Ultrafiltration of Orange Juice: Effect on Soluble Solids, Suspended Solids, and Aroma

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Freshly squeezed orange juice was ultrafiltered in a hollow fiber cross-flow ultrafiltration system. The suspended solids (pulp) in the juice were completely separated with a membrane cutoff of 5×10^5 molecular weight. The membrane retained most of the pectin material, and the viscosity of the permeate (juice serum) was appreciably reduced. Concentration of permeate by evaporation was achieved up to 75 °Brix. No pectinesterase activity was detected in the permeate. Some aroma compounds, particularly hydrocarbons, remained in the retentate. Oxygenated aroma components such as alcohols, esters, and aldehydes remained in the permeate.

INTRODUCTION

Ultrafiltration is now widely used in the food industry. Specific commercial applications, membrane terminology, materials, and equipment have been reviewed by Mohr et al. (1988). Ultrafiltration is particularly suitable for the separation of suspended solids in liquid foods and has replaced the use of filter aids, i.e., diatomaceous earth and filter paper, to clarify fruit juices and wines. Clarification of apple juice, in conjunction with enzyme treatment, was reported by Hernandez and Schwartzberg (1984). Ultrafiltration has been used by Yu and Chiang (1986) as a clarification step prior to the concentration of passion fruit juice. These workers showed that important flavor components are held in the retentate and the evaporation process is improved as a result of removal of the suspended solids. Lue and Chiang (1989) used ultrafiltration as a step prior to deacidification of passion fruit juice; the removal of suspended solids facilitated the passage of the juice through the ion-exchange column and prevented fouling of the resin.

Ultrafiltration of orange juice is used as a step prior to the debittering of navel orange and grapefruit juices with adsorptive resins (Wethern, 1991). Clarification of the juice facilitates the flow of liquid through the adsorption column. Ultrafiltration is also used as a step prior to concentration by reverse osmosis. The removal of suspended solids allows for concentration of orange juice to levels above 42 °Brix (Cross, 1989). Koseouglu et al. (1990) reviewed the use of membranes in citrus processing and studied changes in composition of orange and grapefruit juices after ultrafiltration.

Suspended and dissolved solids are important factors affecting the flow properties of fruit juices. Viscosity is an important factor in the concentration and handling of high-density orange and fruit juices in general. Ezell (1959) studied the effect of concentration and pulp content on the apparent viscosity of orange juice concentrates, reporting a direct relationship between pulp content and apparent viscosity. The effect of pulp on the apparent viscosity of orange juice concentrates has been described by exponential relationships (Vitali and Rao, 1984). Rouse and Albrigo (1974) found a high correlation between pectin content and viscosity of orange juice concentrates.

Radford et al. (1974) studied the distribution of volatiles between the pulp and the serum of orange juice, separating the pulp from the serum by centrifugation. Shaw et al. (1991) used the same techniques to monitor changes in volatile juice components during controlled-atmosphere storage of fresh oranges. Nisperos-Carriedo and Shaw (1990) analyzed flavor volatiles in fresh, pasteurized, frozen concentrate, aseptically packed concentrate, and reconstituted orange juice using head space analysis.

The purpose of this work is to study the effect of ultrafiltration on the suspended solids in the permeate and retentate of orange juice, i.e., pectin content, soluble solids, and viscosity, using a pilot plant ultrafiltration system. Since pectin methylesterase (PME) has an important effect on the stability of the suspended solids in the orange juice, samples of unpasteurized fresh juice, permeate, and retentate were analyzed for PME activity. The distribution of aroma compounds in the fresh juice, the permeate, and the retentate was also analyzed by head space gas chromatography.

MATERIALS AND METHODS

Ultrafiltration System. Samples of Valencia orange juice were processed in a pilot ultrafiltration (UF) system (Romicon, Inc., Woburn, MA). The UF system consisted of three hollow fiber ultrafiltration cartridges connected in parallel (Romicon) (polysulfone, 5×10^5 molecular weight cutoff, 4.68 m^2, 0.75 mm i.d.), and a 15 HP recirculation pump was used to sustain the pressure in the system. The system was operated at 15 psig transmembrane pressure and 25 °C. A tube and shell heat exchanger, placed after the recirculation pump, was used to maintain the temperature of the feed juice constant.

Freshly squeezed, pasteurized, and finished Valencia orange juice (600 L) was processed for each run. A run to test for PME retention was conducted without a pasteurization step prior to ultrafiltration. Samples of feed, clarified serum, and retentate were collected at different time intervals for later analysis. Unless otherwise stated, juice samples were ultrafiltered at a 8:1 (permeate/retentate) concentration ratio. Samples of orange juice and juice permeate were concentrated in a three-effect four-stage pilot TASTE evaporator for viscosity and Brix measurements of juice and permeate concentrates. Juice and permeate were concentrated under the same conditions of temperature and flow rates. Equipment and operation procedures have been described previously by Bates and Carter (1984).

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Table I. Changes in Ultrafiltered Valencia Orange Juice[a]

	soluble solids, °Brix	suspended solids,[b] % vol	pectin, mg_{PGA}/g	viscosity, mPa/s	PME activity, PEu × 10^3
fresh juice	10 ± 0.08	8.0 ± 0.07	1.42 ± 0.051	460.0 ± 5.10[c]	3.4 ± 0.021
permeate	10 ± 0.07	0	$5.7 \times 10^{-3} \pm 9.1 \times 10^{-4}$	12.5 ± 0.083[c]	nd[d]
retentate	10 ± 0.05	>50	13.8 ± 0.083		7.8 ± 0.11

[a] Average of three values ± SD. [b] Sinking pulp method. [c] 45% soluble solids. [d] No PME activity detected.

Analysis of Suspended Solids. *Pectin Methylesterase (PME).* Analysis for PME in the feed juice, permeate, and retentate was done by the titration of the carboxyl groups that result from demethylation of methyl esters in the pectin chains (Rouse and Atkins, 1955). PME activity is reported in microequivalents of hydrolyzed ester per milliliter per minute or PEu units.

Pectin. Pectin content in the feed juice, permeate, and retentate was analyzed as poly(galacturonic acid) by a colorimetric assay utilizing *m*-hydroxydiphenyl as described by Blumencrantz and Asboe-Hansen (1973) and as modified by Ahmed and Labavitch (1977).

Soluble and Free Suspended Solids. Soluble solids were determined with a refractometer as °Brix with a correction for acidity. Suspended solids were determined according to the sinking pulp method (Ting and Rouseff, 1986), by centrifuging a 50-mL sample of juice in a conical test tube at 1000*g* for 10 min.

Viscosity. Viscosities of the single-strength permeate and permeate concentrate were measured with a capillary viscosimeter. Apparent viscosity for the juice concentrate was measured with a Haake RV12 rotoviscosimeter (Haake Buchler Instruments, Inc., Saddle Brook, NY).

Juice Volatile Analysis. Single-strength juice, permeate, and retentate were analyzed for volatiles using the method by Nisperos-Carriedo and Shaw (1990). Samples (2 mL each) were analyzed in triplicate using a Perkin-Elmer Model 8500 gas chromatograph equipped with a FID detector, a Model HS-6 head space sampler, and a Durowax column (0.53 mm × 30 m; 1.0-μm film thickness) with a 6.0 psi helium head pressure (81 cm/s linear gas velocity). The different components were identified by comparison of retention times with those of authentic standards.

All analyses were done in triplicate.

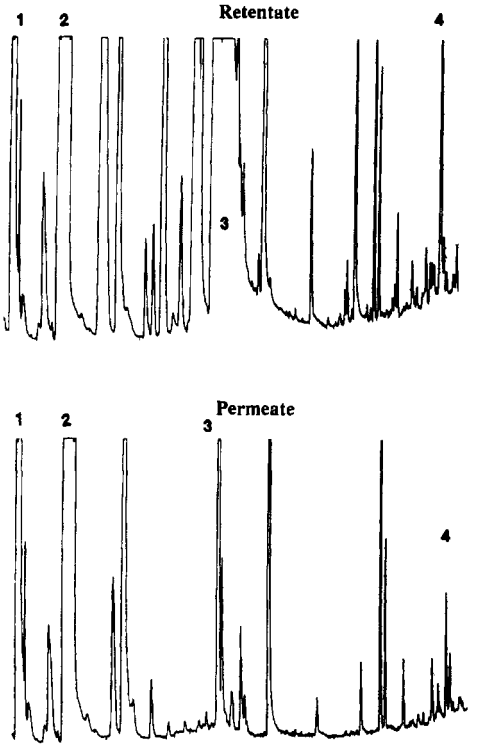

Figure 1. Gas chromatograms of retentate and permeate of orange juice. Peaks: 1, acetaldehyde; 2, ethyl butyrate; 3, limonene; 4, valencene.

RESULTS AND DISCUSSION

Effect on Suspended Solids. Suspended solids in freshly squeezed orange juice were completely removed by ultrafiltration. The resulting serum was a transparent liquid of amber appearance.

Table I shows that most of the pectin in the fresh juice was removed. Our results indicate that it is possible to remove all of the suspended solids and most of the pectin with ultrafiltration membranes of appreciably larger openings. Even though the molecular weight for pectin in orange juice has been measured to be less than 2×10^5 (Kertesz, 1951), it is apparent that the ultrafiltration membrane was capable of retaining most of this component due to association of pectin with protopectin and cellulosic material in the juice. Furthermore, the molecular weight cutoff of the membrane is usually calculated for globular particles; therefore, correlation of pectin retention with molecular weight is not straightforward since the pectin molecular chains are linear and/or branched (Joslyn, 1962). The concentration–polarization effect in the hollow fibers of the ultrafiltration system also allows for the removal of suspended solids of molecular weight lower than that of the membrane's molecular weight cutoff. The gel layer formed on the walls of the hollow fiber can also act as a filtering aid, thus reducing the effective pore size of the membrane.

No PME activity was detected in the permeate (Table I). Apparently the ultrafiltration membrane also removes most of this enzyme. Even though the molecular weight of PME in orange juice has been reported to be 27 500–24 100 (Evans and McHale, 1978), PME in orange juice is generally associated with suspended solids and is a structure-bound insoluble enzyme (Jansen et al., 1960), thus remaining in the retentate during ultrafiltration. Koseouglu et al. (1990) reported an absence of PME activity in the permeate of orange juice using ultrafiltration membranes of 10^5 and 5×10^4 molecular weight cutoff.

The viscosity of the concentrated serum was appreciably lower than that of the concentrated fresh juice. This is not surprising since it has been previously reported that the suspended solids contribute a great deal to the viscosity of the juice, particularly at higher concentrations (Vitali and Rao, 1984). As discussed above, ultrafiltration removed all of the suspended solids in the juice, including most of the pectin material. Therefore, the viscosity of the single-strength and concentrated clear serum was reduced to levels similar to that of sugar solutions.

Reduction in viscosity allowed the TASTE evaporator to concentrate the orange juice permeate to higher Brix, i.e., 56–58 °Brix for the untreated juice vs 72–75 °Brix for the serum at similar conditions of temperature and flow rates in the evaporator. Similar results were reported by Peleg and Mannheim (1970) for the concentration of orange juice from centrifugally separated pulp using a centritherm evaporator. This further illustrates the importance of pulp in the flow and thermal characteristics of orange juice during evaporation.

Effect on Aroma Components Distribution. Head space chromatograms of permeate and retentate (Figure

Table II. Flavor Volatiles from Orange Juice, Permeate, and Retentate[a]

component	fresh juice	permeate	retentate
acetaldehyde	11.9 ± 0.18	11.3 ± 1.3	12.4 ± 1.47
hexanal	0.10 ± 0.012	0.05 ± 0.006	0.09 ± 0.0026
octanal	0.78 ± 0.051	0.57 ± 0.052	0.08 ± 0.039
decanal	0.61 ± 0.021	0.10 ± 0.0099	0.78 ● 0.018
ethyl butyrate	0.54 ± 0.0082	0.56 ± 0.073	0.53 ± 0.014
ethyl hexanoate	0.023 ± 0.0025	0.018 ± 0.0018	0.034 ± 0.0042
methanol	26 ± 4.8	16 ± 0.26	47 ± 4.8
ethanol	515 ± 81.1	366 ± 69.6	526 ± 60.2
linalool	0.68 ± 0.017	0.85 ± 0.064	0.71 ± 0.020
limonene	106 ± 8.6	7.5 ± 0.94	161 ± 8.3
α-pinene	1.0 ± 0.072	0.25 ± 0.060	1.8 ± 0.074
valencene	3.6 ± 0.37	1.2 ± 0.10	5.4 ± 0.21

[a] Average of three values (ppm) ± SD.

1) showed that some aroma compounds in the juice are retained in the pulp fraction during the ultrafiltration process. Table II shows a comparison of aroma components in fresh juice, permeate, and retentate. It was found that most of the more water soluble compounds passed through the membrane, namely aldehydes, esters, and alcohols. However, the less polar aroma compounds like limonene and valencene tended to remain in the retentate. This effect was more pronounced for limonene, where less than 5% of this hydrocarbon ended up in the permeate. The same trend was observed with valencene and α-pinene. The chromatogram for fresh juice was similar to that of retentate except for lower concentration of hydrophobic compounds (see Table II).

The general distribution of aroma compounds was similar to results for aroma distribution in pulp and serum reported by Radford et al. (1974). These authors also found that the more fruity aroma compounds in the juice such as the oxygenated components were associated with the serum and the hydrocarbons are associated with the pulp. The distribution of aroma components during the ultrafiltration stage is an important factor when permeate and retentate are to be processed separately, e.g., debittering and heat treatments.

Conclusions. Processing of orange juice with an ultrafiltration membrane, 5×10^5 molecular weight cutoff, effectively removed all suspended solids. Despite their relatively lower molecular weights, most of the pectin and PME were removed by the membrane from the juice. The viscosity of the concentrated serum was appreciably lower than the viscosity of the concentrated juice. The viscosity of the single-strength and concentrated permeate tended to be similar to the viscosity of sugar solutions. Concentration by evaporation was greatly facilitated by the removal of pulp from the juice by ultrafiltration. Some of the aroma components in the juice tended to be unevenly distributed in the permeate and the retentate. Oxygenated aroma compounds flowed freely through the membrane with the permeate. Hydrocarbons and less polar components tended to be associated with the pulp and stayed in the retentate.

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Registry No. PME, 9025-98-3; pectin, 9000-69-5; acetaldehyde, 75-07-0; hexanal, 66-25-1; octanal, 124-13-0; decanal, 112-31-2; ethyl butyrate, 105-54-4; ethyl hexanoate, 123-66-0; methanol, 67-56-1; ethanol, 64-17-5; linalool, 78-70-6; limonene, 138-86-3; α-pinene, 80-56-8; valencene, 4630-07-3.