of the ultrafiltered grape juice.

There was an exponential decay of the permeate flux at VCR 1 to VCR 9 for each of the membranes tested, then levels off at VCR 10 to VCR 12, where a possible real steady state was reached. The decay of the permeate flux was stronger for PM-100 membrane, while PM-30 and PM-10 showed similar decreasing trends for permeate flux behavior.

The PM-50 membrane was found to be the most suitable for clarification of grape juice. Since it gave the best balance between operation time and retention characteristics.

The decrease in permeate flux with viscosity is due to the increase in the concentration of macromolecules rejected by the membrane (Figure 11) which is aggravated by the fouling of the membrane, being stronger for the PM-100 membrane at lower retentate viscosity. The fouling of the membrane combined with the increasing retentate viscosity caused the observed decrease in permeate flux, and they were the limiting factors for the permeate flux during the UF of grape juice.

Pectins were retained in the range of 80-93% for the PM-100 and the PM-50 membranes. This retention may be attributed to the formation of protein-phenolics and protein-pectins complexes at the gel layer. This pectin retention could account for that increase in viscosity in the retentate stream.

The pH, sugar content and titratable acidity of the grape juice were not significantly affected by any of the MWCOFF during UF processing (Table 3). Haze reduction of 91-93% was achieved with the four different membranes. All four membranes produced a sparkling clear pale yellow-golden grape juice. Hunter "L," "a," "b" were used to confirm that there were no detectable differences in grape juice color produced by the four different membrane cartridges.

BIBLIOGRAPHY

Amicon Corporation. 1980. Ultrafiltration and microporous filtration systems catalog. Publication 550.

Blatt, W. F., David A., Michales, A. S., and L. Nelsen. 1970. Solute polarization and cake formation in membrane ultrafiltration:causes, consequences, and control techniques. In Membrane Science and Technology, (J. E. Flinn, ed.). Plenum Press, New York. pp. 47-97.

Blumenkrantz, N. and G. Asboe-Hansen. 1973. New method for quantitative determination of uronic acids. Anal. Bioch. 54:484-489.

Breslau, B. R. 1976. Advances in ultrafiltration processing technology as related to application in the dairy industry. Paper presented at the 1976 Whey Products Conference. October 14, 1976. Atlantic city, New Jersey.

Breslau, B. R. 1982. Ultrafiltration, theory and practice. Paper presented at the 1982 Corn Refiners Association Scientific Conference. Lincolnshire, Illinois, June 16-18, 1982.

Breslau, B.R. Training program notes. Ultrafiltration. principles and practice. Romicon, Inc., Woburn, Massachusetts.

Breslau, B. R., Agranat, E. A., Testa, A. J., Messinger, S., and R. A. Cross. 1975. Hollow fiber ultrafiltration. Chem. Engr. Progr. 71:12.

Breslau, B. R., and B. M. Kilcullen. 1977. Hollow fiber ultrafiltration of cottage cheese whey: performance study. J. of Dairy Sci. 9(9):1379-1386.

Breslau, B. R., Kilcullen, B. M., and R. A. Cross. 1975. Hollow fiber ultrafiltration of cottage cheese whey. Paper presented at the 70th Annual Meeting of the American Dairy Science Association. June 23, 1977. Kansas State University.

Breslau, B. R., Testa, A. J., Milnes, B. A., and G. Medjanis. 1980. Advances in hollow fiber ultrafiltration technology. In Ultrafiltration Membranes and Application. Polymer Science and Technology, (A. R. Cooper, ed.). Vol. 13. Plenum Press, New York. pp. 109-128.

Bruin, S., Kikkert, A., Weldring, J. A. G., and I. Hiddink. 1980. Overview of concentration polarization in ultrafiltration. Desalination : 35(1):129-147.

Cheryan, M. 1977. Mass transfer characteristics of hollow fiber ultrafiltration of soy protein systems. J. Food Process. Eng. 1:269-287.

Cheryan, M. and D. J. Nichols. 1980. Optimization of flux in laminar flow ultrafiltration. In Food Process Engineering. Vol. 1 — Food Processing Systems, (P. Linko, Y. Malkki, J. Olkku, and J. Larinkari, eds.). Applied Science Pub., London. U. K. pp. 572-579.

Cheryan, M. and J. E. Schlesser. 1978. Performance of hollow fiber systems for the ultrafiltration of aqueous extract of soybeans. Lebensn.-Wiss.u.-Technol. 11:65-69.

de Filippi, R. P. 1977. Ultrafiltration. In Filtration Principles and Practices, (C. Orr, ed.). Vol. 1. Marcel Dekker, Inc., New York. pp. 475-518.

de Filippi, R. P. and R. L. Goldsmith. 1970. Application and theory of memebrane processes for biological and other macromolecular solutions. In Membrane Science and Technology, (J. E. Flinn, ed.). Plenum, Press. New York. pp. 33-46

Doshi, M. R. 1980. Boundary layer removal in ultrafiltration. In Ultrafiltration Membranes and Applications. Polymer Science and Technology, (A. R. Cooper, ed.). Vol. 13. Plenum Press, New York. pp. 231-246.

Drioli, E. and F. Belluci. 1978. Concentration polarization and solute-membrane interactions affecting pressure driven membrane processes. Desalination. 26(1):17-36.

Eakin, D. E., Singh, R. P., Kohler, G. O., and B. Knuckles. 1978. Alfalfa protein fractionation by ultrafiltration. J. Food Sci. 43(2):544-547.

Eykamp, W. 1978. Fouling of membrane in food processing. Food, pharmaceutical and bioengineering. 1976/77. A.I.Ch.E. Symposium Series. 74(172):233-235.

Fenton-May, R. I., Hill, G. G., and C. H. Amundson. 1971. Use of ultrafiltration adn reverse osmosis for the concentration and fractionation of whey. J. Food Sci. 36:14-21.

Fombin, J. F. 1983. Ultrafiltration of grape juice: effects on composition, quality, and preservation. M.S. Thesis. Oregon State University.

Friedrich, A., Driancourt, C. N. and L. Monnerie. 1981. Asymmetric reverse osmosis and ulrafiltration membranes prepared from sulfonated polysulfone. Desalination. 36(1):39-62.

Glimenius, R. 1980. Membrane process for water, pulp and paper, food state of art. Desalination. 35(1):259-272.

Glover, F. A., Skudder, P. J., Stothart, P. H., and E. W. Evans. 1978. Reviews of the progress of dairy science: reverse osmosis and ultrafiltration in dairying. J. of Dairy Research. 45:291-318.

Green G., and G. Belfort. 1980. Fouling of ultrafiltration membranes: lateral migration and the particle trajectory model. Desalination. 35(1):129-147.

Griffith, D. L. 1981. Use of ultrafiltration in procesing of fruit juices. In Proceedings of the Symposium on Technological Problems of Fruit Juices Concentrates. March 19-20, 1981. OSU Ag. Expt. Stn. Tech. Publ. 6234.

Goldsmith, R. L. 1971. Macromolecular ultrafiltration with microporous membranes. Ind. Eng. Chem. Fundam. 10(1):113-120.

Hanbury, W. T., Yuceer, A., Tzimopolous, M., and C. Byagambi. 1981. Pressure drops along the pores of hollow fiber membranes - their measurement, prediction and effect on fiber bundle performance. Desalination. 38(1):301-318.

Harper, W. J. 1980. Factors affecting the applications of ultrafiltration membranes in the dairy industry. In Ultrafiltration Membranes and Applications. Polymer Science and Technology, (A. R. Cooper, ed.). Vol. 13. Plenum Press, New York, pp. 321-342.

Heatherbell, D. A. 1976a. Haze and sediment formation from starch degradation products in apple wine and clarified apple juice. Confructa. 21(1/2):36.

Heatherbell, D. A. 1976b. Haze and sediment formation in clarified apple juice and wine. Alimenta, 15:151-154.

Heatherbell, D. A. 1981. Cause and prevention of haze and sediment formation in fruit juices and concentrates. In Proceedings of the Symposium on Technological Problems of Fruit Juice Concentrates. OSU Ag. Exp. St. Tech. Publ. 6234.

Heatherbell, D. A. 1983. FST. Dept. Oregon State University. Personal communication.

Heatherbell, D. A., Short, J. L. and P. Struebi. 1977. Clarification of apple juice by ultrafiltration. Confructa. 22(5/6):157-169.

Hermans, J. J. 1978. Physical aspects governing the design of hollow fiber modules. Desalination. 26(1):45-62.

Hodgson, J. 1981. Ultrafiltration of pear juice: chemical and phsyical analysis. M.S. Thesis. Oregon State University.

Howell, J. A. and O. Velicangil. 1980. Protein ultrafiltration: theory of membrane fouling and its treatment with immobilized proteases. In Ultrafiltration Membranes and Applications, (A. R. Cooper). Plenum Press, New York. pp. 217-230.

Jonsson, G. 1980. Overview of theories for water and solute transport in ultrafiltration/reverse osmosis membranes. Desalination. 35(1):21-38.

Jonsson, G., and C. E. Boessen. 1975. Water and solute transport through cellulose acetate reverse osmosis membrane. Desalination. 17(1):145-165.

Kirk, D. 1983. Ag. Eng. Dept. Oregon State University Personal communication.

Kortekaas, M. G. 1980. Clarification of pear juice by hollow fiber ultrafiltration. M.S. Thesis. Oregon State University.

Mans, J. 1981. Membrane processing — cost, efficiency spark interest in new technology. Proc. Prep. Food 5:59-63.

Matthiason, E. and B. Sivik. 1980. Concentration polarization and fouling. Desalination 35(1):59-103.

Merin, U. and M. Cheryan. 1980. Ultrastructure of the surface of a polysulfone ultrafiltration membrane. J. Appl. Poly. Sci. 25:2139-2142.

Michaels, A. S. 1974. Tailored membranes. In Advances in Preconcentration and Dehydration of Foods, (A. Spicer, ed.). Wiley, New York. pp. 213-250.

Michaels, A. S. 1968. Ultrafiltration. In Progress in Separation and Purification, (E. S. Percy, ed.). Wiley, New York. Vol. 1. pp. 297-334.

Michaels, A. S. 1980. Membrane technology and biotechnology. Desalination. 35(1):329-351.

Michaels, A. S. 1980. Fifteen years of ultrafiltration: problems and future promises of an adolescent technology. In Ultrafiltration Membranes and Applications. Polymer Science and Technology, (A. R. Cooper, ed.). Vol. 13. Plenum Press, New York. pp. 1-20.

Mott, R. L. 1972. Applied fluid mechanics. 2nd. ed. Merril Publishing Co., Columbus, Ohio. 8:163-166.

Nichols, D. J. and M. Cheryan. 1981. Production of soy isolates by ultrafiltration: Process engineering characteristics of the hollow fiber systems. J. of Food Proc. Eng. 5:103-118.

Nielsen, W. K. and R. F. Madsen. 1980. Use of thin channel systems for ultrafiltration and hyperfiltration. Desalination. 34(1):113-130.

Niketić-Aleksić, G. and M. M. Jaksić. 1980. Application of selective membranes in grape juice stabilization. Desalination. 35(1):317-327.

Omosaiye, O. and M. Cheryan. 1979. Ultrafiltration of soybean water extracts: Processing characteristics and yields. J. of Food Sci. 44:1027-1031.

Pace, G. W., Schorin, M. J., Archer, M. C. and D. J. Goldstein. 1976. The effect of temperature on the flux from a stirred ultrafiltration cell. Separation Science. 11(1):65-77.

Paterson Candy International Ltd. 1982. Membrane applications in the fruit juice industry. Hampshire, U. K.

Pepper, D. 1980. Membrane life, capacity and costs. Desalination. 35(1):338-396.

Probstein, R. F., Schen, J. S. and W. F. Leung. 1978. Ultrafiltration of macromolecular solutions at high polarization in laminar channel flow. Desalination. 24(1):1-16.

Porter, M. C. 1972. Ultrafiltration. Ind. Eng. Chem. Prod. Res. Develop. 11:234-248.

Porter, M. C. 1975. Filtration-separation: Selecting the reight memebrane. Chem. Engr. Progress. 71(12):55-61.

Porter, M. C. and A. S. Michaels. 1971. Membrane ultrafiltration. Part 5. Chem. Tech. 1:56.

Randahn, H. 1976. The flow properties of skim milk concentrate obtained by ultrafiltration. J. of Texture Studies. 7:205-217.

Robertson, G. L. 1979. The fractional extraction and quantitative determination of pectic substances in grapes and musts. Am. J. Enol. Vitic. 30(3):182-186.

Romicon, Inc. Hollow fiber ultrafiltration. Literature packet. Woburn, Massachusetts.

Romicon, Inc. Operating instructions Romicon model HFXS-MXII ultrafiltration system. Woburn, Massachusetts.

Rwabahizi, S. 1983. Effects of mold contamination and ultrafiltration on the color stability of strawberry juice and juice concentrate. To be published in J. of Food Sci.

Sayavedra, L. A. 1983. FST. Dep. Oregon State University. Personal communication.

Setti, D. 1976. Effect of operating parameters on permeate rate. Lebensm.-Wiss.u.-Technol. 9:29-32.

Short, J. L. 1983. Romicon, Inc. Woburn, Massachusetts. Personal communication.

Smith, C. V. and D. di Gregorio. 1970. Ultrafiltration water treatment. In Membrane Science and Technology (J. E. Flinn, ed.). Plenum Press, New York. pp. 209-219.

Snedecor, G. W. and W. G. Cochran. 1982. Statistical methods. 7th ed. The IOWA State Univ. Press. Ames, Iowa.

Strathman, H. 1980. Development of new membranes. Desalination. 35(1):39-58.

Water, A. G. and A. G. Fane. 1981. Initial flux and rejection characteristics of partially permeable ultrafiltration membranes. J. of App. Poly. Sci. 26(9):3007-3914.

Wilson, E. L. and D. J. W. Burns. 1983. Kiwifruit juice processing using heat treatment techniques and ultrafiltration. J. of Food Sci. 48(4):1101-1105.