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MEMBRANE CONCENTRATION OF ORANGE JUICE

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Additional index words. reverse osmosis, ultrafiltration.

Abtract. **A process to concentrate orange juice to levels above 42° Brix with quality close to fresh juice is discussed. Using ultrafiltration and reverse osmosis in a patented process, concentrate of superior quality can be produced. An overview of how membrane characteristics influence the design, selection and operation of the process is presented along with operating economics.**

In 1985, FMC and DuPont began a joint research program to develop a membrane process which could concentrate orange juice to 58° Brix and retain the fresh juice flavor.

The process, called FreshNote™ combines ultrafilration, reverse osmosis, pasteurization and blending to produce an orange juice concentrate of very high quality. The unique hybrid process is what sets FreshNote™ apart from prior membrane concentration efforts with orange juice and is the basis of U.S. patent # 4643902. This paper will describe the non-proprietary aspects of the process and some of the issues relating to its design and optimization.

Traditionally, orange juice has been concentrated using a thermal process. Such a process results in a loss of flavor top notes, color degradation, and a cooked taste. The citrus industry compensates for the product degradation through essence recovery, careful process control and blending to produce a good quality concentrate which, although readily distinguishable from fresh juice, has received broad consumer acceptance. FreshNote™ helps to close the flavor gap between fresh and concentrated orange juice and makes top quality orange juice conveniently available to consumers.

The membrane process was designed to produce a concentrated orange juice with fresh juice flavor and commercial levels of stability. These two objectives impose different and sometimes conflicting requirements upon the process. Only through the proper selection and operation of the membrane separation process can both objectives be achieved.

Successful processing of orange juice requires that some compounds be heated to ensure stability, while other compounds be kept cold to preserve quality. The ultrafiltration (UF) process used in FreshNote™ is the first technology to allow separation of the compounds which we want to heat from those we do not want to heat. This is the crucial first step in the process, as shown in Figure 1. When fed with single strength orange juice, the UF process produces two streams: one of clarified serum and a second stream of concentrated pulp. With careful membrane selection and system operation the serum stream will contain the great majority of the delicate flavor compounds and be commercially sterile. The pulp stream will contain all of the suspended solids, pectins, bacteria, molds and yeasts.

After ultrafiltration, the serum is concentrated in the reverse osmosis (RO) section. The concentration is accomplished at 50°F to minimize the loss or degradation of flavor compounds. Using proprietary membranes provided to SeparaSystems by the DuPont Company, it is possible to concentrate the serum to more than 60° Brix. Because the water is removed by selective passage of water molecules through the membrane and not evaporation, the flavor molecules are retained in the product stream and the fresh flavor is preserved.

All of the compounds in the raw juice feed stream which require heat stabilization are concentrated in the pulp stream. The product is quickly heated using a scrape surface heat exchanger, and then cooled to provide a commercially stable product with minimal flavor or color degradation. Because most of the delicate fresh orange flavors are isolated in the serum stream away from the heat of pasteurization, they are protected from degradation.

The final process of blending combines the pasteurized retentate with the concentrated serum. The processor can then blend in finisher pulp, peel oil and/or essence to produce a concentrated product tailored to his particular market needs. When reconstituted, the juice consistently scores higher in flavor than any thermally concentrated product, and is often indistinguishable from the feed juice.

It is important to note that both the RO and UF processes will work on other streams besidecs orange juice. The RO concentration capability has been demonstrated on apple juice, grape juice, wine, vinegar, gelatin, apricot juice, cranberry juice, pineapple juice, tomato juice, and various berry juices. The UF process also has broad application in the food industry for clarification and fractionization of various streams.

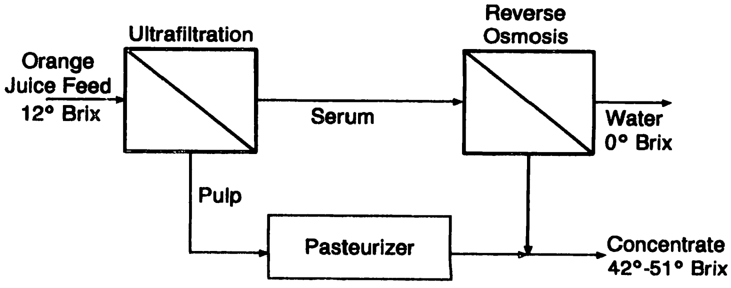

Fig. 1. FreshNote® System Diagram (U.S. Patent #4643902).

Membrane Concentration

Other researchers have concentrated products such as orange juice using reverse osmosis membranes designed to handle the high pulp content of single strength orange juice. While direct and simple because it uses only a single membrane process, this approach has several drawbacks:

A. The solids and pectin content in orange juice create a very viscous stream when concentrated. The high viscosity combined with the high osmotic pressure of the concentrated sugars results in low membrane permeate rates and low levels of concentration (<30° Brix).
B. Pasteurization of the stream is necessary for product stability; this will also expose the flavor compounds to heat, leading to reduced quality.

Our process overcomes these obstacles by isolating various steps in the process and applying technologies specifically designed for each step. The UF system is designed for the high viscosity of concentrated pulp, the UF membrane is selected to allow passage of the delicate flavors, the RO system is designed to achieve high sugar concentrations, and the pasteurizer acts only on the products needing heat treatment.

To understand why the process works as it does, one must have an appreciation for basic membrane processing. Optimal design and operation of the system hinges upon many subtleties of membrane operation.

Membrane processes. Membrane separations are different from depth filter separations due to the formation of the membrane surface and the way they are applied. Traditional filters, or depth filters, use a "thick" filtration bed which mechanically traps particles with certain sizes or shapes in the body of the filter. As a result, the filter retains the removed particles and will become obstructed with use, resulting in higher pressure drops and reduced flow rates. Depth filters are typically used in a perpendicular flow arrangement where the feed stream flows through the filter and retained particles are accumulated in and on the filter material. Automobile filters, bag filters and D.E. filters are perpendicular flow depth filters. If one wishes to recover the retained solids in a perpendicular flow arrangement it is typically necessary to stop the process and do a batch recovery.

In contrast to the uniform construction of the depth type filters, most membranes have an asymmetric structure as shown in Figure 2. A thin skin on the top of the membrane (0.1-0.2 m) forms the rejecting layer, with a thicker sponge-like support layer formed below. A backing of sailcloth or other suitable material provides mechanical strength to the membrane.

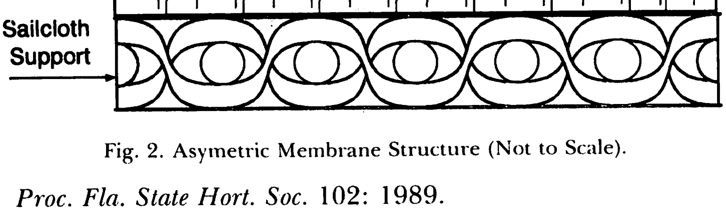

Fig. 2. Asymetric Membrane Structure (Not to Scale).

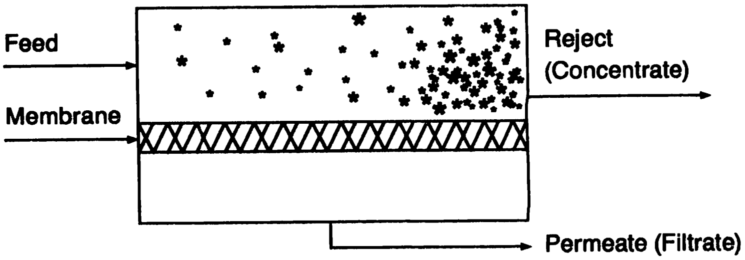

Fig. 3. Cross Flow With a Membrane.

In the asymmetric arrangement where the rejecting layer is on top, there is little tendency for rejected compounds to become trapped in the pores of the membrane. When used in a cross flow configuration as shown in Figure 3, much higher levels of concentration and higher flux rates are possible than with depth filters for applications where the feed stream has a high concentration of compounds to be rejected, or when it is necessary to concentrate the compounds to a high level.

A cross flow system can run in a batch or continuous mode. Batch operation, shown in Figure 4, is used to concentrate a product to a desired level. A starting volume of product is processed and the concentrate removed at the end of the run. With continuous operation, as shown in Figure 5, the concentrated stream is removed continuously, allowing extended runs under constant conditions.

The orange juice concentration process uses a multistage continuous process to provide a constant flow of rejected pulp to the pasteurizer.

Three types of membranes. Membranes are typically classified into one of three categories: microfiltration, ultrafiltration, or reverse osmosis (hyperfiltration).

Microfiltration is a class of membranes which are typically homogenous in structure and are designed to retain particles in the range of 0.1 micron to 10 micron. Most microfilters are not asymmetric, so their use in cross flow systems is limited to applications where the feed stream lacks particles in the size range which would become trapped in the body of the membrane.

Microfilters typically operate at pressures of 20 to 80 PSI. Higher pressures will only force the rejected compounds into the body of the membrane leading to fouling and a loss of flow. Most microfilters are used as cartridge depth filters where trace amounts of impurities must be removed from a stream.

Ultrafilters are designed to reject macromolecules as well as suspended solids down to the 0.001 to 0.02 micron

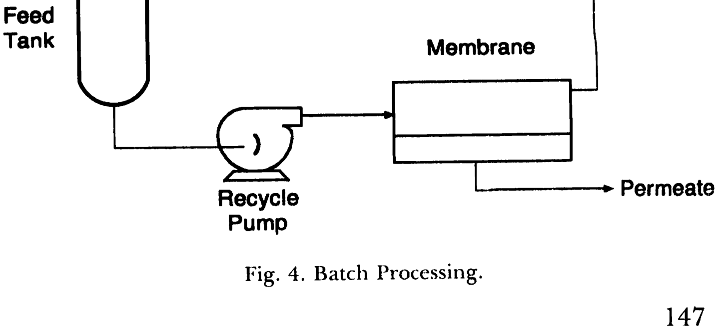

Fig. 4. Batch Processing.

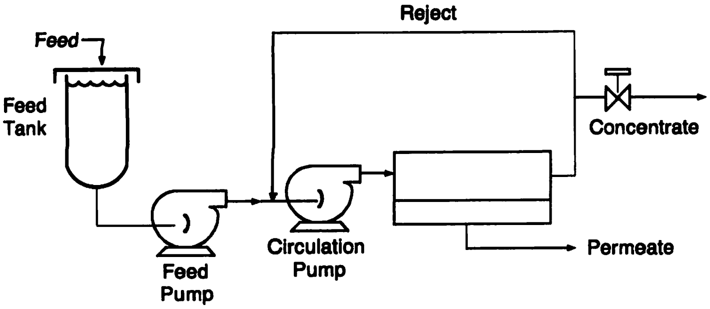

Fig. 5. Continuous Or Feed And Bleed Process.

range. Ultrafilters are available with either homogenous or asymmetric structure, though the asymmetric structure is more common. There are many more manufacturers of UF membranes than MF, and a large variety of pore sizes, materials, and configurations are available.

UF systems typically operate at pressures of 40 to 200 PSI.

Reverse osmosis membranes are much tighter than UF, rejecting dissolved molecules as small as common salt (NaCl). RO is different than MF and UF in that the membrane has no actual pores in its skin. Instead, the solvent molecules pass through the membrane by diffusion.

If a suitable membrane is placed between two solutions, one a sugar serum and the other plain water, the water will pass through or permeate the membrane to dilute the serum in a process called osmosis. If the serum were to be fortified during the osmosis process so the sugar concentration remains unchanged, the osmosis would continue and the column height on the serum side would grow. Eventually the hydrostatic head would create a sufficient pressure at the membrane to stop the osmotic flow of water. The hydrostatic head required is related to the concentration of sugar and is called the osmotic pressure of the serum. If the pressure on the serum side is increased beyond the osmotic pressure of the solution then water will flow from the serum into the water chamber in the process of reverse osmosis (Figure 6).

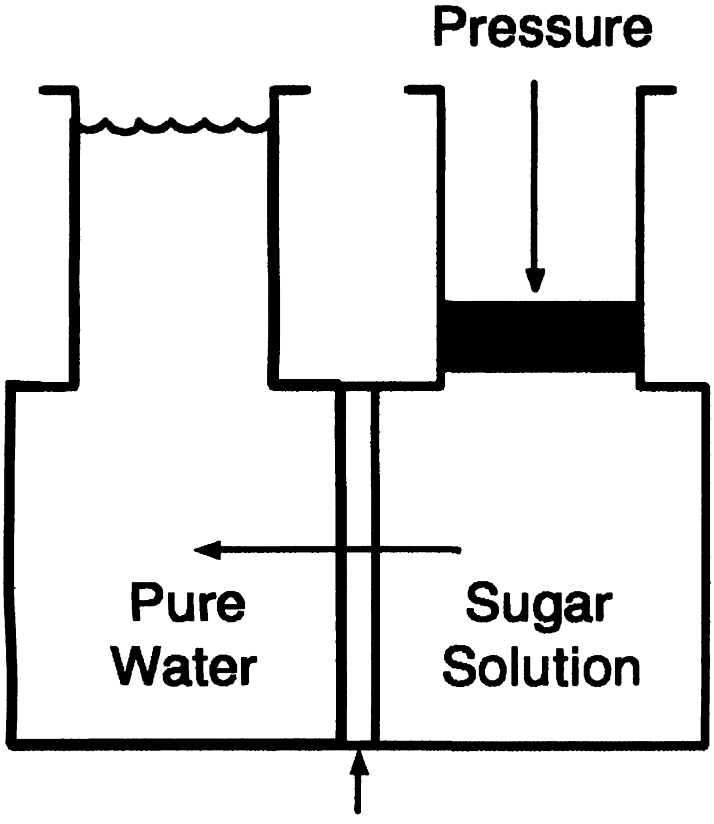

Fig. 6. Reverse Osmosis.

The osmotic pressures for orange juice, sucrose and glucose are shown in Figure 7. Since osmotic pressure is dependent upon the molecular concentration of the solute, monosaccharides will have higher osmotic pressure than disaccharides at a given weight concentration. This accounts for the difference in the osmotic pressure curves for glucose and sucrose. Since orange juice contains some disaccharides and some monosaccharides, it has an osmotic pressure between sucrose and glucose at the same weight concentration.

Selecting membranes. In designing our membrane separation process we took a number of factors under consideration, including:

— Membrane selectivity
— Membrane compatibility
— Configuration.

Selectivity and compatibility are straight forward criteria for screening membranes for a particular application. Selecting a configuration is more complex because more issues come into play. Product viscosity, the presence of suspended solids, the availability of a desired membrane in a particular configuration, hold-up volume and concentration polarization (RO only) are important factors.

When selecting a membrane for a given application, concerns of membrane selectivity and compatibility must be addressed first. Selectivity of a membrane relates to the size and type of compounds which it will pass or reject. Compatibility of a membrane relates to possible chemical interactions between the product or cleaning agents and the membrane and support structure itself.

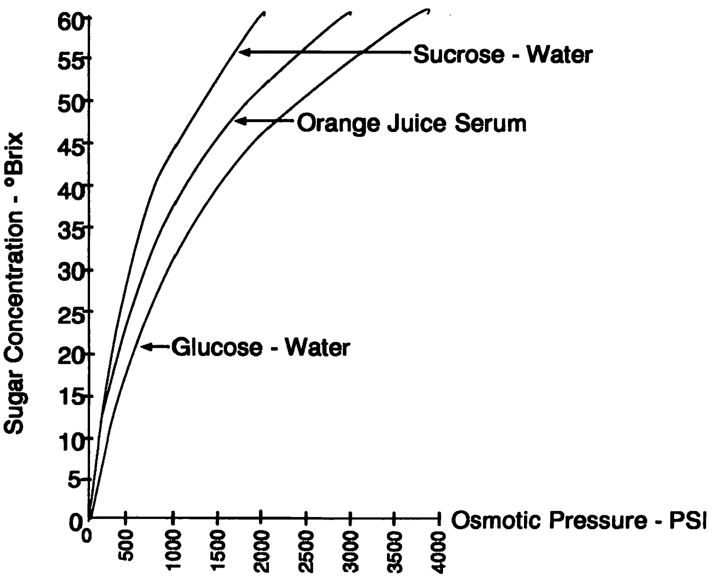

Fig. 7. Osmotic Pressure versus Sugar Concentration.

Selectivity. MF, UF, and RO membranes are available in a wide variety of pore sizes. A preliminary membrane selection can be made based upon the pore size rating of the membrane and a knowledge of the molecular weights of the compounds to separated. Unfortunately, the selection is not always so straightforward because of other factors. The shape and charge of the molecules or particles in the stream, membrane characteristics such as pore and support geometry, and the polymer characteristics can all affect the actual passage of a particular component. Knowledge of these factors can speed and focus membrane testing but not eliminate it.

Compatibility. Membrane compatibility is an issue with citrus juices in general due to the presence of peel oil (which contains d-limonene) and the use of caustic for cleaning. There are various polymers used in membrane and support formulations, with differing tolerance to temperature, pH, and oxidizing agents. For example, cellulose acetate membranes are degraded by peel oil and therefore are not an acceptable membrane for citrus. Most polymeric membranes can tolerate 100-120°F as a maximum operating temperature so heat is not an issue for our process.

In the early days of membrane science, pH was a very limiting factor in membrane applications. The cellulosic membranes are generally limited to pH 4-6, and were the only type commercially available until 1974. New polymers have a much wider pH tolerance. For example, polysulfone can tolerate pH 2-12. In orange juice processing, using high pH caustic cleaners will restrict membrane selection more than the low pH of the product will. Many polymeric membranes are still very sensitive to oxidizing agents such as chlorine, and these compounds must be excluded from the process.

Configuration. Each available membrane configuration has advantages and disadvantages, depending upon the particular application. The selection of a particular configuration will depend upon product viscosity, suspended solids, membrane availability, hold up volume and cost. With reverse osmosis membranes where high levels of concentration are desired one must also consider maximum pressure limits for the membrane and its housing.

Product viscosity. Product viscosity is a critical factor in configuration selection. Viscous streams can form gel layers which in some configurations will result in substantial flow loss as well as modification of the separation process.

In the MF or UF process, rejected compounds tend to accumulate at the membrane surface forming a gel layer much the way a heat exchanger can develop boundary layers. The thickness of the gel layer must be minimized by establishing high shear rates at the membrane surface (Figure 8). Inadequate flow rates result in heavy gel layer formation which creates several problems for the separation.

Figure 9 shows the effect on the permeate flow as the product velocity is reduced and the gel layer grows.

Gel layer formation creates several problems in clarification of orange juice. 1) it produces significant flux loss resulting in increased equipment size and cost; 2) it causes formation of a secondary membrane which can interfere with the desired flavor passage; and 3) it can trap and accumulate trace compounds which are important to fresh aroma and taste for the final product.

Flow loss due to gel formation can be dramatic as shown in Figure 9. In addition to increasing the required membrane area for a given capacity with the associated increase in equipment size and cost, it also increases system volume and the holding time for the product. Increased membrane area required to overcome gel formation also produces increased operating costs due to higher pumping costs, higher membrane replacement cost, and higher consumption of cleaning chemicals.

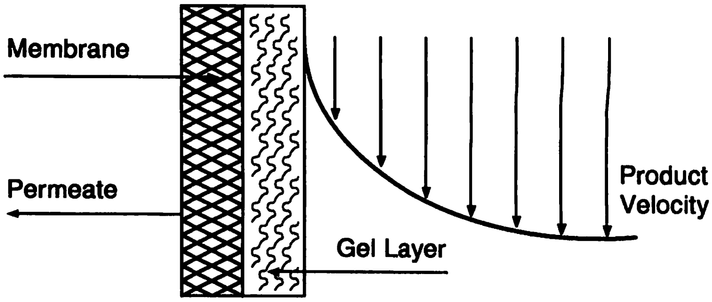

Fig. 8. Gel Layer Formation With UF.

Gel layers can also act as a membrane over the synthetic membrane in some cases. When this happens, molecules which would normally pass the synthetic membrane will be rejected by the gel layer, changing the separation process.

Although data is scarce, we have seen situations where it appears that the gel layer can trap certain trace molecules, effectively removing them from the process. Since the gel layer is only removed during cleaning, the accumulated compounds can be lost.

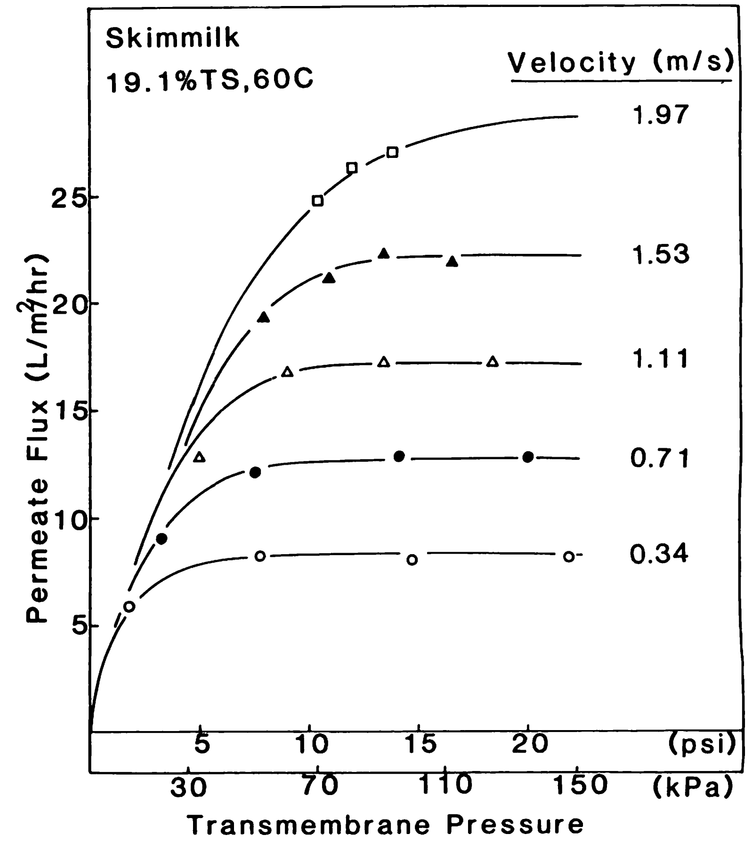

Fig. 9. Gel Layer Formations Influence on Membrane Flux (from Cheryan and Chiang, 1984).

Suspended solids. The presence of suspended solids in a feed stream can influence the configuration selection. The flow channel size varies greatly between different configurations. Hollow fine fiber, hollow fiber, and spiral have the least tolerance of suspended solids. The large diameter tubular systems are most tolerant, with plate and frame somehere in between.

Orange juice is routinely finished in citrus finishers which remove any large particles. The small size pulp particles will plug spiral, inside out hollow fiber or hollow fine fiber modules but cause no problems for plate and frame or tubular systems.

Membrane availability. The membrane industry has developed a wide range of membrane types with subtle differences in their separation characteristics. Each manufacturer works on membranes for their particular configuration, so all types are not available in each configuration. This can become an issue in selecting a particular configuration depending upon the separation desired.

Hold-Up volume. In the processing of sensitive products such as orange juice flavor compounds, the time it takes for the product to complete the process can influence the final quality. Process time is a function of the system hold-up volume and the process flow rate. Configurations with a high hold-up volume to productivity ratio can add substantially to the overall process time, to the detriment of product quality.

Concentration polarization in reverse osmosis. In the RO process one faces concentration polarization (which is similar to MF & UF gel layer formation) and osmotic pressure as performance hurdles.

In reverse osmosis, the flow of water through the membrane can generally be described as:

$$Q = A \times J\,(\Delta P - \Delta\pi) \qquad \text{EQ 1}$$

where:

Q = flow in volume per unit time
A = membrane area employed
J = membrane flux constant
ΔP = differential hydraulic pressure across the membrane
$\Delta\pi$ = differential osmotic pressure across the membrane.

The osmotic pressure of a solution is exponentially related to the molecular concentration of the solute in the solvent. Figure 7 showed the osmotic pressure of orange juice at various concentrations. Most RO systems have a maximum working pressure of 1100 PSI. Under this limition the maximum theoretical concentration achievable would be 39° Brix. While our RO membranes operate at pressures above 1100 PSI, they do not operate at 3000 PSI to make 60° Brix. Rather, by exploiting the unique properties of the hollow fine fiber and the enormous surface area in a module, we are able to achieve our 60° Brix at less than 2000 PSI.

Commercial Configurations

Plate & frame. The plate and frame configuration is offered by several manufacturers for UF, MF, and RO. The basic arrangement is shown in Figure 10, where flat sheets of membrane are placed between porous plates with the product flow between facing membranes and permeate collected in the plates. This arrangement is well suited for highly viscous streams or streams with a lot of solids such as orange juice. The equipment allows for a fair degree of flexibility in controlling flow velocities and pressure drop which is critical in viscous applications.

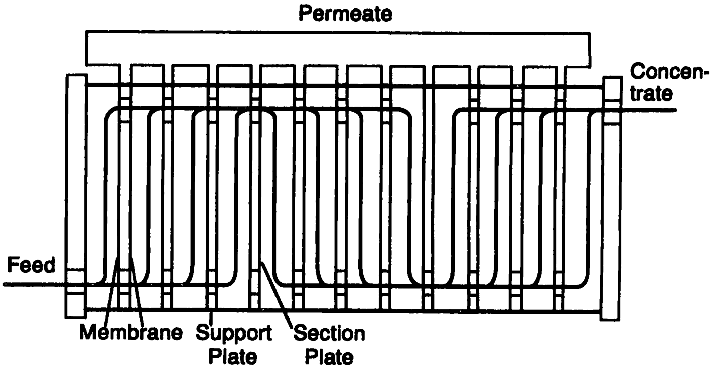

Fig. 10. Plate and Frame.

Flat sheet systems have moderate holdup volume per square meter of membrane area and are moderate to high in cost. Some plate and frame systems allow use of any flat sheet membrane so offer high versatility for clarification.

RO plate and frame systems have smilar characteristics to the UF systems. For orange juice concentration, however, they are too limited in pressure to achieve the desired concentration levels.

In head to head testing, we have found the plate and frame UF system to perform better than any other configuration in the orange juice clarification process.

Tubular. In the tubular configulation (Figure 11) the membrane is formed inside support tubes of 1/2 inch to 3 inch I.D. This configuration is well suited to streams with high solids because it is very resistant to plugging. The flow conditions in a tube are not as easily controlled as in a flat sheet system, hence the tubular configuration is not ideal for highly viscous streams, though it is better than spiral or outside in hollow fiber.

Tubular configurations are limited to each manufacturers particular membrane offerings since there are no standard sizes. We have not yet found a tubular membrane with the desired passage characteristics for the UF process.

Spiral wound. In this configuration a flat sheet membrane is rolled into a "jelly roll" as shown in Figure 12. This results in a low cost system with low holdup volume. It is generally the preferred configuration for traditional desalination of brackish water due to the low cost. Many manufacturers make spiral membranes, so there is a wide

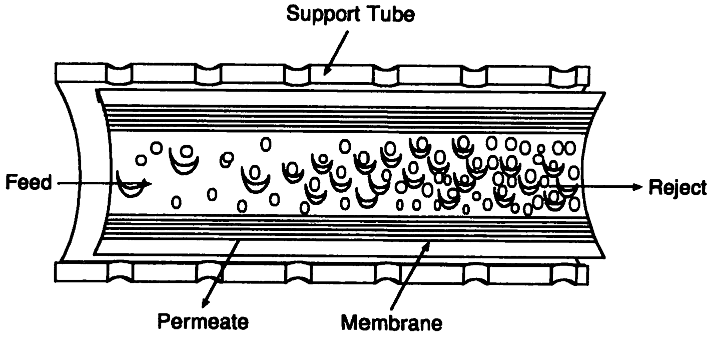

Fig. 11. Typical Tubular Configuration.

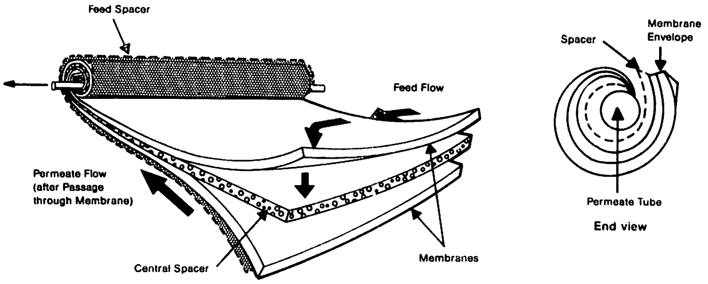

Fig. 12. Spiral-Wound Cartridge

variety available. However, the arrangement is unsuited for highly viscous streams or high solids streams because the flow channels are small and prone to plugging. Cleaning is also difficult.

Hollow fiber. The hollow fiber classification describes polymer fibers with an ID of 1 to 3 millimeters for UF and MF, or an OD of around 85 micron for RO. Fibers are available for outside in or inside out flow. Packing density is very high so the holdup volume and costs are low. The systems tend to be sensitive to plugging if solids are present and viscous streams can be difficult to handle for outside in fibers because product shear rates are difficult to control at the membrane surface.

In the hollow fine fiber RO system (Figure 13) there are millions of hair-like fibers with the feed stream on the outside. The surface area in such a module is several orders higher than a comparable spiral unit.

Pasteurization. As mentioned earlier, the concentrated pulp stream from our system's UF unit contains all the pectin, bacteria, mold and yeast from the feed juice. If this stream were to be recombined with the concentrated serum directly, a high quality product would result but stability would be poor. Pasteurization of the pulp stream alone will result in a concentrated product with stability comparable to commercial standards when combined with the "sterile" concentrated serum.

Pasteurizing the pulp stream is somewhat complicated by its high viscosity (3500 cp). Traditional plate or shell and tube type heat exchangers are unsuited for products this thick. Scrape surface heat exchangers, however, can handle the stream without trouble. Pasteurizing the pulp stream at 180°F for 30 seconds produces an acceptable level of stability without harming the flavor. Accelerated abuse tests of 24 hours at 78°F have consistently shown zeo gelation for the fresh concentrate and also after extended storage (0°-5°F). The pectinesterase enzyme activity test has also shown acceptable stability for fresh and stored product; readings of 1 to 2 are typical.

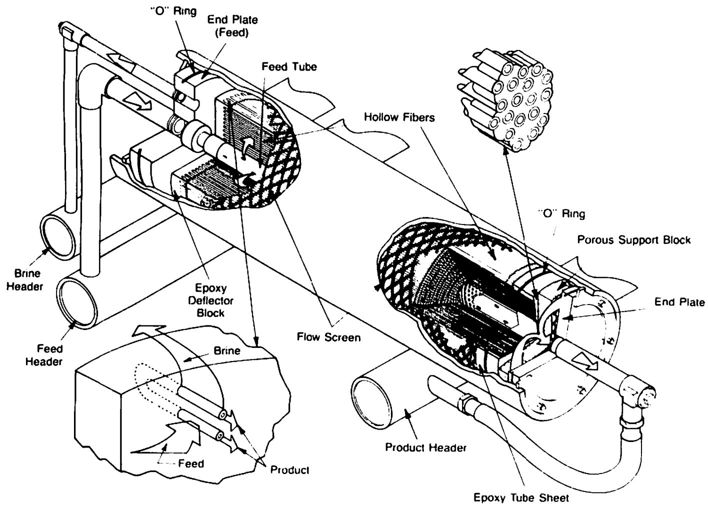

Fig. 13. Hollow Fine Fiber Permeator.

Blending. When the pasteurized pulp and concentrated serum are recombined, a very high quality product results. Our tests on reconstituted RO concentrate give the product very high flavor scores. It is, however, not necessarily a final product.

Several opportunities exist to use current orange juice blending technology to produce a product with particular characteristics. The addition of pasteurized finisher pulp can modify the texture and mouthfeel of the final product. In the UF process the large pulp is broken down so the addition of finisher pulp may be desired.

Peel oil may also be added to standardize the product for seasonal or varietal fluctuations. Additional blending opportunities exist with seasonal blending, adding cut back juice, or blending with juice concentrated with other processes.

Flavor results. The overall FreshNote™ process was first experimentally demonstrated in 1986. Since then numerous taste tests have shown the high quality product which could be produced. In-house panels, outside flavor consultants and consumer tests have ranked the product flavor above available retail concentrate and at or above that available from the freeze concentration process.

Figure 14 shows the relative flavor ratings for evaporator pump out, blended retail concentrate, FreshNote™ concentrate, freeze concentrate, and fresh juice, as compiled from our various tests. The FreshNote™ product used for these flavor tests was sampled as it came from our machine without the benefit of any blending. Even without blending, the product quality has been consistently ranked superior to commercially available concentrate, and very near to fresh juice.

Economics. Table 1 gives a projected cost breakout for a 20,000 lb/hr membrane concentration process designed to produce 42° Brix orange juice. These estimates are probably conservative, reflecting demonstrated capabilities from the '87-'88 season pilot program.

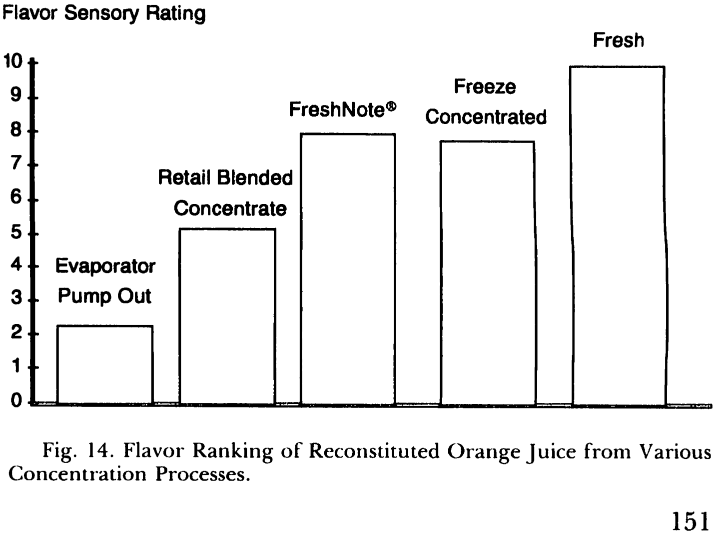

Fig. 14. Flavor Ranking of Reconstituted Orange Juice from Various Concentration Processes.

Table 1. Projected Processing Costs For FreshNote® Process.

Operating Costs	$/Gallon of Feed
Utilities	
Electricity	0.018
Refrigeration	0.007
Water	—
Supplies	
Chemicals	0.007
Miscellaneous	0.002
Labor $20/hr	
Operator @ 4 hrs/day	0.001
Subtotal	0.035
Lease & Royalty (5 yr. service/membrane replacement)	0.070
Total	$0.105/gal.
Capital Depreciation	$0.05-0.08/gal.
Total Cost	$0.15-0.18/gal.

Table 2. Projected Cost Assumptions.

- 20,000 lbs/hr water removal rate
- 2,000 operating hours per year
- 8,900,000 gallons feed per year
- Electricity @ 10.06/KWH
- Refrigeration @ $2/ton/day
- Water @ $1/1,000 gallons
- Labor @ $20/hr

Cost assumptions are shown in Table 2. As one can see, the total cost is now projected to 15¢ to 18¢/gallon of raw juice feed. Operating costs for utilities, supplies and labor are 3.5¢/gallon. The balance of the cost is capital depreciation for the equipment and lease and royalty costs for service and membrane replacement.

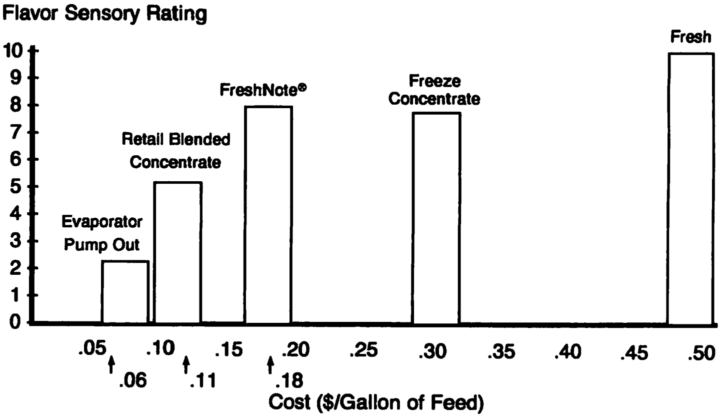

Fig. 15. Flavor/Cost Comparison for Various Concentration Technologies.

Assessing the value of a new technology requires that one not only consider the cost, but also the benefit. Figure 15 shows a ranking of thermal, membrane, and freeze concentrators for cost and product quality. Fresh juice is included as a flavor reference only. The FreshNote™ process offers significant flavor improvement at a reasonable cost increment.

Development programs. The membrane concentration process is now available for commercial use. Systems up to 20,000 lbs/hr, concentrating to a minimum 42° Brix are being discussed in the Mediterranean and Florida markets where there is strong customer interest. Our goal, however, is to improve the process so it can be adopted by a large percentage of the citrus industry. With this in mind we have set our R&D objectives to raise the final product concentration level to the point that the product can be stored in existing tank farms (58° B) and reduce the cost to the processor to 12¢/gallon of feed. We feel that opportunities exist for significant advances in the UF and RO segments which bring our objectives within reach.

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EFFECTS OF TEMPERATURE ON PULP REMOVAL FROM ORANGE JUICE BY CENTRIFUGATION

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Additional index words. oranges, commercial, extraction, finishing.

Abstract. **During the 1985-86 and 1986-87 Florida citrus seasons, several harvests of Hamlin, Pineapple, and Valencia oranges were made. The juice from these varieties was subjected to centrifuging at ambient and 195°F temperature using a Westfalia separator. Statistical evaluations showed significant differences in pulp removal between the two temperatures in the Valencia juice for both seasons and from Pineapple juice during the 1985-86 season. In both cases, the juice centrifuged hot yielded the highest pulp removal. No significant difference was found in the pulp removal from Hamlin juice samples. However, in both seasons the percentage of pulp removed from the Hamlin juice was highest from the juice centrifuged at the higher temperature.**

The centrifuge has played an important role in the citrus industry as an aid to manufacturing. Its role in the manufacture of byproducts has been reported by various investigators (2, 5, 6). Peleg and Mannheim (8) evaluated a process for the production of orange concentrate based on centrifugal separation of the juice into pulp and serum.

Murdock (7) reported on the use of centrifuges in some citrus plants for the removal of pulp solids from orange juice.

The purpose of this study was to determine the effect of centrifuging juice at ambient and approximately 195°F on pulp removal.