Permeability of Cane Juice in Ultrafiltration Membranes of Acrylic Vinyl Co-Polymer and Cellulose Acetate†

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The effects of membrane permeability on the flux and quality of raw and limed cane juice on ultrafiltration were studied by 2~3 h long-term testing (of several types with molecular weight cut-off levels from 50 000 to 100 000). The flux through XM-50, XM-100 and A-50 T membranes for raw juice remained at the value of about $0.100 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ until permeation volume of 250 ml, but it then decreased gradually. The flux of A-50 T membrane was the greatest at the initial stage (with $0.140 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$), and then decreased gradually when juice limed to pH 8.1 at 10°C was used. The flux of juice limed to pH 7.0 at 85°C showed remarkably high value (at the initial stage), however it decreased rapidly with increasing permeate volume. The flux of A-50 T membrane showed comparatively lower value than that of XM-membranes. The sucrose rejection of the permeate with the XM-50, XM-100 and A-50 T membranes was 2, 2~5 and 5~7% for juice limed to pH 7.0 at 85°C, respectively.

A number of studies have been done on the application of low energy techniques in sugar processing, because cane manufacturing is one of the most energy-intensive processes in the food industry¹⁾. One of such technique is the ultrafiltration of raw and limed juice^{2)~5)}. As reported in the preceding papers^{6)~8)}, addition of lime to cane juice proved effective for increasing the flux. When ultrafiltration was carried out with a PM-10 membrane at 80°C after liming at 10, 30 and 85°C, the greatest flux and highest permeate quality based on purity, and the optimum contents of CaO and P_2O_5 were obtained at pH 8.1, 7.8 and 7.0, respectively⁶⁾. Such optimum conditions were also found for PM-30, YM-5 and YM-2 membranes⁷⁾. Furthermore, we reported previously on the membrane permeabilities of raw and limed cane juice through two types of mem-

branes (PM and YM) with molecular weight cut-off levels from 5 000 to 30 000 by the long-term testing, and concluded that the YM-30 membrane with a nominal molecular weight exclusion limit of 30 000 was suitable for ultrafiltration of raw juice, while the YM-5 membrane (5 000) was more suitable for that of limed juice (limed to pH 7.0 at 85°C)⁸⁾. This indicated that the membrane permeabilities of cane juice was not proportional to the molecular weight cut-off levels in a type of cellulose derivative membrane. On the other hand, the membrane of acrylic vinyl copolymer are also developed by many membrane manufacturing companies as well as those of cellulose derivatives⁹⁾.

We report here the effects of membrane permeability, with types of XM-membrane and cellulose acetate membrane with molecular

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weight cut-off levels from 50 000 to 100 000, on the flux and quality of raw and limed juice on ultrafiltration, as studied by long-term testing for 2~3 h, and discuss the applicability of the membrane process in the cane sugar industry.

Materials and Methods

Cane Juice

Sugar cane (variety N : Co 310) grown in the fields of the University of the Ryukyus was pressed twice with a test mill to obtain the juice, which was filtered through cotton wool.

Liming the cane juice

The cane juice (400 ml) was limed to pH 8.1 at 10°C and pH 7.0 at 85°C by adding $\text{Ca}(\text{OH})_2$ (3.4 g/l) as previously reported^{6,7,8}.

Operation and conditions for ultrafiltration

The apparatus used for ultrafiltration was a UHP-76 (Toyo Kagaku Sangyo Co., Ltd.), which was a batch-type filtration unit equipped with a stirrer. Three membranes of two types were used in this study : XM-50 and XM-100 (Amicon Co., Ltd.), and A-50 T (Bioengineering Co., Ltd.). These membranes had nominal molecular weight exclusion limits of 50 000, 100 000, and 50 000, and the flow times of water for the initial 10 ml were 2.0, 4.0, and 8.0 sec, respectively. The XM and A-50 T membranes are reportedly made of an acrylic vinyl co-polymer and cellulose acetate, respectively. The juice applied (400 ml) was ultrafiltered until a permeation volume of 370 ml was reached (700 rpm, 4.0 kg/cm², and 67 and 55°C). As the maximum temperature for A-50 T membrane was 55°C, ultrafiltration was performed at 55°C when the membrane was used.

Sucrose measurements

The Brix (Bx) degree of the permeated juice was measured with a refractometer and a spindle without clarification. The sucrose content was also measured with a saccharimeter after clarification with dry basic lead acetate for raw and limed juice.

Results

The flux rate is shown in Fig. 1 as a

function of the permeate volume of the raw juice for the XM-50, XM-100 and A-50 T membranes. The flux rate through the all of membranes used remained at a value of 0.09–0.100 ml · cm⁻² · min⁻¹ until a volume of 250 ml was reached, but it then decreased gradually. A decreasing flux rate may be due to the deposit of some colloids such as proteins and polysaccharides on the membrane surface^{7,8}.

The qualities of the permeates are summarized in Table 1. The permeates thus obtained were of 17–20° Bx and 87–90% purity. Sucrose rejection was high, 5–9%, with the A-50 T membrane, while XM-50 and XM-100 membranes showed low values, 2–3%. This may be due to the adsorption of proteins and polysaccharides as mentioned above, and these results agree with the flux data shown in Fig. 1.

Effect of degree of liming on flux through the XM-50, XM-100 and A-50 T membrane is shown in Fig. 2. Liming was performed at 10 and 85°C and flux was calculated on basis of the first 50 ml of permeate. The largest flux of permeate was obtained at pH 8.1 and pH 7.0 when liming was performed at 10 and 85°C, respectively. This result agreed with that

Fig. 1 Permeation flux of raw juice as a function of permeation volume at 67 and 55°C

The membranes used were XM-50, XM-100 and A-50 T membranes. Ultrafiltration was performed under the following conditions : Pressure, 4.0 kg/cm² ; stirring speed, 700 rpm ; temperature, 67°C for XM-50 and XM-100 membrane and 55°C for A-50 T membrane.

○, XM-50 ; ◐, XM-100 ; ●, A-50 T.

obtained from PM and YM membranes as reported previously⁽¹⁷⁾. Furthermore, flux rate of juice limed at 85°C, showed very large values, about twice as large as those of juice limed at 10°C. This indicates that hot liming, at 85°C, is more efficient for increasing the flux than cold liming, and these results agree with the results obtained from PM-10, YM-5 and YM-2 membranes as reported previously⁽¹⁷⁾.

The limed juice adjusted to pH 8.1 at 10°C

Fig. 2 Effect of degree of liming on flux at 67 and 55°C

Juice was limed at 10 (---) and 85 (—) °C. Flux was calculated on basis of the 50 ml of permeate.

○, XM-50; ⊙, XM-100; ●, A-50 T.

Table 1 Sucrose contents of raw juice permeated with XM-50, XM-100 and A-50T membranes at 67 and 55°C

	Sucrose (% w/v)*	Bx (Spindle)	Bx (Ref)
XM-50			
Sucrose	18.2	18.0	18.8
Sucrose rejection (%) ^a	3.1	5.0	2.1
XM-100			
Sucrose	18.2	20.5	18.6
Sucrose rejection (%) ^a	2.7	2.4	3.2
A-50T ^b			
Sucrose	17.8	18.5	17.6
Sucrose rejection (%) ^a	9.4	7.5	5.1

* Measurement was performed after clarification with dry basic lead acetate.

^a Sucrose rejection = (1 - permeated juice/feed juice) × 100

^b Ultrafiltration was performed at 55°C.

was ultrafiltered through the XM-50, XM-100 and A-50 T membranes, and the flux obtained are shown in Fig. 3. The A-50 T membrane gave the greatest value of $0.14 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ at the initial stage, however the value decreased gradually with increasing permeate volume. The flux with the XM-100 membrane was lower than that for non-treated juice as shown in Fig. 1. This may be due to the occurrence of considerable colloids adsorption on the membrane materials.

Figure 4 shows the flux-permeate relationship of juice limed to pH 7.0 at 85°C. The flux through the XM-50 and XM-100 membranes

Fig. 8 Permeation flux of juice limed to pH 8.1 at 10°C as a function of permeation volume at 67 and 55°C

○, XM-50; ⊙, XM-100; ●, A-50 T.

showed remarkably large values at initial stage. However, it decreased rapidly until a volume of 100 ml was permeated and remained constant at $0.100 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$. On the contrary, the A-50 T membrane gave comparatively lower values than XM-50 and XM-100 membrane at the initial period, the greatest value among the three membranes being given

Fig. 4 Permeation flux of juice limed to pH 7.0 at 85°C as a function of permeation volume at 67 and 55°C
○, XM-50; ◐, XM-100; ●, A-50 T.

after a permeation volume of 200 ml had been reached.

The quality of juice limed to pH 8.1 (7.0) at 10 (85)°C and ultrafiltered through the various membranes is summarized in Table 2. The sucrose rejection with XM membranes was higher than that with A-50 T membrane in cold liming (10°C) test. However, in hot liming (85°C), the reverse correlation was observed; namely, the A-50 T membrane which had a molecular weight cut-off level of 50 000 showed the highest sucrose rejection of 5.2~7.0%. Whereas the sucrose rejection was 2.5~3.5% with the XM-100 membrane, which had a molecular weight cut-off level of 100 000, it was the lowest, 2.1~2.4%, with the XM-50 membrane, which had a molecular weight cut-off level of 50 000.

Experimental results were also obtained for a pure sucrose solution (17.5%, w/v), as shown in Fig. 5. In both experiments with XM-50 and XM-100 membranes, the flux was observed to be remarkably high during the initial period, and then it decreased with increasing permeate volume. As for the A-50 T membrane, a comparatively large increase in the flux was observed as compared to that of the cane juice limed to pH 7.0 at 85°C (Fig. 4). The sucrose rejection for pure sucrose

Table 2 Sucrose contents of limed juice permeated with XM-50, XM-100 and A-50 T membranes at 67 and 55°C

		Sucrose (% w/v)	Bx (Spindle)	Bx (Ref)
XM-50	Limed to pH 7.0 at 85°C	18.2	20.5	18.6
	Sucrose rejection (%) ^a	2.1	2.4	2.1
	Limed to pH 8.1 at 10°C	17.2	17.0	16.6
	Sucrose rejection (%) ^a	14.9	10.0	4.1
XM-100	Limed to pH 7.0 at 85°C	18.1	20.0	18.0
	Sucrose rejection (%) ^a	3.5	2.5	3.1
	Limed to pH 8.1 at 10°C	18.4	17.5	16.8
	Sucrose rejection (%) ^a	12.1	11.0	11.8
A-50 T ^b	Limed to pH 7.0 at 85°C	16.3	18.0	16.6
	Sucrose rejection (%) ^a	7.0	5.2	5.6
	Limed to pH 8.1 at 10°C	16.3	17.5	16.6
	Sucrose rejection (%) ^a	12.2	7.9	5.7

^aSucrose rejection = $(1 - \text{permeated juice/feed juice}) \times 100$

^bUltrafiltration was performed at 55°C.

Fig. 5 Permeation flux of a sucrose solution as a function of permeation volume at 67 and 55°C

The sucrose solution used was 17.5 % w/v.

○, XM-50; ⊙, XM-100; ●, A-50 T.

solutions was very low, 0 ~ 2.0%, with both XM and A-50 T membranes (not shown in the Table).

Discussion

In order to compare the flux and quality of cane juice permeated with XM-50, XM-100 and A-50 T membranes with those with YM membranes, experiments were performed under the same conditions as in the previous study⁸⁾. In spite of the greater flux through the YM-30 membrane⁸⁾, which had nominal molecular weight exclusion limit of 30 000, and was reportedly made of a cellulose derivative, the A-50 T membrane, which had nominal molecular weight exclusion limit of 50 000, and was made of cellulose acetate, showed lower values for raw juice. The result obtained was contrary to our expectation. This suggests that the cellulose acetate membrane (A-50 T) became more liable to adsorb some colloids such as proteins and polysaccharides even of being formerly globular in shape, when its molecular weight exclusion limit of 50 000 was used. However, for juice limed to pH 8.1 at 10°C, the A-50 T membrane gave the greatest flux during ultrafiltration, and furthermore it

showed larger values than those with YM-5 membrane⁸⁾ for juice limed to pH 7.0 at 85°C.

Although, XM-membranes (XM-50 and XM-100) showed low flux for the raw juice and the juice limed to pH 8.1 at 10°C, for the juice limed to pH 7.0 at 85°C, it gave very large flux, showing 0.390 and 0.330 ml·cm⁻²·min⁻¹ at the initial stage. The values were twice as large as PM-30, PM-10, YM-5⁸⁾ and A-50 T membranes at the period, while it then decreased rapidly with increasing permeate volume, the value being 0.120 and 0.110 ml·cm⁻²·min⁻¹ at the permeation volume of 200 ml. After that, it remained constant until the volume of 370 ml, at which, however, the flux was larger than with YM-5 membrane as reported previously⁸⁾.

In spite of showing larger flux with A-50 T membrane than with YM-5 membrane⁸⁾, the sucrose rejection for the former membrane was greater than that for the latter one for juice limed to pH 7.0 at 85°C. This indicates that there is a remarkable difference in sucrose concentration between the residual and permeated juice when ultrafiltration is performed with A-50 T membrane. This may be due to the remarkable adsorption of proteins and polysaccharides that takes place on the membrane surface. It cannot be concluded whether the result depends on the quality of the membrane material (cellulose acetate) or on the operation temperature (55°C). Thus, A-50 T membrane is difficult to use in the sugar industry. The lowest sucrose rejection was obtained with the XM-50 membrane, the value being 2.1% for the juice limed to pH 7.0 at 85°C, while it remained at 2.5 ~ 3.5% with the XM-100 membrane.

On ultrafiltration of limed juice with all of membrane used, some dark brown deposit was formed on the membrane surface. The deposit on the XM-50, XM-100 and A-50 T membranes was removed by washing with 0.05 N NaOH at 50°C for 20 min, and the membrane capacity was restored. A big problem in ultrafiltration is the fouling of membrane⁴⁾. This could cause serious disruption of sugar production and limit the economic viability of

the process.

Thus, on the basis of Results and Discussion, we conclude that the XM-50 membrane which is reportedly made of an acrylic vinyl co-polymer is suitable for juice limed to pH 7.0 at 85°C (hot liming). The next stage in this study is large scale operation with an XM membrane, using a batch-type filtration apparatus and other systems such as tubular, spiral wound and hollow-fibre ones.

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ポリアクリル・ビニール共重合および酢酸セルロース膜 による限外濾過での甘蔗汁の膜透過性

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分画分子量の異なる XM 膜 (ポリアクリル・ビニール共重合; 分画分子量 50 000 および 100 000) および A-50 T 膜 (酢酸セルロース; 50 000) を使用して甘蔗汁および石灰添加汁の限外濾過を長時間行い、透過性を検討した。生甘蔗汁の膜透過性はいずれの膜も透過流量が $0.100 \text{ ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ 前後で、透過量の増大に伴って徐々に減少した。10°C で pH 8.1 に水酸化カルシウムによって調製した甘蔗汁は A-50 T 膜の流量が最も高く、次いで XM-50, XM-100 膜の順に高い値を示した。85°C で pH 7.0 に調製した甘蔗汁の初流量は XM-50 および XM-100 膜が著しく高い値を示したが、透過量の増大に伴って急激に減少した。XM-50, XM-100 および A-50 T 膜の透過液 (pH 7.0, 85°C ライミング) の蔗糖の阻止率は 2.1, 2.5~3.5 および 5~7% であった。このような結果から、XM-50 膜は石灰添加汁 (ホットライミング) の限外濾過に適する可能性が示唆された。