

AN ABSTRACT OF THE THESIS OF

Marjan G. Kortekaas for the degree of Master of Science  
in Food Science and Technology presented on May 2, 1980

Title: CLARIFICATION OF PEAR JUICE BY

HOLLOW FIBER ULTRAFILTRATION

Abstract approved: \_\_\_\_\_

Dale E. Kirk

Hollow fiber ultrafiltration was successfully applied to obtain a clear, amber-colored pear juice.

For the three hollow fiber membrane cartridges tested (50, 000, 30, 000, and 10, 000 molecular weight cut-off), the process parameters were optimized and found to be similar. The permeate-flux versus pressure behavior after the formation of a gel layer was bell-shaped. The permeate flux reached a maximum at an average transmembrane pressure of  $1.6 \text{ kg/cm}^2$  ( $P_{in} = 1.78 \text{ kg/cm}^2$  and  $P_{out} = 1.41 \text{ kg/cm}^2$ ) with a flow rate of  $0.15 \text{ m/s}$ . The permeate flux decreased linearly with the logarithm of the concentration. Higher flux rates were obtained at higher temperatures within the temperature limitations of the membrane.

Clarification of Pear Juice by Hollow  
Fiber Ultrafiltration

by

Marjan G. Kortekaas

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

Completed May 2, 1980

Commencement June 1980

APPROVED:

---

Professor of Agricultural Engineering in charge of major

---

Head of Department of Food Science and Technology

---

Dean of Graduate School

Date thesis is presented May 2, 1980

Typed by Opal Grossnicklaus for Marjan G. Kortekaas

## ACKNOWLEDGEMENTS

I would like to express my thanks and appreciation for the guidance and assistance given by professor Dale E. Kirk in this research and the preparation of this thesis.

Special thanks are due to Dr. Morris W. Montgomery for serving on my graduate committee and his assistance, to Dr. David A. Heatherbell for his advice and assistance, and to Dr. Paul E. Kifer for providing financial support during the course of this investigation.

## TABLE OF CONTENTS

### SECTION I

	<u>Page</u>
INTRODUCTION	1
REVIEW OF LITERATURE	3
Clarification of Pear Juice	3
Membrane Separation Processes	5
Membranes	7
Theory of Membrane Transport	12
Application of Ultrafiltration	19
BIBLIOGRAPHY	21

### SECTION II

#### RESEARCH PAPER

INTRODUCTION	26
EXPERIMENTAL	29
RESULTS AND DISCUSSION	32
Transmembrane Pressure Effects	32
Flow Rate	36
Concentration Effects	38
Viscosity and Temperature	41
CONCLUSIONS	44
REFERENCES	45

## LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
SECTION I		
A	Principles of ultrafiltration and reverse osmosis.	6
B	Useful ranges of various separation processes	8
C	Scanning electron photomicrograph (400x) of conventional flat sheet membrane (left) and hollow fiber of similar porosity (right).	11
D	Schematic description of hollow fiber ultrafiltration process.	13
E	Schematic description of concentration gradient	16
F	Schematic description of gel layer and concentration gradient.	18
SECTION II		
1.	Flow sheet for hollow fiber ultrafiltration unit	30
2.	Effect of average transmembrane pressure and flow rate on permeate flux for PM-50 membrane at 50°C.	32
3.	Relation between permeate flux and average transmembrane pressure and effect of volume concentration ratio for PM-50 membrane at 50°C.	37
4.	Effect of volume concentration factor and pore size of membrane on permeate flux at 50°C and $\Delta P_t = 1.6 \text{ kg/cm}^2$ .	39
5.	Decline of permeate flux with time for a PM-50 membrane at an average transmembrane pressure of $1.6 \text{ kg/cm}^2$ and at 50°C.	50

Figure

Page

6. Relation between viscosity and volume concentration ratio for pear juice at 50°C. 42
7. Relationship between permeate flux and temperature for a PM-50 membrane at  $\Delta P_t$  of 1.6 kg/cm<sup>2</sup> and a VCR of 2. 43

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	Some commercially available UF membranes.	10

# CLARIFICATION OF PEAR JUICE BY HOLLOW FIBER ULTRAFILTRATION

## INTRODUCTION

The fruit juice industry in the Pacific Northwest region (where the world's largest producers of pears and pear concentrates are located) has been searching for better methods of clarifying fruit juices. Increasingly, this interest is being channeled towards pear juice, due to its being an excellent source of natural sugars. When combined with other fruit juices, pear juice improves the body of the mix; also, its substitution for sugar-syrup in canned fruits creates a more natural product.

However, a requisite for the last application is a clear, light-colored pear juice. Obtaining these characteristics for pear juice presents difficulties, since existing, conventional clarification methods (Doesburg 1965) are slow and inconsistent (Beavers and Youtz 1976, Chang 1979).

In an attempt to find better clarification methods, the following pilot-scale study evaluates the feasibility of utilizing hollow fiber ultrafiltration in pear juice clarification. The prime concern was to optimize process parameters such as average transmembrane pressure, flow rate and temperature. Not covered in this research were the composition of the juice or changes that might occur

during processing. These chemical analyses are currently being researched, and will be reported elsewhere (Youtz, in progress).

## REVIEW OF LITERATURE

### Clarification of Pear Juice

While numerous strides have been made towards improving clarification methods of fruit juices in general, little effort has been directed at pear juice due to various hindering factors (Beavers and Youtz 1976, Chang 1979). Consequently, the literature on apple juice clarification will be reviewed, since it uses more conventional methods.

Fruit juice clarification has two endemic problems, being haze and sediment formation. These problems have been well recognized, but according to Curl and Talbut (1954) not well understood.

The major compounds responsible for these haze and sediment formations are pectins, starches, polyvalent cations, polyphenolics and proteins. These are described by Heatherbell (1976a and b) in great detail. He indicates that the pivotal factor for preventing cloud formation in apple juice and apple wine lies in the removal of pectin and starch. Where the removal of pectin and starch cannot be accomplished through physical processes such as fining, centrifugation and filtration, enzymatic hydrolysis should be used.

Yamasaki et al. (1964) have reported that positively charged colloids will improve apple juice clarification. These positively

charged colloids will improve apple juice clarification. These positively charged particles, such as gelatin, have the ability to attach to large colloidally-suspended pectin molecules and thus remove the haze and assist in the clarification.

As for applying Yamasaki's theory in clarifying pear juice, Beavers and Youtz (1976) obtained good results with acidification. Their attempts to obtain filtration without acidification proved to be nearly impossible. They did find that by properly concentrating, gelatin would improve the clarification and increase the filtration rate. However, the results of this experiment were heavily weighted by independent factors such as crop year and pear variety. Consequently this method would not have particular value in industrial applications.

Another method for clarifying apple juice was introduced by Heatherbell et al. (1977). This was using ultrafiltration (UF), which selectively removes essentially all polysaccharide materials (i. e. , pectin and starch) without adversely affecting other juice constituents. The result was a "sparkling clear" apple juice.

When comparing conventional clarification methods to UF, Heatherbell's research indicated that the latter possesses a unique advantage. It leads to a "cold sterilization" by removal of all microorganisms which, in turn, promotes preservation. This can reduce

quality losses that are incurred when conventional thermal processing or sterilization methods are used.

### Membrane Separation Processes

Ultrafiltration (UF) and Reverse Osmosis (RO) are pressure-activated membrane processes (Porter and Michaels, 1971a), where different size molecules are fractionated by filtration without involving a phase change or interphase mass transfer.

While there are similarities in these two separation processes, important differences exist. Unfortunately, there is considerable confusion about these distinctions. One of the better explanations is given by Michaels (1968) and Glover et al. (1978) (see also

Figure A):

Reverse Osmosis is a process for separating low molecular weight ( $< 500$ ) solutes from their solvents. Since the membranes are impermeable (or only slightly permeable) to inorganic ions and organic compounds, osmotic pressure effects are significant. Operation pressures are in the region of 5 to 50 kg/cm<sup>2</sup>.

Ultrafiltration is a sieving process, can be compared with normal filtration, in which macromolecules with a molecular weight of more than 500 are retained. A low pressure (0.5 to 5 kg/cm<sup>2</sup>) is applied to the feed solution on one side of a highly permeable membrane. The molarity of macromolecular solutions is usually so low that osmotic pressure effects are negligible.

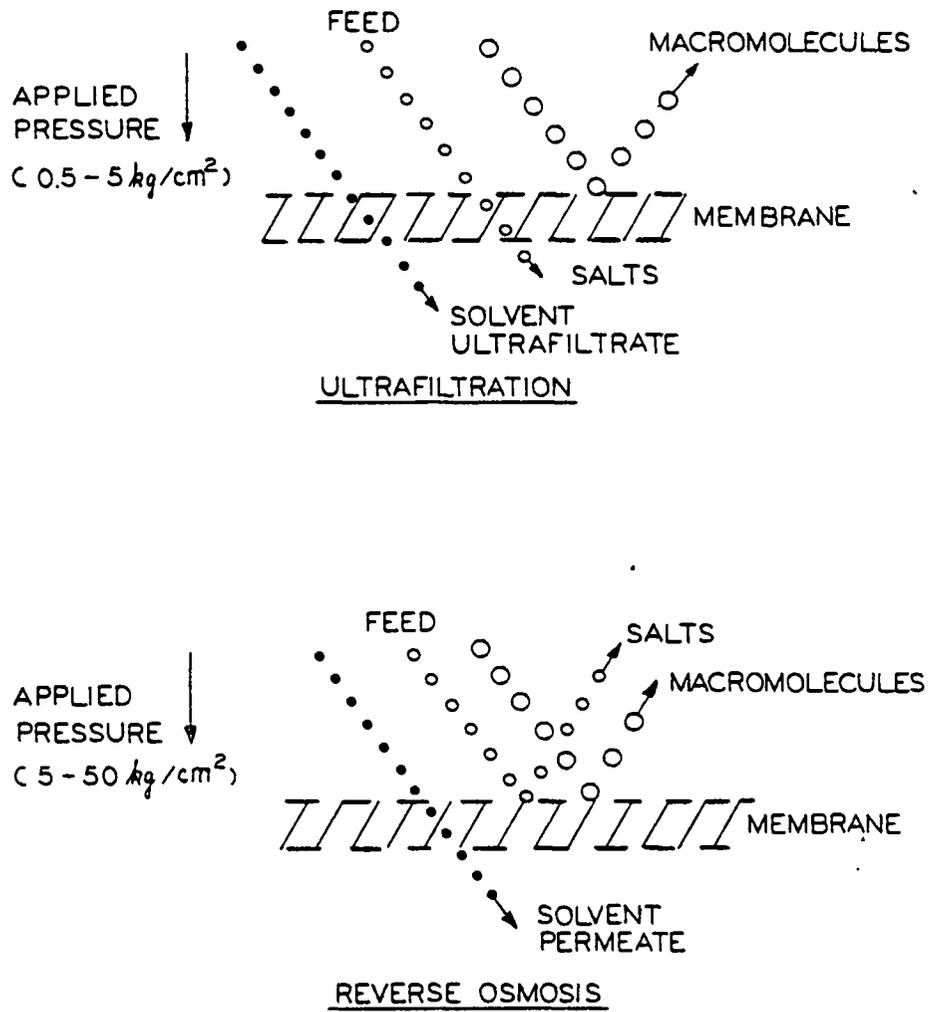


Figure A. Principles of ultrafiltration and reverse osmosis.

Figure B ranks UF and RO. It can be seen that UF retains particles in the size range  $2 \times 10^{-3}$  to 10 microns. In contrast, the smallest particles that can be recovered by conventional filtration are greater than 10 microns. For a frame of reference, the molecular weights of pectic substances lie in the macromolecular range, from about 10,000 to 400,000 (Doesburg, 1965).

Much has been published about membrane separation processes. In order to cover what is pertinent, for an adequate understanding of the research done in this paper, the following background information has been divided into three different sections.

### Membranes

Because of the structure of UF and RO membranes all rejection of solutes occurs at the membrane surface (Porter and Nelson 1971 and Michaels 1974). This makes the membrane and its properties one of the most important parts of the whole clarification process.

Not until the late 1950's did the industrial applications of UF and RO become important. The breakthrough came with the development of anisotropic cellulose-acetate membranes by Loeb and Sourirajan (1963). Their design consisted of a thin solute rejecting skin on a supporting porous structure, having a reasonable flux and

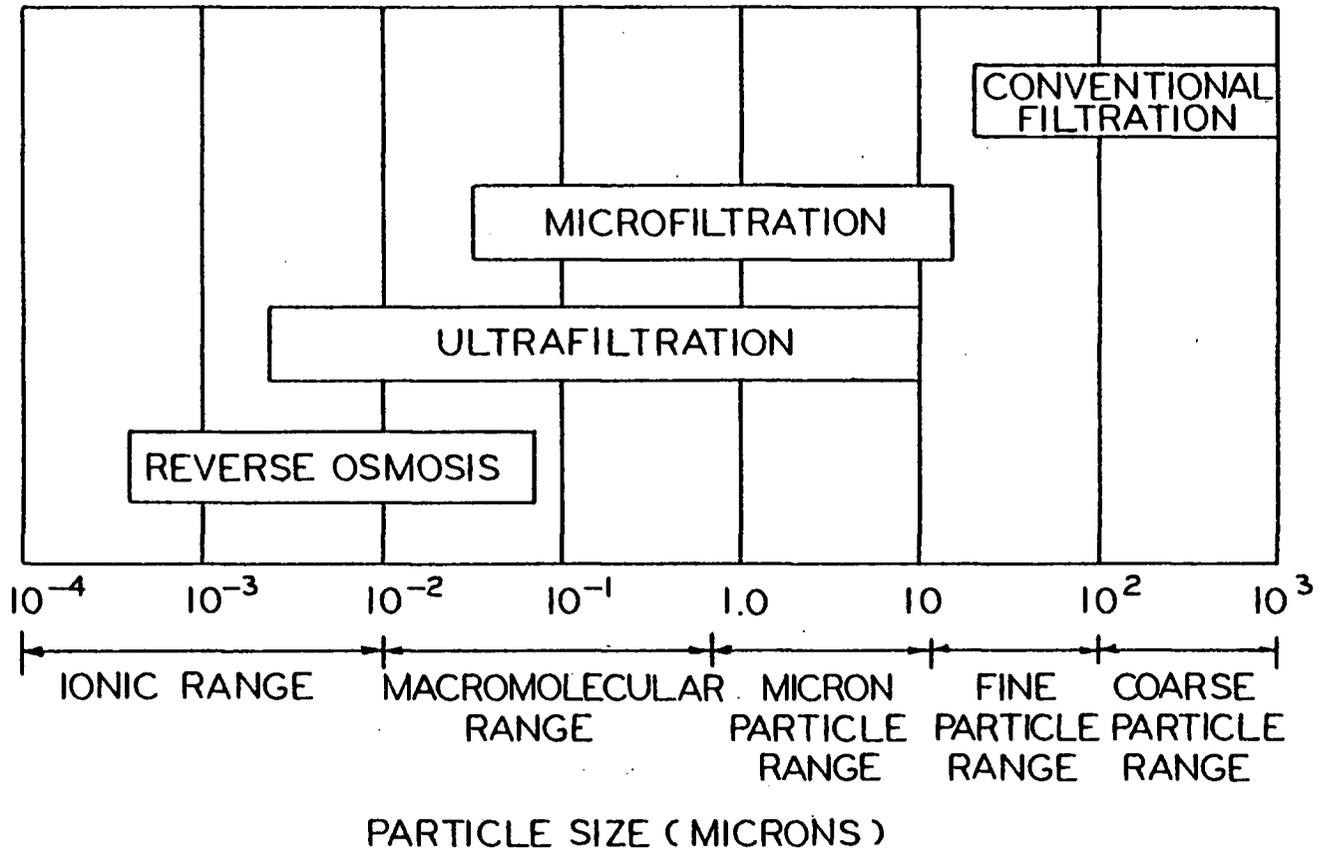


Figure B. Useful ranges of various separation processes.

fairly high hydraulic permeability. Merten (1966) and Michaels (1968) described the initial experimental processes, which were plagued with membrane fouling and limited membrane lives.

In more recent years, polymeric membranes of polymers other than cellulose acetate have been produced especially for UF (Michaels 1971).

While there is a plethora of literature about the manufacture of RO membranes, there is scanty information about the production and development of successful UF membranes of other polymers. To date, a number of polymeric membranes have been designed for UF. These are summarized in Table 1 (Glover et al. 1978).

Besides different membrane compositions, there is also a wide variety of configurations. Since only the hollow fiber geometry is used for this research project, the following will preclude discussion about other available geometries.

Porter (1975) and Blatt et al. (1970) describe hollow fiber UF membranes as being a single fiber of active membrane surface, which, because of its construction, can withstand pressure on either side. The hollow fibers are made with a thin interior skin ( $0.1\mu$ ) and have a sponge-like outer support (Figure C). The latter allows for ready removal of surface fouling when the direction of the fluid flow is reversed.

TABLE 1. SOME COMMERCIALY AVAILABLE UF MEMBRANES.

Membrane configuration of module	Composition	Cut-off minimum mol. wt.	Manufacturer	Remarks
Hollow fibres	modakryl	10,000 to 50,000	Romicon	Compact. Susceptible to plugging
Tubular	cellulose acetate + derivate	10,000 to 22,000	Abcor PCI Calogen Havens	Not prone to plugging. Preferred in food processing due to ease of cleaning.
Thin or flat channel	polysulphonic acrylic copolymers	15,000 to 18,000	Romicon Iopor (Dorr-Oliver) (DDS)	Fairly compact. More economic for viscous solutions.
Spiral wound	polysulfone cellulose-acetate	600 to 1000		Compact. Susceptible to plugging.



Figure C. Scanning electron photomicrograph (400x) of conventional flat sheet membrane (left) and hollow fiber of similar porosity (right).

The operation of a hollow fiber UF unit is explained by Blatt (1972), Breslau and Kilcullen (1977). As shown in Figure D, a feed solution is pumped into a hollow fiber membrane. Under the impressed pressure gradient across the supported membrane wall, the feed solution is separated into two streams. A permeate stream of solvent and smaller solute particles passed through the membrane, and a concentrated stream of larger solutes is retained by the membrane.

One outstanding feature about hollow fiber membranes is the ability to utilize a high velocity laminar flow to minimize buildup of material on the membrane surface. This is important, as retained material can form a gel layer and cause a significant decline of permeate flux during processing.

In clarifying fruit juice, the UF membrane retains the cloud stabilizing polysaccharides while allowing water, sugars, flavor and aroma compounds to pass through and be collected as permeate (Heatherbell et al. 1977).

### Theory of Membrane Transport

The theory of ultrafiltration has not changed significantly since Ferry's review in 1936. More recent reviews were made by Blatt et al. (1970), Lonsdale (1972), and Madsen (1977). The following describes

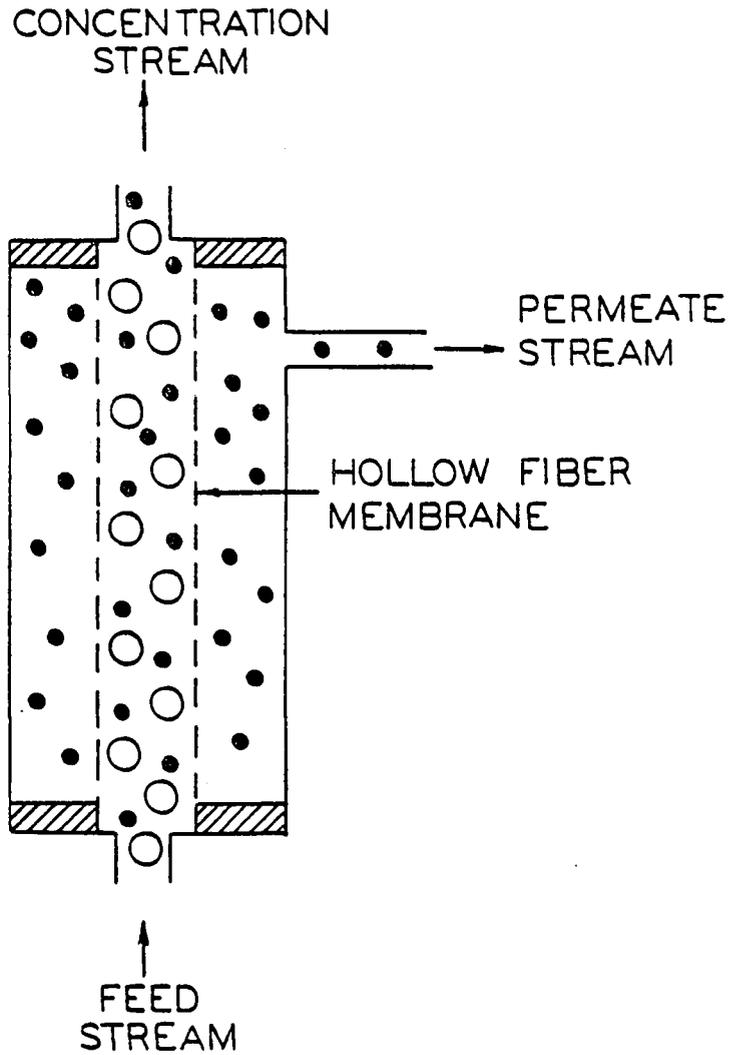


Figure D. Schematic description of hollow fiber ultrafiltration process.

the more important aspects of the theory of membrane transport.

A number of theoretical approaches are used to describe the various mechanisms of membrane transport. They are the solution-diffusion model, irreversible thermodynamics, and the pore-model (Lonsdale 1972). The last model has been most widely used in explaining UF.

In the pore-model equation, the permeate flux, the flow through the membrane is given in terms of Poiseuille's Law for viscous flow:

$$J = \frac{A(\Delta P_t - \Delta \pi)}{\eta} \quad \text{Eq. 1}$$

Where:  $J$  = the permeate flux, the flow rate per unit of membrane area

$\Delta P_t$  = transmembrane pressure, the average of inlet and outlet pressures on the retentate side of the membrane. The permeate is at atmospheric pressure

$\Delta \pi$  = the transmembrane osmotic pressure of the rejected solute against which the driven force  $\Delta P_t$  is applied

$\eta$  = the viscosity of the feed

$A$  = membrane permeability coefficient characteristic of a particular membrane

Several studies (Michaels 1968, De Filippi and Goldsmith 1970, Goldsmith 1971, and Porter 1975) have found that this simple relation between permeate flux and applied pressure difference was not valid

for UF systems. It was observed that the permeate flux became independent of the applied transmembrane pressure. This phenomenon, known as "concentration polarization", is a direct consequence of solvent transport through the membrane.

The model based on concentration gradient has been described by Michaels (1968). In any UF system, solution bulk flow toward the membrane is accompanied by solute being retained adjacent to the membrane surface. Thus, a solute concentration gradient is formed, as shown in Figure E.

At steady state, a mass balance of the solute requires that the solute transport to the membrane surface be counterbalanced by back diffusion of solute from the concentration polarization layer into the bulk liquid. This yields the equation:

$$J = K \ln \frac{c_w - c_p}{c_f - c_p} \quad \text{Eq. 2}$$

Where:  $J$  = permeate flux, flow rate per unit of membrane area

$K$  = mass transfer coefficient

$c_w$  = solute concentration at membrane surface

$c_f$  = solute concentration in the feed

$c_p$  = solute concentration of the permeate

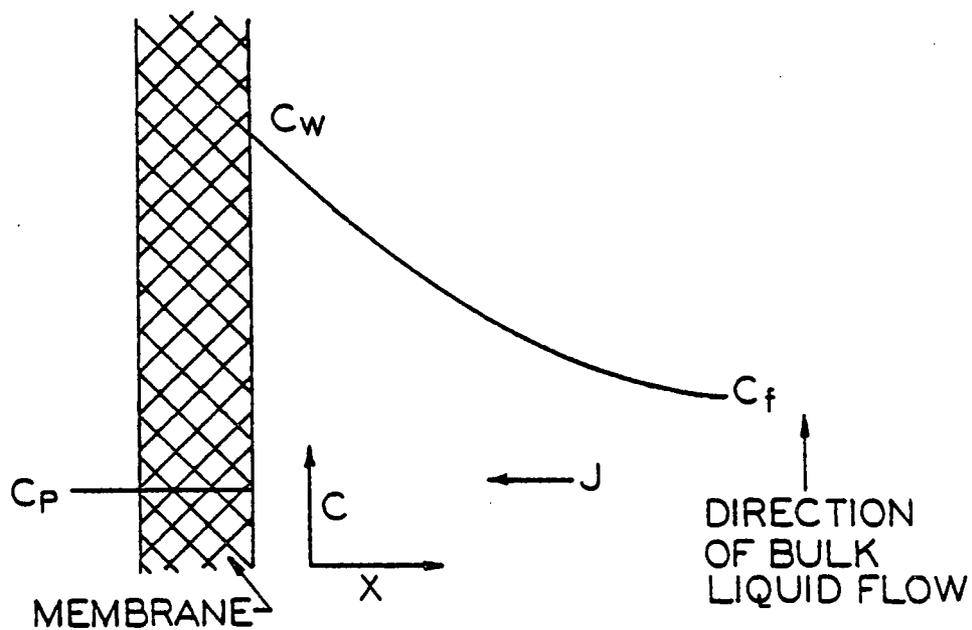


Figure E. Schematic description of concentration gradient.

For high flux membranes (UF) or higher molecular weight solutes, the  $c_w$  could exceed the solute solubility limit, and a gel layer could be formed adjacent to the membrane. This is shown in Figure F.

The presence of the gel layer introduces a hydraulic resistance which is significantly greater than that of the membrane. Consequently, transport through the membrane is now controlled by the permeability properties of the gel layer. Thus, equation 2 now becomes:

$$J = K \ln \frac{c_g - c_p}{c_f - c_p} \quad \text{Eq. 3}$$

Where  $c_w = c_g$ , is the solute concentration of the gel layer.

$$J = K \ln \text{VCR} \quad \text{Eq. 4}$$

Where VCR is the volume concentration ratio, defined as the initial volume divided by retentate volume at any time.

Equation 4 (Breslau and Kilcullen 1977) is a working equation used in UF practice.

The permeate flux is directly proportional to the mass transfer coefficient,  $K$ , and decreases logarithmically with the VCR.

The above mechanism also predicts that when the gel layer reaches a steady state condition the permeate flux becomes

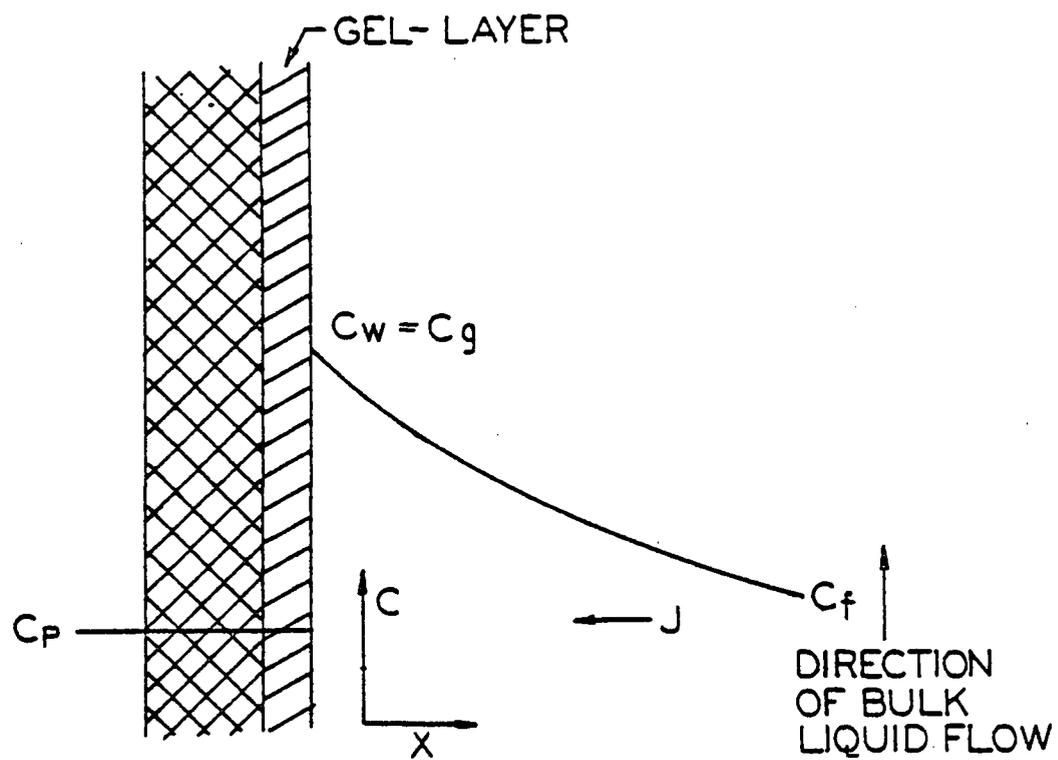


Figure F. Schematic description of gel layer and concentration gradient.

independent of the applied transmembrane pressure.

### Application of Ultrafiltration

Industrial applications of UF can be divided into the following categories: concentration, fractionation, and purification. These methods are being increasingly applied within the food processing industry, and have been documented by Porter and Michaels (1971a, b, c, d 1972).

One of the more important applications is the processing of dairy products. Horton et al. (1972) describes the first commercial scale plant. Also, UF applications have been used in the recovery of protein from cheese-whey (Horton 1974), and the production of milk-concentrates (Fenton-May et al. 1972, Thompson and deMan 1975). More recent applications in dairy industry are reviewed by Glover et al. (1978).

A number of other UF applications have achieved at least a pilot-scale level. These operations include soy protein recovery (Cheryan 1977, Omosaiye and Cheryan 1979), protein recovery in food processing wastes (Pepper), recovery of starch wastes (Bambridge et al. 1975, Oosten 1976), UF of animal blood (Ericksson and von Bockelmann 1975), and, as previously described, Heatherbell's (1977) recent successful UF application in clarifying apple juice.

Overall, UF has shown promise in solving a number of important problems in the food industry. This encompasses not only pilot-scale operations, but also potential improvements and economies over alternative processing methods.

## BIBLIOGRAPHY

- Bambridge, H., Chudack, M., Farre, A. G., Fell, C. J. D., 1975. Starch waste concentration with ultrafiltration. Third National Chemical Engineering Conference. Mildura, Victoria, Australia (August 20-23).
- Beavers, D. V. and Youtz, J. A., 1976. Investigating juice clarification and filtration procedure for juices made from fruit wastes and surplus fruits. Research Report Number 2 to Tri Valley Growers, Oregon Agric. Exp. Stn. Corvallis, Ore.
- Blatt, W. F., David, A., Michaels, A. S., Nelson, L., 1970. Solute polarization and cake formation in membrane ultrafiltration: causes, consequences, and control techniques. In Membrane Science and Technology, (Ed. J. E. Flinn). p. 47, Plenum Press, New York.
- Blatt, W. F., 1972. Hollow Fibers: A transition point in membrane Technology. American Laboratory Publication.
- Breslau, B. R., Kilcullen, B. M., 1977. Hollow Fiber Ultrafiltration of Cottage Cheese Whey: Performancy Study. J. Dairy Sc. 60. pp. 1371-86.
- Chang, Y. H., 1979. Chemical Analysis of Acid Precipitated Colloid of Ripe Bartlett Pear Juice. M.S. Thesis. Oregon State University, Corvallis, Ore.
- Cheryan, M., 1977. Mass Transfer Characteristics of Hollow Fiber Ultrafiltration of soy protein systems. J. of Food Process Engineering 1, pp. 269-287.
- Curl, A. L., and Talburt, W. F., 1954. Deterioration in storage. In Fruit and Vegetable Juice Production. (Ed. Trepler, D. K., Yoslyn, M. A.) p. 247, Avi Publishing Co. New York.

- Doesburg, J. J., 1965. Pectic substances in Fresh and Preserved Fruits and Vegetables. p. 24 and 119. Institute for Research on Storage and Processing of Horticultural Produce. Wageningen, The Netherlands.
- Ericksson, G., and von Bockelmann, J., 1975. Ultrafiltration of Animal Blood Serum: Technology and Microbiology. *Process Biochemistry*. 9. pp. 11-14.
- Fenton-May, R. I., Hill, C. G. J., Amundson, C. M., Lopez, M. H., and Anclair, P. D., 1972. Concentration and fractionation of skim-milk by reverse osmosis and ultrafiltration. *J. Dairy Sci.* 55, pp. 1561-1566.
- Ferry, J. O. (1936). *Chem. Revs.*, 18, 373.
- De Filippi, R. P., and Goldsmith, R. L., 1970. Application and theory of membrane processes for biological and other macromolecular solutions. In *Membrane Science and Technology* (Ed. J. E. Flinn) pp. 33, Plenum Press, New York.
- Glover, F. A., Skudder, P. J., Stothart, P. H., and Evans, E. W., 1978. Reviews of the progress of Dairy Science: reverse osmosis and ultrafiltration in dairying. *J. of Dairy Research*, 45, 291-318.
- Goldsmith, R. L., 1971. Macromolecular ultrafiltration with microporous membranes. *Ind. Eng. Chem. Fundam.* 10, pp. 113-120.
- Heatherbell, D. A., 1976a. Haze and sediment formation from starch degradation products in apple wine and clarified apple juice. *Confructa* 21:36.
- Heatherbell, D. A., 1976b. Haze and sediment formation in clarified apple juice and apple wine. I: The role of pectin and starch. *Fd. Tech in New Zealand*, May.
- Heatherbell, D. A., Short, J. L. and Struebi, P., 1977. Apple Juice Clarification by Ultrafiltration. *Confructa*, 22(5/6). pp. 157-169.

- Horton, B. S., Goldsmith, R. L. and Zall, R. R., 1972. Membrane processing of cheese whey reaches commercial scale. *Food Technol.* 36(2):30.
- Horton, B. S., 1974. Ultrafiltration of whey and milk for protein recovery. In *Proceedings, IV International Congress Food Sci. Technol.* Vol. IV, pp. 322-331. Instituto de Agro., Valencia, Spain.
- Loeb, S. and Sourirajan, S., 1963. *Advances in Chemistry Series* 38, 117.
- Lonsdale, H. K. 1972. Theory and practice of reverse osmosis and ultrafiltration. In *Industrial Processing with Membranes* (Eds. R. E. Lacey and S. Loeb) Wiley Interscience, New York.
- Madsen, R. F., 1977. *Hyperfiltration and ultrafiltration in Plate- and Frame Systems.* Elsevier Scientific Publishing Company, Amsterdam. The Netherlands.
- Merten, U., 1966. *Desalination by Reverse Osmosis,* MIT Press, Cambridge, England.
- Michaels, A. S., 1968. Ultrafiltration. In *Progress in Separation and Purification* (Ed. E. S. Percy) Wiley, New York. Vol. 1, pp. 297-334.
- Michaels, A. S., 1971. Preparation and Properties of Ultrafiltration membranes. Conference on Reverse Osmosis and Ultrafiltration. Chemical Center, Lund University, Lund, Sweden May 17.
- Michaels, A. S., 1974. Tailored Membranes. In *Advances in Pre-concentration and Dehydration of Foods* (Ed. A. Spicer) Wiley, New York. pp. 213-250.
- Omosaiye, O., and Cheryan, M., 1979. Ultrafiltration of soybean water extracts: Processing Characteristics and Yields. *J. of Food Sci.* 44, pp. 1027-31.
- Oosten, B. J. 1976. Ultrafiltration of Potato Juice Results in High Yield of Protein. *Die Stärke* 28:4. pp. 135-137.

- Pepper, D., (?). The Use of Membranes in the Treatment of Beverages and Food Plant Wastes. Paterson Candy International Ltd., Lavenstoke Mills, Wentchurch, Hampshire, England.
- Porter, M. C., and Nelson, L., 1971. Ultrafiltration in the chemical, food processing, pharmaceutical and medical industries. In Recent Developments in Separation Science (Ed. N. N. Li). pp. 227, RC Press, Cleveland, Ohio.
- Porter, M. C. and Michaels, A. S., 1971a. Membrane Ultrafiltration Part 1 Chem. Technol. January: 56.
- Porter, M. C. and Michaels, A. S. 1971b. Membrane Ultrafiltration Part 2. Chem. Technol. April:248.
- Porter, M. C. and Michaels, A. S. 1971c. Membrane Ultrafiltration Part 3. Chem. Technol. July 1971:440.
- Porter, M. C. and Michaels, A. S. 1971d. Membrane Ultrafiltration Part 4. Chem. Technol. October 1971:633.
- Porter, M. C. and Michaels, A. S. 1972. Membrane Ultrafiltration Part 5. Chem. Technol. January 1972:56.
- Porter, M. C., 1975. Selecting the Right Membrane. Chemical Engr. Progress. 71, No. 12, pp. 55-61.
- Thompson, S. J. and de Man, J. M., 1975. Concentration and Fractionation of Milk by Ultrafiltration. Can. Inst. Food Sci. Technol. J. Vol. 8. No. 2.
- Yamasaki, M., Yasui, T. and Akima, K. 1964. Pectic enzymes in the clarification of apple juice. Part I. Study on the clarification in a simplified model. Agr. Biol. Chem. 28:779.
- Youtz, Y. A., in progress. Oregon State University. Corvallis, Ore.

CLARIFICATION OF PEAR JUICE BY HOLLOW  
FIBER ULTRAFILTRATION

M. G. Kortekaas and D. E. Kirk

Department of Food Science and Technology

Oregon State University

Corvallis, OR 97331

## INTRODUCTION

Pear juice is an excellent source of natural sugars. Added to other fruit juices it gives more body to the mix and as a substitute for sugar-syrup in canned fruit, it provides a more natural product. Many of these applications require a clear, light-colored pear juice. The existing conventional methods for clarification of fruit juices (Doesburg 1965) are slow and inconsistent for pear juice (Beavers and Youtz 1976, Chang 1979).

The major compounds involved in haze and sediment formation in fruit juices are generally believed to be pectins and starches (Pilnik and Voragen 1970). These cloud-stabilizing compounds need to be removed by physical processes such as fining, centrifuging, filtration or by enzymatic hydrolysis.

Heatherbell et al. (1977) successfully introduced ultrafiltration (UF) to clarify apple juice and obtained a stable clear juice. UF has also the advantage of achieving a "cold sterilization", which permits cutting down on processing time and at the same time improving the quality of the juice.

UF has many applications in the food industry. Today the processing of dairy products is one of the most important (reviewed by Glover et al. 1978), but a number of other applications have been

made in at least pilot-scale operations. These include recovery of soy proteins (Cheryan 1977, Omosaiye and Cheryan 1979), and recovering of proteins and starches in food processing wastes (Bambridge et al. 1975, Ericksson and von Bockelmann 1975).

The main problem in most practical applications of UF of macromolecular solutions is a decline in permeate flux or flow through the membrane by building up of a gel layer on the membrane surface due to concentration polarization. Most recent studies of the flux behavior of UF systems, therefore, are conducted to optimize the flowrate parameters.

Many investigators working with proteins (Cheryan 1977, Omosaiye and Cheryan 1979, Fenton-May et al. 1971, Setti 1976) report that after an initial period permeate flux becomes independent of transmembrane pressure. Dejmek (1975) found for proteins that the resistance of the gel layer is proportional to the amount of deposit and increases with transmembrane pressure.

Not much information, however, is available on the behavior of permeate flux for solutions containing pectins and starches. Although Heatherbell et al. (1977) investigated the clarification of apple juice and reported the effect of concentration on flux and juice composition. He did not investigate the optimizing of process parameters.

This study is conducted to determine the feasibility of clarifying

pear juice using hollow fiber UF, and to optimize process parameters such as transmembrane pressure, flow rate along the membrane, and temperature.

## EXPERIMENTAL

The experiments were performed on a Romicon pilot-scale hollow fiber ultrafiltration unit (model HFXS MX11), equipped with three sizes of membrane cartridges (PM-50, PM-30, and PM-10, with a molecular weight cut-off of 50,000, 30,000 and 10,000 respectively).

The unit was operated as a circular batch system, schematically shown in Figure 1. The feed stream (1) was pumped from a temperature controlled ( $\pm 2^\circ\text{C}$ ) steam kettle (2) into the hollow fibers (3). The permeate stream (4) was collected and the concentrate stream (5) recirculated back into the feedtank (2). For total recycling tests both permeate and concentrate streams were recirculated to the feedtank.

In order to minimize fluctuations in test results the operation and cleaning procedures were standardized. Prior to each experiment the membranes were conditioned by flushing with recycled tap water at  $70^\circ\text{C}$  for 30 minutes.

The cleaning procedure was: flush juice out with tap water, run TERG-A-ZYME (Alconox, Inc.) detergent solution (30 g/10 l) for 15 min, flush with tap water, run with bleach solution (0.003%) for 15 min, and flush with tap water for 15 min. All solutions were at

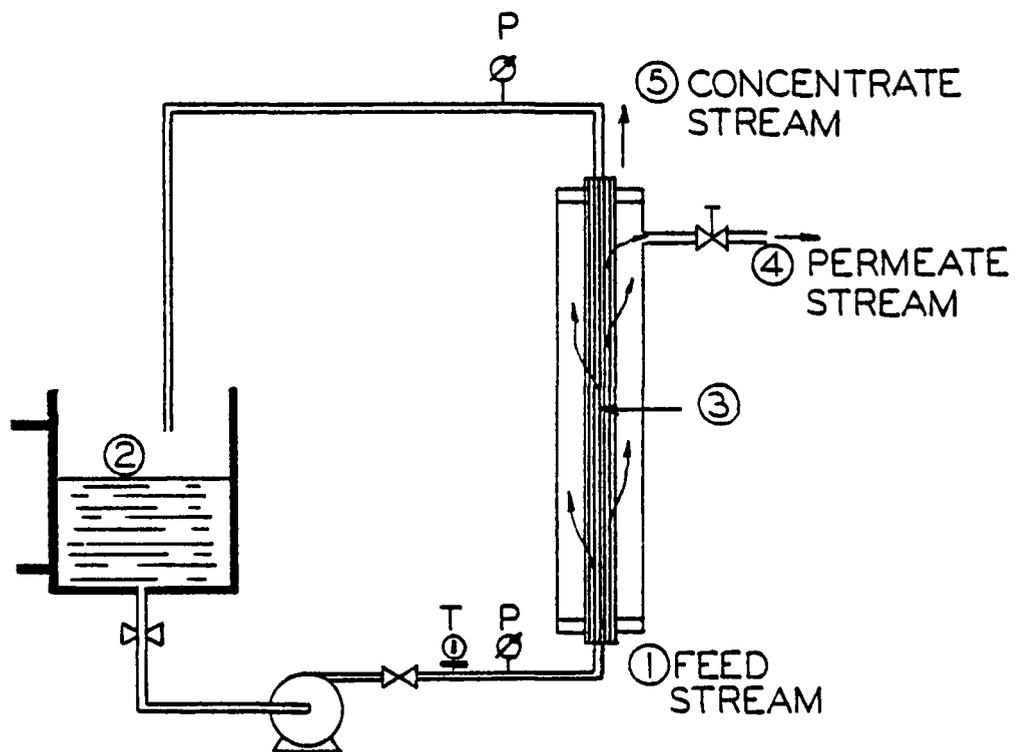


Figure 1. Flow sheet for hollow fiber ultrafiltration unit.

70°C and an average transmembrane pressure of 1.6 kg/cm<sup>2</sup>  
(P<sub>in</sub> = 1.78 kg/cm<sup>2</sup> and P<sub>out</sub> = 1.41 kg/cm<sup>2</sup>).

For flux measurements, the stopwatch and cylinder method was used. The repeatability was within 0.5 sec. Viscosity measurements were carried out with a Brookfield Synchro-lectric viscometer.

The pear juice was obtained from commercially-grown fresh, ripe Bartlett pears from California. The fruit was mixed with 1% filterpaper and 1% ricehulls, ground in a hammermill, immediately pressed in a rack-and-cloth hydraulic press, and frozen until needed. Before running in the UF unit, the pear juice was prefiltered in a Schenk plate and frame filterpress, using paper path and diatomaceous earth filtercell.

## RESULTS AND DISCUSSION

Data were obtained for the three different membranes (PM-50, PM-30, and PM-10) at four different temperatures (30, 40, 50 and 60°C), and at different average transmembrane pressures. Total recycling was used except for concentration experiments, which were a batch operation. Since they showed sufficient similarity, not all data obtained are presented here.

All the membranes tested produced a crystal-clear, amber-colored pear juice. There was no visible difference in juice color between the three membranes. This could indicate that the pore size of the membrane within the 50,000 to 10,000 molecular weight range has no influence on color or chemical composition of the pear juice. However, this should be verified with some additional experiments (Youtz, in progress).

### Transmembrane Pressure Effects

Figure 2 shows the effect of transmembrane pressure,  $\Delta P_t$ , on the permeate flux,  $J$ . Transmembrane pressure is defined as the average of inlet and outlet gauge pressures, with the permeate at atmospheric pressure.

The permeate flux increased initially with applied transmembrane pressure, and then decreased with continued increase in the

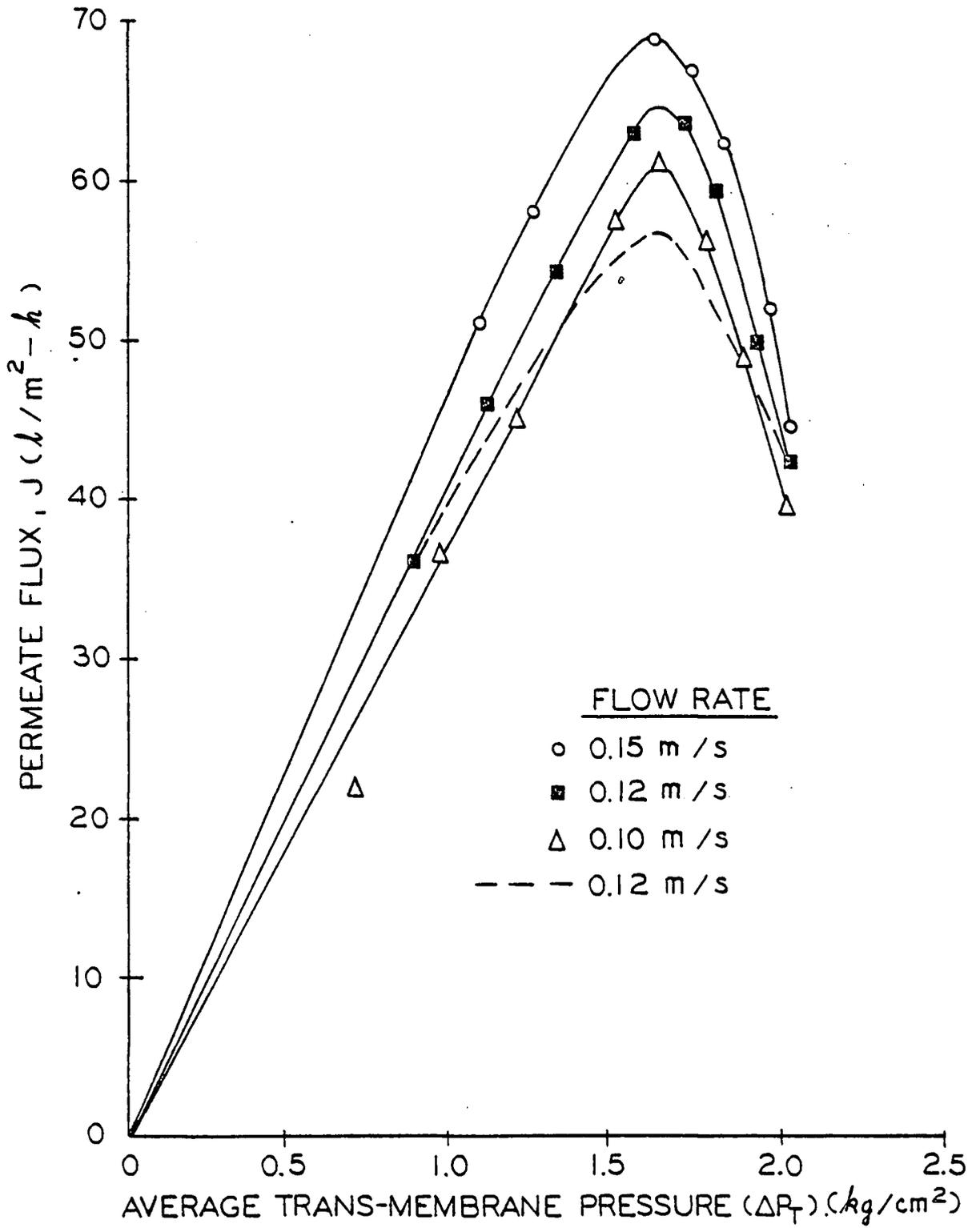


Figure 2. Effect of average transmembrane pressure and flow rate on permeate flux at 50 °C for P1-50 membrane.

transmembrane pressure. The point at which the permeate flux is maximal is considered the optimum transmembrane pressure. In these experiments it occurred at  $1.6 \text{ kg/cm}^2$  ( $P_{in} = 1.78 \text{ kg/cm}^2$  and  $P_{out} = 1.41 \text{ kg/cm}^2$ ), for all three membranes. The optimum transmembrane pressure was not greatly influenced by temperature or flow rate.

The bell-shaped permeate flux-pressure behavior for ultrafiltration of pear juice is in contrast to what many investigators have found for protein solutions (Setti 1976, Cheryan 1977, and Omosaiye and Cheryan 1979). They report that the permeate flux at higher pressures becomes independent of the applied transmembrane pressure.

This phenomenon appears to be a direct consequence of the building up of a gel layer of retained macromolecules on the membrane surface, initiated by concentration polarization.

The concentration polarization effect can be described by the following two simplified equations (Lonsdale 1972):

$$J = \frac{A(\Delta P_t - \Delta \pi)}{\eta} \quad \text{Eq. 1}$$

$$J = K \ln \frac{c}{c_f} \quad \text{Eq. 2}$$

where:  $J$  = permeate flux, flow rate per unit of membrane area

$\Delta P$  = average transmembrane pressure

$\eta$  = viscosity of the feed

$\Delta \pi$  = the transmembrane osmotic pressure

$A$  = membrane permeability coefficient

$K$  = mass transfer coefficient

$c_g$  = solute concentration of gel layer

$c_f$  = solute concentration in the feed stream

The presence of the gel layer introduces a hydraulic resistance which can be significantly greater than that of the membrane. In this case, the mechanical properties of the gel layer, rather than that of the membrane itself, may become the controlling factor.

Pectic substances and proteins have differences in character causing differences in mechanical properties of the gel layer, which could explain the observed effects. Proteins can be visualized as having a spheric shape. When an elastic gel layer is building up, this shape leaves channels through which the solution can pass. Upon applying pressure these channels never totally close off, explaining the asymptotic behavior. Pectic substances in a gel are, according to Doesburg (1965) and Pilnik and Voragen (1970), chain-like combinations of galacturonic acid units aggregated by hydrogen bridges. When the gel layer is compressed, the H-bridges collapse and the chains stick together closing off the membrane. This explains the decrease in permeate flux, but not the almost total restoring of the flux upon pressure release as shown by the dotted line in Figure 2.

Another experiment (Figure 3) showed the optimum transmembrane pressure for maximum permeate flux does not change when the process stream becomes more concentrated. The change in concentration over a long period of time (10-12 h.) is expressed as a volume concentration ratio (VCR), which is the initial batch volume divided by the volume of the retentate. Knowledge of the optimum transmembrane pressure is very important when operating on an industrial scale. The transmembrane pressure does not need to be adjusted to stay in the maximum permeate flux range during a process operation.

#### Flow Rate

The flow rate, or the velocity of the feed stream past the membrane also influences the permeate flux. The permeate flux increases with higher flow rate, which is illustrated in Figure 2. The maximum flow rate obtained for this system was 0.15 m/s.

This is in agreement with what Setti (1976) found. He reported that the flow rate affects the buildup of the gel layer by sweeping off retained material, resulting in a higher permeate flux. The sweeping off effect becomes more important at higher flow rates, and is optimal when turbulence is induced. The velocities used in this experiment are in the laminar flow region, corresponding to Reynolds numbers of one to five.

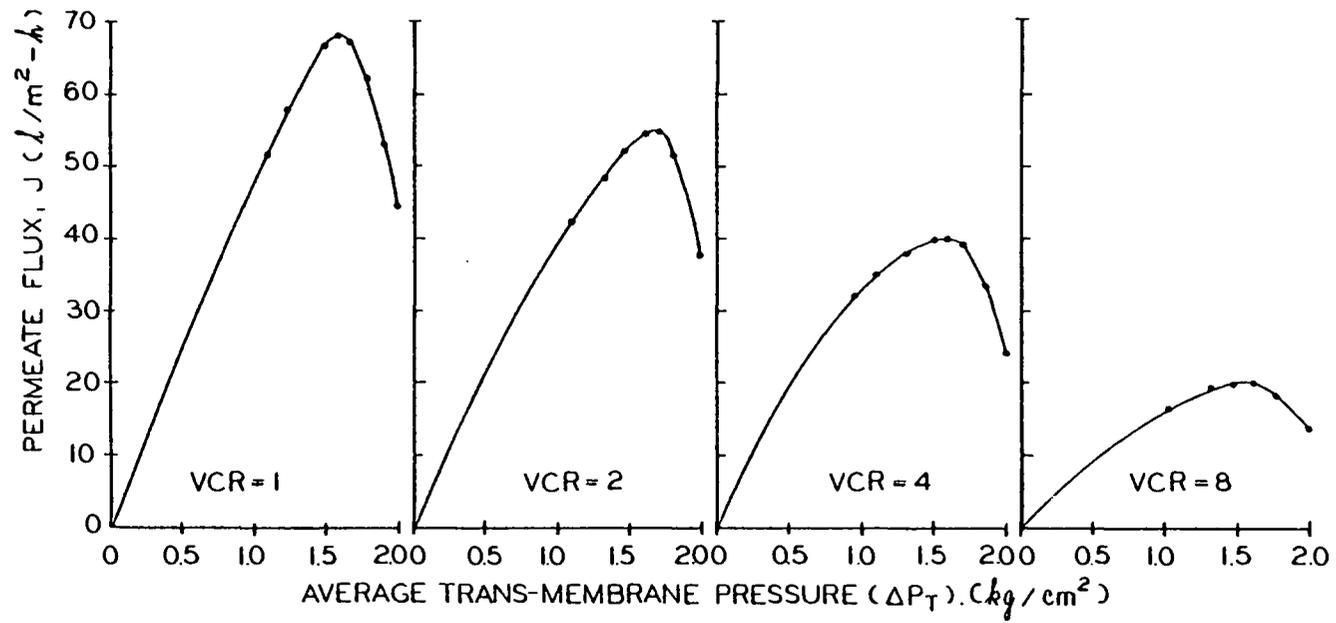


Figure 3. Effect of feed stream concentration on permeate flux at various average transmembrane pressures.

### Concentration Effects

When permeate was collected (batch operation), the process stream became more concentrated as the juice was processed. This concentration effect affected the permeate flux greatly.

In a recycling system the gel layer can not reach a steady state, since the concentration of the feed stream increases and the gel layer keeps growing. Consequently, the hydraulic resistance of the gel layer increases, and the permeate flux decreases.

Figure 4 shows that the permeate flux decreases linearly with the logarithm of the concentration and obeys the relationship formulated by Breslau and Kilcullen (1977)

$$J = K_1 - K_2 \ln VCR \quad \text{Eq. 3}$$

Where VCR is the volume concentration ratio, defined as the initial volume divided by retentate volume at any time.  $K_1$  and  $K_2$  are experimental constants. This logarithm flux-concentration relationship is also in agreement with what Heatherbell et al (1977) found for apple juice.

The flux-decay can also be expressed as a function of time (Figure 5).

Figure 4 illustrates the pore size of the membrane in the 50,000 to 10,000 molecular weight range has only a slight effect on the

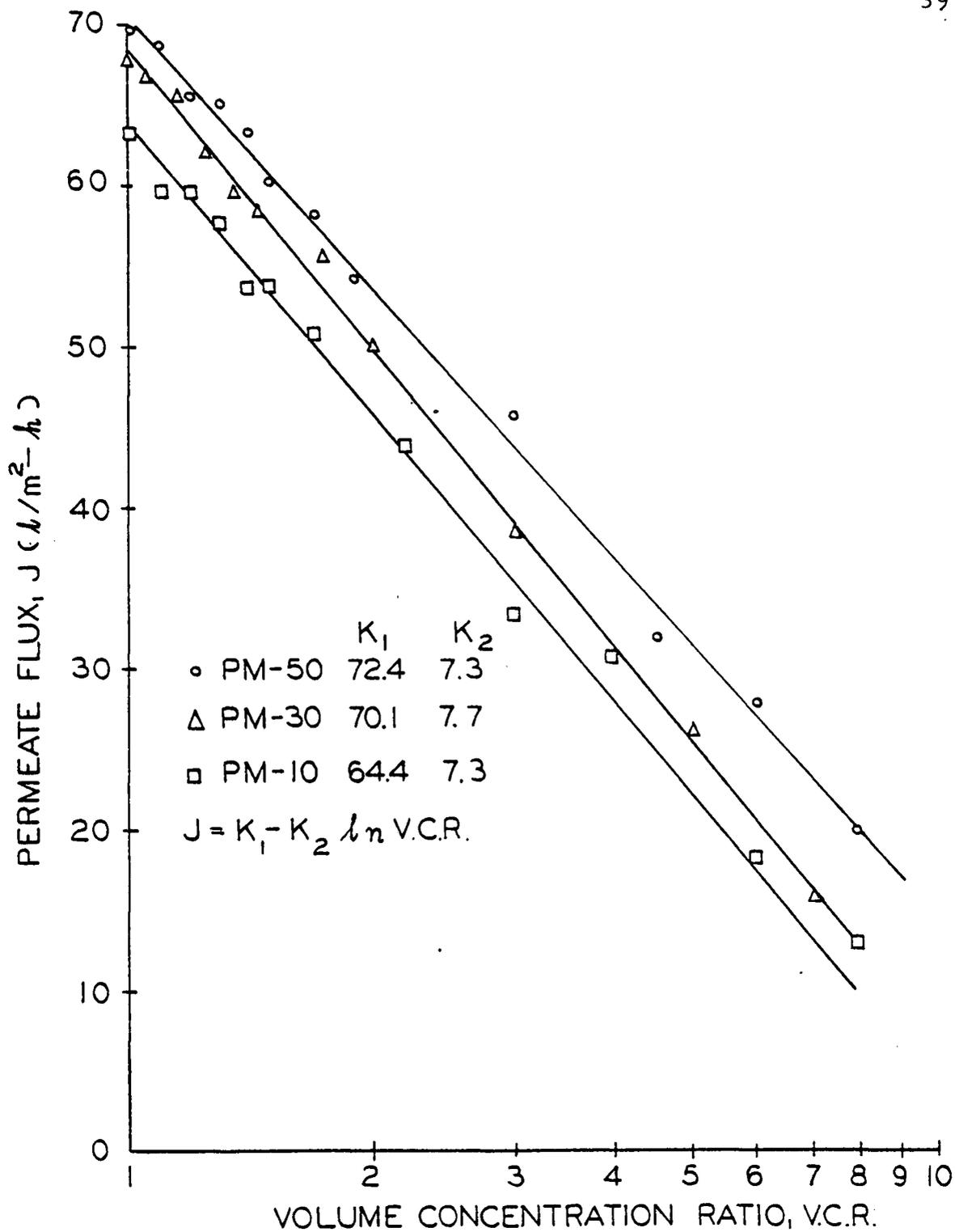


Figure 4. Effect of volume concentration ratio and pore size of membrane on permeate flux at  $50^\circ C$  and  $\Delta P_t = 1.6 \text{ kg/cm}^2$ .

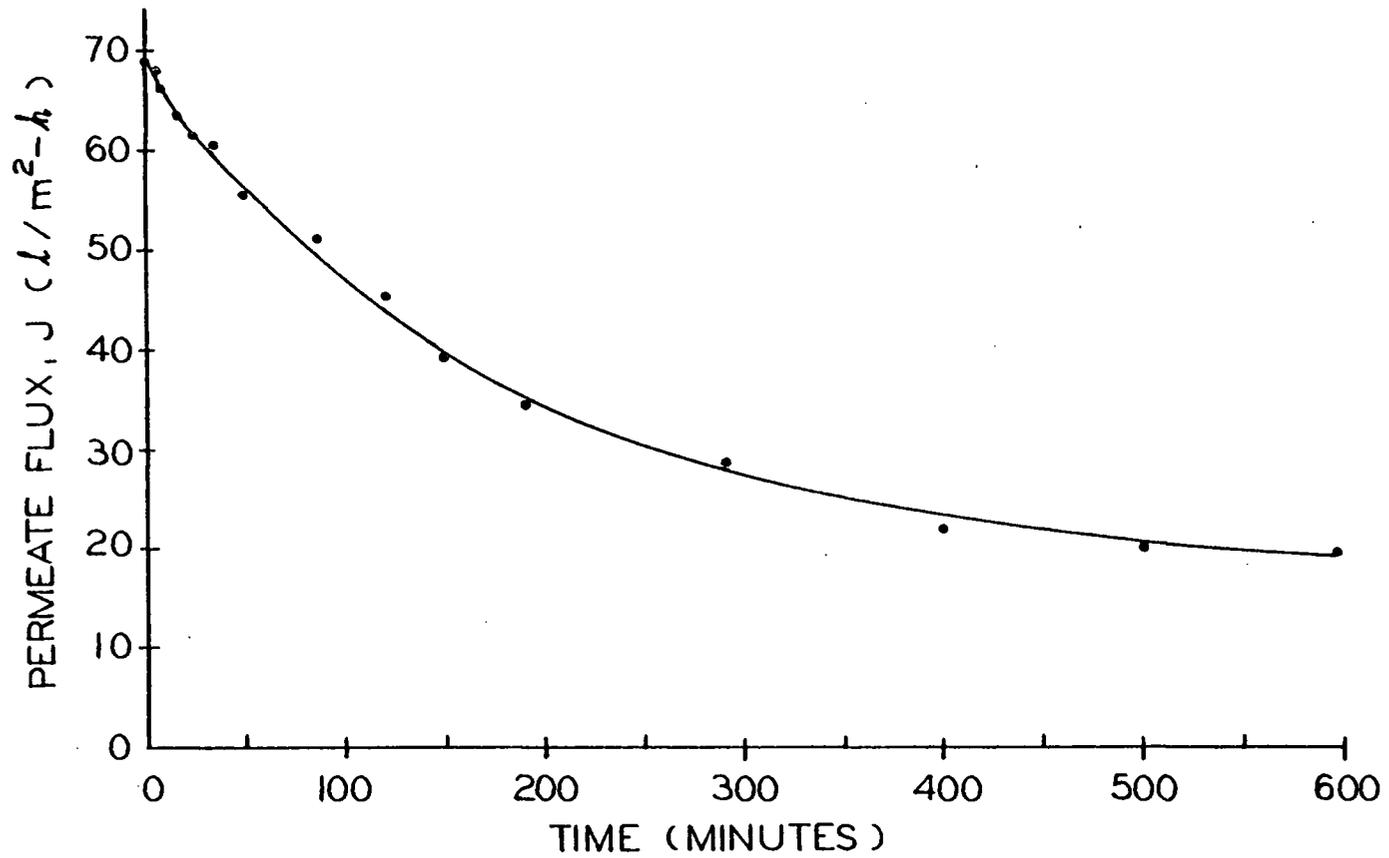


Figure 5. Decline of permeate flux with time for a PM-50 membrane at an average transmembrane pressure of  $1.6 \text{ kg/cm}^2$  and  $50^\circ\text{C}$ .

permeate flux rate. At present there are no data available on the effect of pore size on chemical composition (Youtz, in progress).

### Viscosity and Temperature

The viscosity is affected by two factors, the temperature and the concentration of the process stream during processing.

Saravacos (1974) reports that cloudy fruit juices are non-Newtonian in behavior. The viscosity increases exponentially at higher concentrations, which is illustrated in Figure 6. The effect of viscosity on permeate flux is explained by eq. 1 and is in accordance with what was observed for pear juice.

The temperature has a relatively smaller effect on the apparent viscosity and permeate flux. Figure 7 shows essentially a linear relationship between permeate flux and temperature. For a maximum permeate flux, the temperature should be as high as possible, but limited by such factors as membrane stability, pear juice quality and energy costs. Therefore most experiments were arbitrarily operated at 50°C.

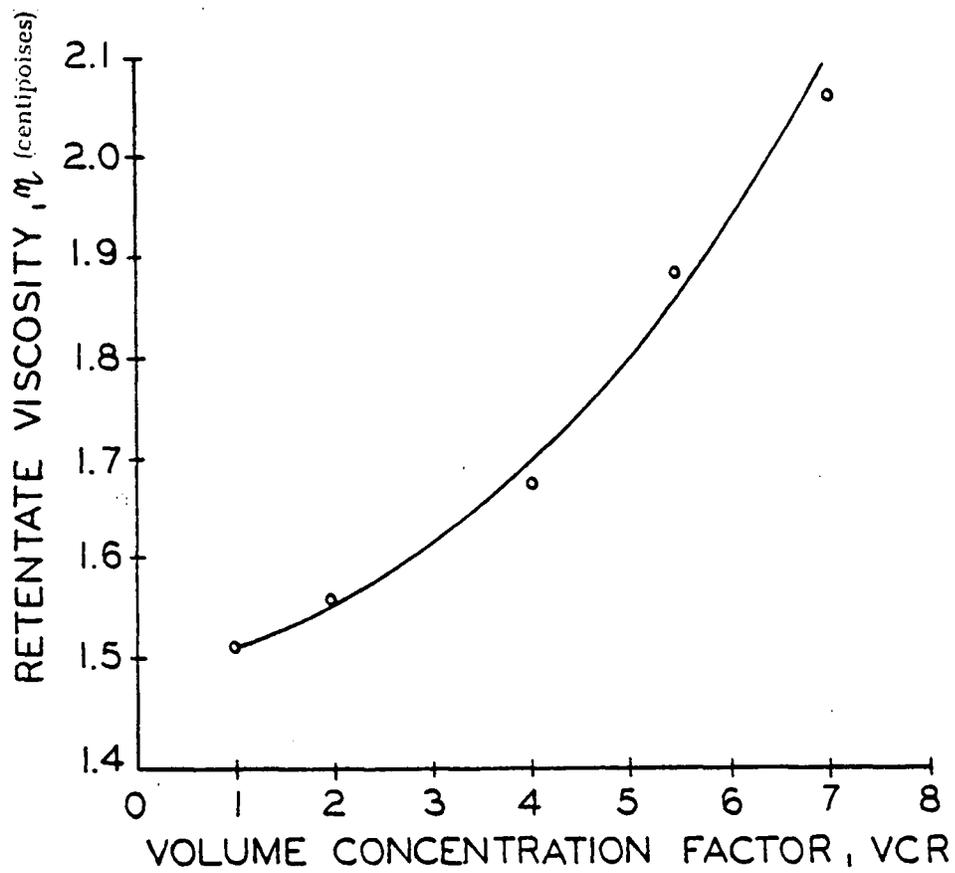


Figure 6. Relation between viscosity and volume concentration ratio for pear juice at 50 °C.

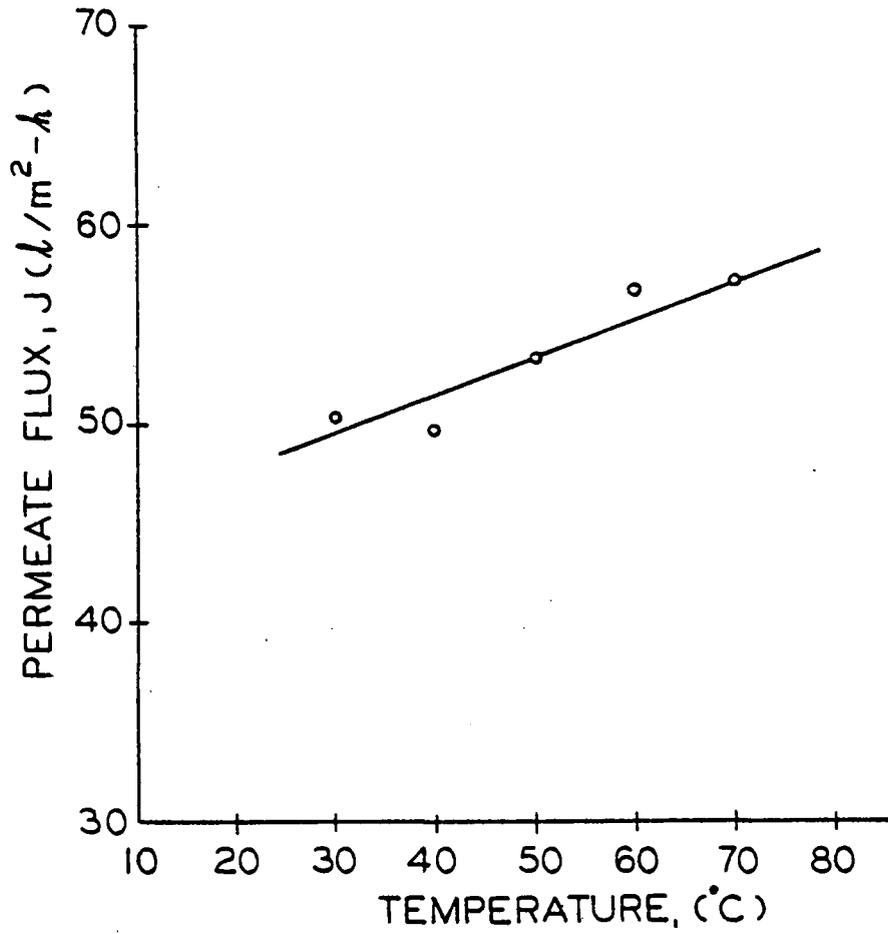


Figure 7. Relationship between permeate flux and temperature for a PM-50 membrane at a  $\Delta P_t$  of  $1.6 \text{ kg/cm}^2$  and a VCR of 2.

## CONCLUSIONS

This study showed that it is possible to clarify pear juice by using hollow fiber ultrafiltration.

The pore size of the tested membranes within the 50,000 to 10,000 molecular weight range had no significant influence on permeate juice color and optimal process parameters. These optimum parameters were found to be a transmembrane pressure of  $1.6 \text{ kg/cm}^2$  and a flow rate of  $0.15 \text{ m/s}$  when restricted to a temperature of  $50^\circ\text{C}$ .

It should be recognized, however, that a full understanding of membrane ultrafiltration for solutions containing pectic substances has yet to be achieved, especially in relation to the chemical changes of the pear juice.

Further, no single equipment design or membrane configuration will be optimum for all applications in fruit juice clarification. Each application requires a basic set of experimental data when application is considered for use as an industrial scale. Economic factors may indicate a desirable deviation from these optimum process parameters, when considering trade-offs between production rates and overall costs. These factors probably will determine the applicability of clarification of pear juice on an industrial scale.

## REFERENCES

- Bambridge, M., Chudack, M., Farr, A. G., Fell, C. G. D., 1975. Starch waste concentration with ultrafiltration. Third National Chemical Engineering Conference. Mildura Victoria, Australia (August 20-23).
- Beavers, D. V., and Youtz, F. A. 1976. Investigating juice clarification and filtration procedure for juices made from fruit wastes and surplus fruits. Research Report Number 2 to Tri Valley Growers. Oregon Agric. Exp. Stn. Corvallis, Ore.
- Breslau, B. R., Kilcullen, B. M., 1977. Hollow fiber ultrafiltration of cottage cheese whey: Performance Study. J. Dairy Sc. 60. pp. 1371-86.
- Chang, Y. H. 1979. Chemical analysis of acid precipitated colloid of ripe Bartlett pear juice. M.S. Thesis. Oregon State University, Corvallis, Ore.
- Cheryan, M., 1977. Mass transfer characteristics of hollow fiber ultrafiltration of soy protein systems. J. of Food Process Eng. 1, pp. 269-287.
- Dejmek, P. (1975). Permeability of the concentration polarization layer in ultrafiltration of macromolecules. Symposium on Separation Processes by Membranes, Ion-exchange and Freeze concentration in Food Industry. Paris. March.
- Doesburg, J. J., 1965. Pectic substances in Fresh and Preserved Fruits and Vegetables. p. 24 and 119. Institute for Research on Storage and Processing of Horticultural Produce Wageningen The Netherlands.
- Ericksson, G. and von Bockelmann, Y. 1975. Ultrafiltration of Animal Blood Serum. Technology and Microbiology Process Biochemistry 9. pp. 11-14.

- Fenton-May, R. I., Hill, C. G. and Amundson, C. H. 1971. Use of ultrafiltration reverse osmosis systems for the concentration and fractionation of whey. *J. Food Sci.* 36 pp. 14-21.
- Glover, F. A., Skudder, P. J., Stothart, P. H. and Evans, E. W. 1978. Reviews of the progress of Dairy Science: reverse osmosis and ultrafiltration in dairying. *J. of Dairy Research*, 45, pp. 291-318.
- Heatherbell, D. A., Short, J. L. and Stauebi, P., 1977. Apple juice clarification by ultrafiltration. *Constructa*. 22 (516) pp. 157-169.
- Lonsdale, H. K., 1972. Theory and practice of reverse osmosis and ultrafiltration. In *Industrial Processing with membranes* (eds. R. E. Lacey and S. Loeb) Wiley Interscience, New York.
- Omosaiye, O. and Cheryan, M., 1979. Ultrafiltration of soybean water extracts. Processing characteristics and yield. *J. of Food Sci.* 77, pp. 1027-31.
- Pilnik, W., and Voragen, A. G. J., 1970. Pectic Substances and other Uronides. In *The Biochemistry of Fruits and their Products* (Ed. A. C. Hulme). Academic Press, London, England. Vol. 1, pp. 53-89.
- Saravacos, G. D., 1974. Rheological Aspects of Fruit Juice Evaporation. In *Advances in Preconcentration and Dehydration of Foods* (Ed. A. Spicer). Wiley, New York.
- Setti, D., 1976. Effect of Operating Parameters on Permeate Rate. *Lebensm. -Wiss, u-Technol.* 9, pp. 29-32.
- Youtz, Y. A., in progress. Oregon State University, Corvallis, Ore.