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Pre-concentration of Apple Juice with Different Reverse Osmosis Membranes

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역삼투막을 이용한 사과쥬스의 예비농축

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Abstract

The clarified apple juice was pre-concentrated by reverse osmosis system as a trial for reduction of heat treating time and quality drop in concentration of the juice. The permeate fluxes through CA 865 and CA 960 membranes were higher than those of HR 95 and HR 98 membranes even at the low operating pressure. In the concentration limit depended on the membranes used, HR membranes operated at 60 bar showed 29.0°Brix, and the time required to reach the limit was 86 min for HR 95 and 71 min for HR 98. In cases of CA membranes run at 30 bar, the juice concentration was linearly increased without the limit, and longer time to reach the same concentration was required in comparison with HR membranes. As the juice concentration was increased, the loss of soluble solids was increased, and the average contents of soluble solids in the permeate passed through HR 95, HR 98, CA 865 and CA 960 were 1.3 , 0.5 , 7.5 and 2.3° Brix, respectively, in the juice concentration range of 20.0 -25.0° Brix. The lower amounts of sugars, total acid and flavor volatiles were involved in the permeate through HR membranes, especially HR 98 than in the permeate through CA membranes.

Key words: reverse osmosis membranes, apple juice, pre-concentration.

Introduction

Apple juice is one of the most popular fruit juices and the consumption quantity of the juice is increased every year in the world[1]. Juices are watery mixtures of mostly unstable flavor volatiles and organic compounds. It is expensive to package and store single strength juice. Hence, it is desirable to remove a part or all of the water from juice to reduce volume of juice. The concentration of juice, however, is a delicate process since it is sensitive to heat treatment and many of their components are unstable even at moderate temperature. Recently the reverse osmosis (RO) system has claimed much attention for pre-concentration of fruit juices. This system has several advantages with respect to water removal over traditional evaporation techniques[2-4]. As the heat treatment is eliminated, thermal damage such as production of phenolic compounds and change in flavor volatiles of the products can be minimized[5-6]. Therefore, the pre-concentrated apple juice processed by RO system has a better quality than that prepared by vacuum evaporator at concentration range of 20 to 25° Brix. Several works about the fundamental and physico-chemical criteria approach to the problems of recovery of flavor components and sugars in fruit juices during concentration by RO system were studied

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by Matsura *et al.*[9-13]. Sheu *et al*[7,8] demonstrated that the RO system using pilot scale equipment was technically feasible for concentrating 10° Brix apple juice to 20-25° Brix at 20℃ with good retention of apple flavor volatiles. They also reported that both temperature and pressure had a significant effect on solute recovery during RO process.

Although the RO system had been developed and industrialized twenty years ago, the optimum extent in pre-concentration by RO process which may replace the evaporation method for pre-concentration of apple juice has not yet been established clearly[8]. The objectives of this study were to measure the changes in permeate flux and juice concentration depended on the membranes used, and losses of sugars, total acid and flavor volatiles of apple juice were also checked as the extent of permeate increased during RO process.

Materials and Methods

Preparation of single strength apple juice

Fuji apples were purchased from local grower, Chungnam province, at March 1987. Apples were crushed with chopper (General Slicing Company, U.S.A.), and the juice was extracted with basket type hydraulic press(Hein Werner Corp., U.S.A.). The extracted juice was heated to 50℃, and pectinase (0.003%, w/v, Ultrazyme 100, Swiss Ferment Company Ltd. Swiss) was added for clarification of the juice, kept for 2hr, and stored for 24hr at 5℃. The juice was filtered through filter press and pasteurized for 30 sec at 100℃. The finished single strength juice contained 0.21% total acid and 12.0° Brix soluble solids. The five liters of 12.0° Brix single strength apple juice were pre-concentrated by RO system for each operation.

Apparatus and Membranes

RO module used in the experiments was a DDS(De Danske Sukkerfabrikker, Copenhagen, Denmark) Lab Module-20 plate-and-frame membrane processing system. The RO system was run with only the single type membrane set(HR 95, HR 98, CA 865 and CA 960) with an effective membrane area of 0.18m². The cleaning process after each operation of RO system was followed by 1.0% of P3 Ultrasil 10(A Henkel Company, Iowa). The specifications of membranes and operating conditions used in this study are listed in Table 1.

Table 1. Specifications of RO membranes and operating conditions

Type	Permeability % NaCl	Recommended operating conditions			Experimental operating conditions		
		pH	°C	bar	pH	°C	bar
HR95	5	2-11	0-60	0-60	4.2	20°C	60
HR98	2.5	2-11	0-60	0-60	4.2	20°C	60
CA865	66-74	2-8	0-30	0-40	4.2	20°C	30
CA960	36-45	2-8	0-30	0-30	4.2	20°C	30

Analytical

Sugar composition analysis: Major sugars, which exist in permeate, i.e., glucose, fructose and sucrose were determined by high performance liquid chromatography (HPLC, Waters Model 440, Waters Associate, U.S.A.) according to the procedures of Brause and Raterman[14]. A Lichrosorb $-NH_2$ column(Merk, W. Germany) was used for sugar seperation, and an acetonitrile/water(85/15) mixture was used as the elute solvent.

Titratable acidity: The total acid content in permeate sample was analyzed by titration method[15] with 0.01N NaOH solution to pH 8.1 using a pH meter(Fisher Model 750, Fisher Sci., U.S.A.). The titratable acidity of a sample was expressed as percent malic acid by weight.

Soluble solids: Soluble solids in permeate and concentrated juice were measured with refractometer(Erma Optical Works Ltd., Japan) at 20℃.

Flavor analysis : Twenty milliliters of each permeate sample were put into a 50ml reaction vial, sealed, and incubated in a 55℃ water bath before analysis. After allowing 20 min for equilibration of each vial, a 5ml headspace sample was injected a 3m×3.2mm O.D. stainless steel column packed with 10% FFAP on chromosorb AW (80/100mesh) in a Hewlett Packard Model 5890 gas chromatograph(GC) equipped with a flame ionization detector and a Model 3390A computerized terminal recorder (Hewlett Packard, U.S.A.). The other GC conditions for analysis of the flavor were followed by procedures of Hachenberg[16]. The total apple flavor volatiles were determined by summation of the intergrated area from each volatile component peak, and major flavor volatiles were presented as summation of peak area of ethyl-2-methylbutylate, hexanal and trans-2-hexal in the chromatogram[17,18].

Results and Discussion

Changes in permeate flux and juice concentration

Fig. 1 and Fig. 2 show the changes in permeate flux through the RO membranes used and the concentration of apple juice during RO processes under the operating pressure at 30 bar for CA 865 and CA 960 membranes and 60 bar for HR 95 and HR 98 membranes. The permeate flux as a function of operating time was decreased with the different trends depended on the membranes used. The decrease of permeate flux was more rapidly occured in HR membranes than in CA membranes, and HR 98 showed the most considerable reduction in the flux. The flux through HR 98 membrane was dropped drastically up to 4l/m^2 · hr after 43 min from start run of the RO system, and thereafter it was slowly changed. HR 95 showed the similar decreasing trend but the reduction was not much shaper than that presented by HR 98.

When compared with the average processing capacities of HR membranes concentrated to 20 Brix under pressure of 35, 40 and 45 bar[7], higher permeabilities could be obtained by the same membranes pressured at 60 bar in this experiment. In case of CA membranes, the permeability of CA 865 was higher than that of CA 960 at the initial phase in running period and there was no difference between the two membranes after 66 min.

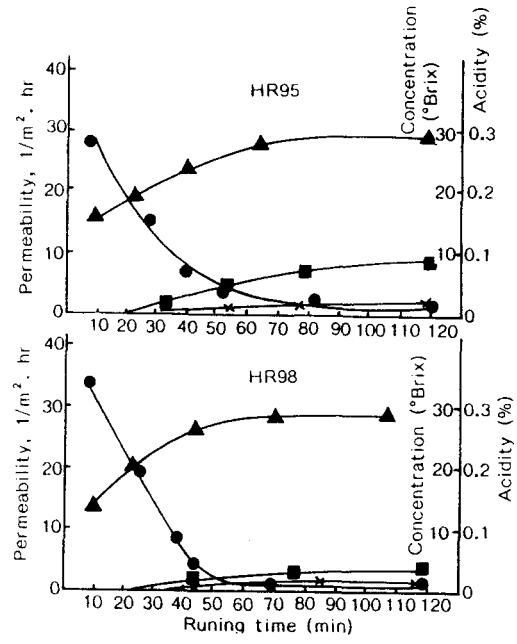

Fig. 1. Changes in permeate flux, concentration of the juice and losses of soluble solids and titratable acid through the permeate during RO processes with HR 95 and HR 98 membranes at 60 bar.
●——● : Permeability of the membrane
▲——▲ : Soluble solids of the concentrate
■——■ Titratable acidity of the permeate
×——× Soluble solids of the permeate

The concentration of feed juice was increased as the operating time of the RO system elapsed, and the juice concentration showed the inverse relationship with permeate flux.

In HR 98, the concentration of the juice was changed rapidly from 12.0° Brix to 20.0° Brix within 23 min, and thereafter the increasing rate of the concentration was reduced as the running time went by. After run for 71 min, the juice was con-

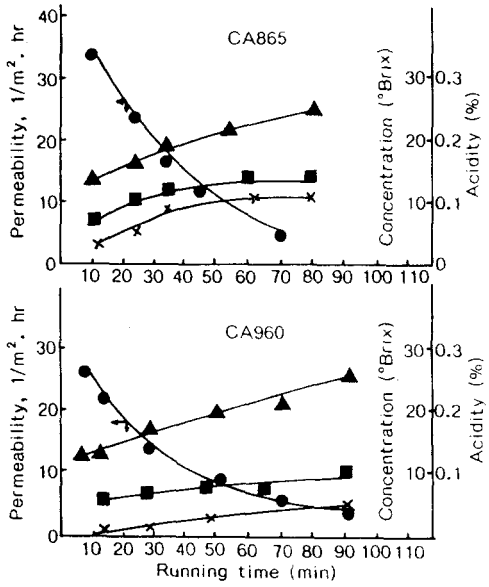

Fig. 2. Changes in permeate flux, concentration of the juice and losses of soluble solids and total acid through the permeate during RO processes with CA 865 and CA 960.

●——●: Permeability of the membrane
▲——▲: Soluble solids of the concentrate
■——■: Titratable acidity of the permeate
×——×: Soluble solids of the permeate

centrated to 29.0° Brix, and the extent of concentration was the concentration limit of HR 98 membrans. The time for concentration of the feed juice of 12.0° Brix to 20.0° Brix with HR 95 was required 2 min longer than the time required by HR 98. This membrane had similar concentration limit as indicated in HR 98, and the limit extent was shown after run for 86 min from the start of the RO system. During the RO processes with CA membranes, the concentration of the juice was linearly increased, and the increasing pattern was quite differed from that given by HR membranes. The consumption time for arrival to 20° Brix from 12° Brix was 45 min with CA 865 and 50 min with CA 960, respectively, and these membranes did not show the concentration limit.

Loss of soluble solids

Soluble solids in feed juice were lost through the membrances, and its amount was increased linearly during RO processes(Fig. 1 and Fig. 2). In RO processes using HR95 and HR98 membranes at 60 bar, the losses through permeate were little occured until the feed juice was concentrated to 20.0° Brix. During concentration of the juice from 20.0° Brix to 25.0° Brix and from 25.0° Brix to 29.0° Brix, the average losses through the permeate were 0.15° and 0.82° Brix for HR98, and they were 0.50° and 1.20° Brix for HR95, respectively. The CA 865 and CA960 membrance were unable to retain as much of soluble solids as the HR membranes in spite of low operating pressure, 30 bar, and this might be caused by differences in pore size and characteristics of the membrances. Concentrating the juice of 20.0° Brix to 25.0° Brix using CA865 and CA960 membrances showed higher loss of soluble solids through the permeate in comparision with the concentration range from 12.0° Brix to 20.0° Brix, and this trend was serious in the membrane of CA865.

Loss of acid

The losses of total acid through membranes during RO processes are also shown in Fig. 1 and Fig. 2. The trends of acid loss were similar to those of soluble solids developed by the same membranes during RO process. The average loss through the permeate was ranged from 0.01% using HR98 to 0.03% using HR95 in the concentration range from 20.0° Brix to 25.0° Brix, and it was 0.03% and 0.057% in the concentration range from 25. 0° Brix to 29.0° Brix, respectivlely.

As the juice was concnetrated to 20.0° Brix CA865 and CA960, the losses were 0.09% and 0.07%. respectively. Concentrating the feed juice to 25.0° Brix with CA960 marked lower acid loss when compared with CA865.

Loss of major sugars

Fig. 3 shows the lost major sugar contents through the each fraction of permeate during RO processes. The data in Fig. are presented as percent losses of sugar contents in permeate against the total amounts of the sugars contained in the original volume of feed juice. The fresh feed juice for this process had average sugar contents of 6.4% fructose, 2.9% glucose and 2.5% sucrose. During the concentration of the juice by RO system with HR 95, HR 98, CA 865 and CA 960 membranes, the amount of each sugar leaked out through the membranes was increased as the extent of permeate amount increased. These sugars were much more permeable through CA 865 and CA 960 membranes than through HR 95 and HR 98 membranes, and glucose and fructose were more easily permeated through membranes in comparison with sucrose. These results could be explained by differences in molecular weight of these sugars and pore size of the membranes[10]. Especially, fructose, the important sweeter in juice was lost considerably through CA 865 membrane and the lost amount was about 5 times higher than that of HR 98 in the permeate extent range of 60%-70%.

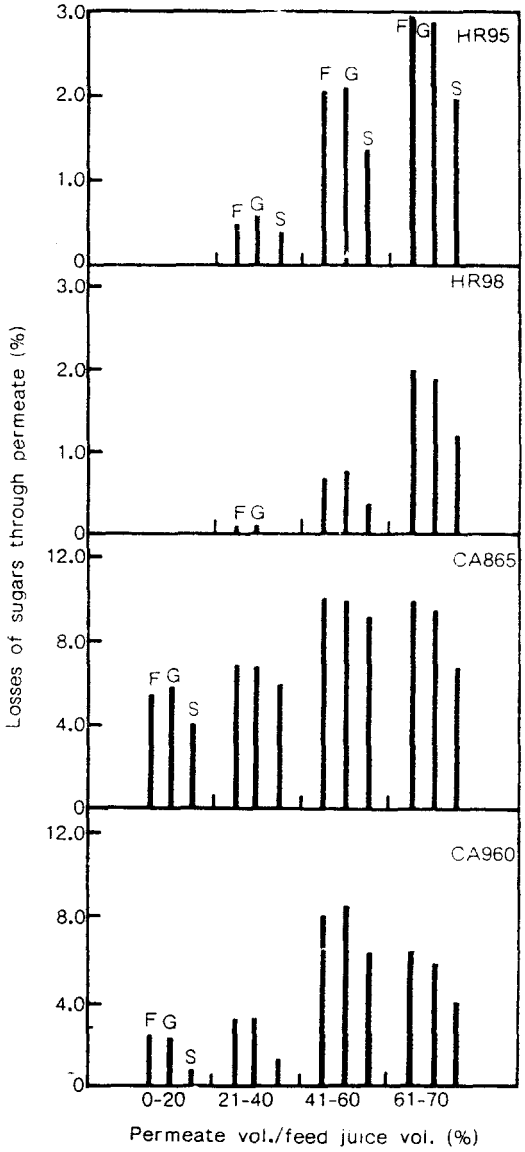

Fig. 3. Percent losses of major sugars as the amount of permeate water increased.
F: fructose
G: glucose
S: sucrose

Loss of flavor volatiles

During RO processes with the different conditions a part of the flavor volatiles in the juice was reduced as shown in Fig. 4 and the results in Fig. were presented as like as the case of sugar losses. The losses of the flavor volatiles were increased until the percent of permeate amount against the initial volume of feed juice was reached to 60% and thereafter the increasing rate of the losses was reduced during RO processes with all the membranes used. In the losses depended upon the membranes, they were much more serious in CA membranes, especially CA 865 than in HR membranes, and the most effective flavor retention was shown in HR 98 membrane used in RO process. When 70% of the initial volume of the feed juice was permeated through the HR 98 membrane, the concentration of juice was about 29.0° Brix, and 36.1% of total and 30.2% of major flavor volatiles were lost through permeate. HR 95 and

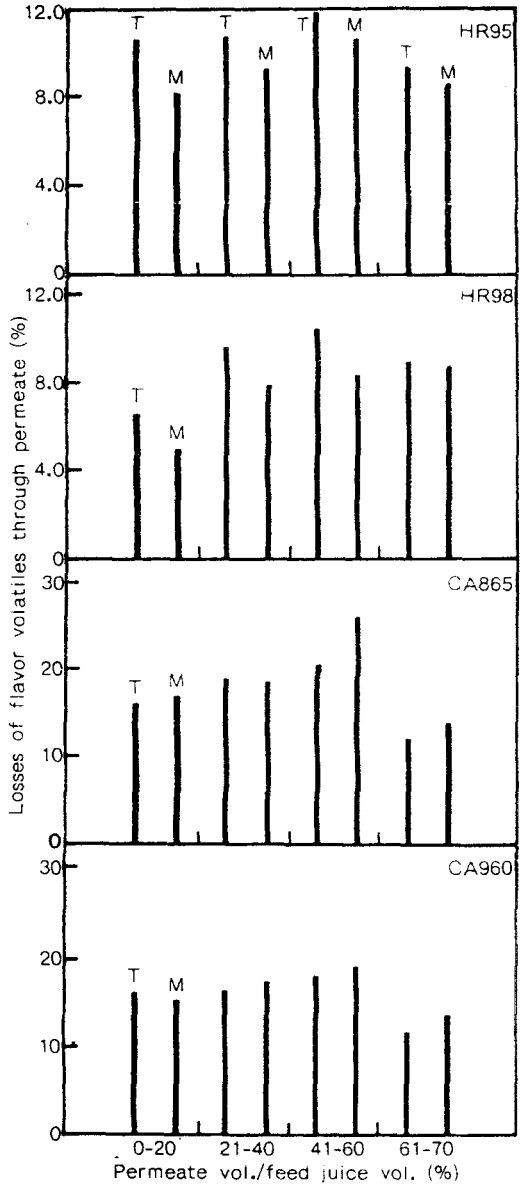

Fig. 4. Percent losses of apple flavor volatiles as the amount of permeate water increased
T: total flavor volatiles
M: major flavor volatiles

HR 98 membranes demonstrated higher retention of the major flavor volatiles than that of the total flavor volatiles as pointed out by Sheu *et al*[8]. The application of CA 865 and CA 960 membranes with their higher losses of flavor volatiles through the permeate resulted in appreciable quality loss, and it seems that this type of membranes might not be suitable for concentration of apple juice.

요 약

청징한 사과쥬스를 역삼투 장치를 이용하여 예비농축을 하였다. 사용한 역삼투막의 종류에 따른 농축한계농도는 HR 95 및 HR 98형의 역삼투막에 60 bar를 가하여 농축하였을 때 29.0° Brix이었으며, 이 농도에 도달하는 데 소요된 시간은 HR 95형이 86분, HR 98형이 71분이었다. CA 865와 CA 960형은 30 bar에서 농축한계농도를 보이지 않고 역삼투압 장치의 가동시간이 경과함에 따라 직선적으로 농도가 증가하였는 데 HR형의 경우에 비하여 동일 농도에 도달하는 시간이 더 많이 소요되었다. 한편 역삼투막을 통하여 손실된 가용성 고형물의 양을 쥬스의 농축농도와 관련지어 비교시 20.0 25.0° Brix의 농축범위에서 HR 95, HR 98, CA 865 및 CA 960의 역삼투막을 통과한 permeate에는 가용성고형물이 각각 평균 1.3, 0.5, 7.5 및 2.3°Brix씩 함유되어 있었으며 HR형 특히 HR 98을 통한 손실이 가장 적은 것으로 나타났다. 또한 총산 및 향기성분의 permeate를 통한 손실도 가용성고형물의 손실에서 보인 경향과 유사하였다.

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