An apparatus for partial ice-melting to improve yield in progressive freeze-concentration

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Abstract

A small test apparatus was made for partial melting of ice at controlled conditions in temperature and stirring speed. Ice cubes from 10 wt% sucrose were partially melted in this apparatus at 4 temperature and 4 stirring speeds. At the lower temperature with relatively faster stirring speed, the initially-melted fractions effectively contained the higher concentration of solute than the later-melted fractions. The partial ice-melting technique was combined with progressive freeze-concentration (PFC) to improve the yield in PFC. Apple juice with 13.7 °Brix was concentrated up to 25.5 °Brix by PFC using a tubular ice system. Then, the partial ice-melting was applied for the ice formed by PFC to improve the yield from 63.8% to 85% by recovering the initial 30% melted fraction. The partial ice-melting was also applied to pear (La France) juice flavor condensate. After 2.36 times concentration of flavor component (butyl acetate) by PFC, the yield was improved from 86.7% to 95% by recovering the initial 35% melted fraction in the partial ice-melting process. Partial ice-melting technique will overcome the major drawback of PFC, in which the yield decreases with an increase in solute concentration because of the solute inclusion in the ice.

Key words: Progressive freeze-concentration, Partial ice-melting, Yield improvement, Solute inclusion in

ice, Freezing-thawing technique

1. Introduction

Freeze-concentration has long being known as the best concentration method in terms of preserving original quality in the concentrated product (Deshpande et al., 1982). The low temperature operation in freeze-concentration prevents undesirable chemical, physical and biological changes that occur in other types of processing. Up to date, commercially available freeze-concentration method is known as suspension crystallization. This method requires a complicated system including surface-scraper heat-exchanger for seed ice, recrystallization vessel for ice crystal growth by Ostwald ripening mechanism, and washing tower to separate ice crystals from concentrated mother solution (Huige and Thijssen, 1972). Complexity of this system along with the high capital cost resulted in the limited practical use of this method for the concentration of liquid food.

Progressive freeze-concentration (PFC) is an alternative freeze concentration method where only a single ice crystal is formed on a cooling plate by a moving ice front (Matthews and Coggeshall, 1959; Shapiro, 1961; Miyawaki et al., 1998). Due to the ease of separation of concentrated solution, this method requires a simple system and a relatively cheap method than the suspension crystallization. A falling film reactor has developed for the scaling up of PFC (Flesland, 1995) and has applied for concentration of variety of liquid food (Hernandez et al., 2009, Hernandez et al., 2010, Sanchez et al., 2010, Sanchez et al., 2011). In this system, the ice crystal grows on a vertically placed cooling plate on which the solution to be concentrated flows as a falling film. Although this system is simple, the limited liquid flow rate on the cooling surface may result in limited mass transfer between the ice and the liquid phases, which limits the separation

efficiency as expected by the concentration polarization theory (Miyawaki et al., 1998). In addition, this reactor has an open air surface which could lead to the loss of volatile flavor components. Retention of flavors is a major advantage in PFC (Ramos et al., 2005). Therefore, the PFC system should be designed in a way to minimize these losses. A closed tubular ice system with a circulating flow was developed for the scale-up of PFC, which provides a good mass transfer and a controlled heat transfer in a closed system (Miyawaki et al., 2005). This system is expected to give a high separation efficiency and a high-quality for the concentrated product especially in the retention of volatile flavors.

The major drawback in PFC system is the decrease in yield with an increase in the concentration, or osmotic pressure of sample because of the solute inclusion in the ice (Gu et al., 2005). To overcome this problem, we proposed partial ice-melting technique (Miyawaki et al., 2012), where the principle in the classical freezing-thawing technique was effectively applied.

In the freezing-thawing process, the initial melted fractions after freezing contains the higher concentration of solute than the later melted fractions. This phenomenon has been known from long time ago as the enrichment of ions from melting snow or ice in natural environment (Johannessen and Henriksen, 1978; Davies et al., 1982; Brimblecombe et al., 1987, 1988). This principle has been applied in desalination from sea water (Johnson, 1993; Khawaji et al., 2008; Mandri et al., 2011; Rich et al., 2012) and recently, various applications in industrial purpose have been explored (Yee et al., 2003, 2004; Nakagawa et al., 2009, 2010; Moreno et al., 2013, 2014). Only by freezing-thawing, however, concentration efficiency is limited so that multiple operations are inevitable (Aider and Halleux, 2008) to obtain a highly concentrated product, which requires a high energy consumption in the process.

To improve the efficiencies in separation and energy, a combination of freezing-thawing process with

PFC will be an attractive option. In the previous paper, we successfully combined the partial ice-melting technique with PFC to improve the yield (Miyawaki et al., 2012). In this case, however, the experimental conditions in the thawing process were uncontrolled. In the present paper, we made a test apparatus for the melting of ice under the controlled conditions in temperature and stirring speed and applied it to improve the yield in PFC by the tubular ice system.

2. Experimental method

2.1 Materials

Sucrose and methyl butanoate were purchased from Kanto Kagaku (Tokyo, Japan). Apple juice was supplied from Ishikawa Agriculture and Forestry Research Center. Pear (La France) juice flavor condensate is a by-product of vacuum evaporation of pear juice and was supplied by Kakoh Fruits and Flavors, Tokyo.

2.2 Preparation of cube ice

Ice cubes ($25 \times 25 \times 30$ mm) were prepared by freezing 10 wt% sucrose solution (550 mL) in an ice cube tray using a freezer (D-396DF3, Nihon Freezer, Japan) operated at -35°C .

2.3 Progressive freeze-concentration

A tubular ice system (Miyawaki *et al.*, 2005) with circulating flow (MFC-10, Mayekawa, Tokyo) was used to concentrate apple juice and pear juice flavor condensate. This system consists of jacketed cylindrical tube (59.5 mm in diameter, 1800 mm $\times$ 2 in length), circulation pump, and feed tank. A coolant, the temperature of which was controlled by a controller and a refrigerator, was supplied to the jacket side of the tube to cool down

the tube to form ice layer inside. Concentration process was controlled by the temperature program of the coolant and the speed of the circulation pump.

For apple juice, which was a solution with relatively high osmotic pressure, the seed ice lining step was necessary to improve the yield. For this purpose, the pure water was firstly introduced into the tubular system to form a small amount of seed ice on the cooling palate and the water was discharged. Then, precooled apple juice sample was introduced into the system to start PFC. After the concentration process, the concentrated solution was removed from the system and the coolant temperature was raised up to 20 °C to melt the ice surface formed in the system. Then, the ice slid out gravimetrically from the bottom of the tube. The ice taken out incorporated the small amount of the seed ice, the contribution of which was neglected in the analysis. The part of the ice was broken down into pieces and used for partial melting by the partial ice-melting vessel.

For pear juice flavor condensate, pre-cooling of the sample and seed ice lining (Miyawaki et al., 2005) was not applied because of the low osmotic pressure of the sample which has a freezing point close to 0 °C.

2.4 Test apparatus for partial ice-melting

A test apparatus (Fig. 1) was made for the partial melting of ice at a controlled temperature and a stirring speed. The apparatus is a jacketed vessel (11cm in diameter, 30 cm in depth) whose temperature was controlled by a circulation type cooler (TRL 108 H, Thomas, NJ, USA). The ice pieces were transferred into the vessel and stirred (SM-102, As one, Osaka) using a 4-blade, paddles blade stirrer (10 cm in diameter). The temperature was controlled at 0, 2, 10, or 20°C and the stirring speed was at 0, 50, 100, or 200 rpm. The melted ice fractions about 50-100 ml were collected at intervals and the volume and the solute concentration were measured.

2.5 Analytical method

The concentrations in °Brix were analyzed for original solution, concentrate after PFC, and partially melted ice fractions by a refractometer (APAL-1, As One, Osaka) for ice cube sample and apple juice. For pear juice flavor condensate, °Brix was measured as a tentative index after concentration and partial ice-melting and flavor analysis by gas chromatography was carried out succeedingly.

The solid phase micro extraction (SPME) was used for the flavor analysis of the pear juice flavor condensate sample. A 10 ml sample, mixed with 40 ppm methyl butanoate as an internal standard and 2.4 g of sodium chloride, was transferred into a 20 ml screw-cap vial and heated up to 45 °C for 5 min and then the SPME fiber (50/30um, DVB/CAR/PDMS (Grey), Supelco Analytical, PA, USA) was inserted into the head space of the vial for the extraction and adsorption of flavor components to the SPME fiber for 15 min. Then, the SPME fiber was removed from the vial and was inserted into the injection port of gas chromatograph (GC) or gas chromatograph/mass spectroscopy (GC/MS) for releasing of flavors for 3 min.

Flavor components of the samples were identified by GC/MS (Focus DSQ II, Thermo Scientific Japan, Yokohama) and quantitatively analyzed by GC (G3900, Hitachi, Tokyo). The same type capillary column (InertCap Wax, GL Sciences, Tokyo) was used both in GC/MS and GC. The initial column temperature was 40 °C, which heated up to 220 °C at a rate of 10 °C /min. The detector of GC was flame ionization detector (FID) kept at 250 °C.

3. Results and discussion

3.1 Partial melting of cube ice

Figure 2A shows the effect of thawing temperature on melting rate of cube ice of 10 wt% sucrose at a constant stirring rate of 100 rpm. As the freezing point of 10 wt% sucrose is -0.625°C (Weast, 1974), the actual driving force for the melting ice is the environmental temperature, controlled by the coolant, plus 0.625°C . The thawing rate was very slow at 0°C and very fast at 10 or 20°C . In all the case, the thawing rate decreased with time because of the decrease in the driving force for ice-melting, which is affected by the freezing point of cube ice. The freezing point of the ice increases with time because of the selective elimination of solute during the thawing process. Figure 2B shows the effect of stirring speed on the melting rate of ice at a constant temperature of 2°C , which was chosen because of the too slow melting rate at 0°C . The melting rate of the ice increased with an increase in the stirring speed because of an increase in heat transfer to the ice phase from the jacket wall.

In Fig.3A, the effect of the thawing temperature is shown on the concentration change with time in the melted fractions. As was expected from the freezing-thawing principle, the initial fractions contain the higher solute concentration than the later fractions. This tendency was the most noticeable at 0°C while the difference among the fractions diminished at 20°C . This suggests that the slow thawing at the temperature close to the freezing point of the sample is desirable to obtain the higher concentration gradient with time for melted fractions. At 0°C , the sucrose concentration of the first melted fraction was 19 %, which was almost two times that of the original solution. This corresponds to the possibility for freeze concentration only by the freezing-thawing technique although the separation efficiency is not so high so that the multiple operations are necessary in practice (Aider and Halleux, 2008). Figure 3B shows the effect of stirring on the concentration gradient with time for melted fractions at a fixed temperature of 2°C . The gradient increased with an increase in the stirring speed but its effect was not so apparent as in the effect of temperature.

Figures 4A and B, respectively, show the effects of thawing temperature (stirring speed at 100 rpm) and stirring speed (thawing temperature at 2 °C) on the change in yield during the partial melting process. At the lower thawing temperature with the higher stirring speed, the discrepancy between the ice-melted fraction and the yield increased. For example, the yield of 64 % was obtained at the ice-melted fraction of 40 % in the partial ice-melting process at the thawing temperature of 0 °C and the stirring speed of 100 rpm (Fig.4A) showing the effectiveness of the partial ice-melting technique for the selective elution and enrichment of solute from the ice. On the contrary, the yield at the thawing temperature of 20°C was almost the same with the fraction of melted ice. This shows that too rapid thawing is not effective to obtain the concentration effect in partial ice-melting.

3.2 Yield improvement in progressive freeze-concentration by partial ice-melting

3.2.1 Apple juice

Although the partial ice-melting itself might be effective for the concentration of solute after freezing, this technique will be most effective if combined with PFC. Therefore, PFC of apple juice was carried out by the tubular ice system. As shown in Table 1, apple juice of 12.18 L was concentrated to 3.50 L (volumetric concentration ratio 3.48) and the concentration increased from 13.7 to 25.5 Brix. In this case, however, the °Brix-based yield was 63.8 % because of the solute inclusion in the ice, which contained solutes at 5.84 °Brix in average.

To improve the yield in PFC, the partial ice-melting apparatus was applied. A part of the ice (724 mL) formed in PFC of apple juice was broken into small pieces and was transferred into the partial ice-melting vessel operated at 0 °C with stirring speed at 100 rpm in consideration of the results in the partial melting of 10 wt% sucrose ice. As shown in Fig.5, the concentrations of solute in the initially melted fractions were higher than those

in the later fractions. By recovering the 30 % of initial melted fractions, the yield improved from 63.8 % up to 85 % and this could be improved up to 90 % if 50 % initial fractions were recovered. This shows the effectiveness of the partial ice-melting technique to improve the yield in PFC.

3.2.2 Pear (*La France*) juice flavor condensate

Pear juice (*La France*) flavor condensate is a by-product of the vacuum evaporation of pear juice so that this contains various flavors as shown in Fig.6 and could be applicable as a high quality source of natural fruits flavors. This is a solution with much lower osmotic pressure than apple juice so that the higher yield is theoretically expected in PFC (Gu et al., 2005; Gunathilake et al., 2013). PFC of pear juice flavor condensate was carried out by the tubular ice system. As shown in Table 2, 12.18 L of original solution was freeze-concentrated to 3.32 L (volumetric concentration ratio 3.67). Although the °Brix-based concentration was tentatively measured, this sample contains no sugars. Therefore, the concentrations after PFC was measured for the concentrate and the ice by the relative concentration, based on the original solution of butylacetate (peak 3 in Fig.6). The yield obtained in this way was 86.7 %, which is much higher than the case with apple juice. For this sample, the partial ice-melting was also applied. The result is shown in Fig.7. By recovering 35% of initially melted fraction, the yield improved up to 95 % through the partial ice melting with the temperature at 0 °C and the stirring speed at 100 rpm.

The major advantage of the partial ice-melting combined with PFC, compared with the simple freezing-thawing technique, is that the concentrate at a certain level is firstly obtained in PFC step then the yield is improved in the partial ice-melting step. The recovered fraction is not necessarily mixed with the concentrate but rather recommended to be mixed with the original solution for the next concentration operation to avoid dilution

of the concentrate. On the contrary, the dilution is inevitable in the freezing-thawing technique if the higher yield is necessary and the concentration level is not so high so that a multi-step operation is necessary to obtain the higher concentration level.

4. Conclusion

Ice cubes from 10% sucrose were partially melted in a small test apparatus for partial melting of ice at controlled conditions in temperature and stirring speed. At the lower temperature with relatively faster stirring speed, the initially-melted fractions contained the higher concentration of solute than the later-melted fractions. This initial enrichment effect of solute in the partial ice-melting could be applicable to the concentration of solutes in a solution in accordance with the principle of classical freezing-thawing technique. The partial ice-melting technique was effectively combined with PFC to improve the yield in PFC, in which a major drawback was the lower yield because of the solute inclusion in the ice, especially for a highly concentrated sample. Apple juice with 13.7 Brix was concentrated up to 25.5 Brix by PFC using a tubular ice system. Then, the partial ice-melting was applied for the ice formed by PFC to improve the yield from 63.8% to 85% by recovering the initial 30% melted fraction. The partial ice-melting was also applied to pear (La France) juice flavor condensate. After 2.36 times concentration of flavor component (butyl acetate) by PFC, the yield was improved from 86.7% to 95% by recovering the initial 35% melted fraction in the partial ice-melting process. The recovered fraction is not necessarily mixed with the concentrate but rather recommended to be mixed with the original solution for the next concentration operation to avoid dilution of the concentrate.

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Table 1 Progressive freeze-concentration of apple juice by tubular ice system

	Volume(L)	Concentration (°Brix)	Yield
Original solution	12.18	13.7	-
Concentrate	3.50	25.5	0.638
Ice	8.68	5.84	0.362
Conc. ratio	3.48	1.86	

Table 2 Progressive freeze-concentration of pear juice flavor condensate by tubular ice system

	Volume(L)	Concentration (°Brix)	Relative conc. of butylacetate	Yield
Original solution	12.18	1.0	1.0	-
Concentrate	3.32	2.7	2.36*	0.867
Ice	8.86	0.7	0.135*	0.133
Conc. ratio	3.67	2.7	2.36	

*) Relative value compared to original solution.

Legends for Figures

Fig. 1 A test apparatus for partial ice-melting.

Fig. 2 Effects of melting-temperature (A: stirring speed, 100rpm) and stirring speed (B: melting temperature, 2 °C) on melting volume of cube ice from 10 wt% sucrose.

Fig. 3 Effects of melting-temperature (A: stirring speed, 100rpm) and stirring speed (B: melting temperature, 2 °C).on concentration distribution among partially melted fractions of cube ice from 10% sucrose

Fig. 4 Dependence of yield-improvement effect on melting-temperature (A: stirring speed, 100rpm).and stirring speed (B: melting temperature, 2 °C) in partial melting of cube ice from 10% sucrose.

Fig. 5 Yield improvement based on °Brix by partial melting of ice formed in progressive freeze-concentration of apple juice (melting temperature, 0°C; stirring speed, 100rpm).

Fig. 6 Head space SPME chromatogram for pear (La France) juice flavor condensate.

Fig. 7 Yield improvement based on butylacetate by partial melting of ice formed in progressive freeze-concentration of pear (La France) juice flavor condensate (melting temperature, 0°C; stirring speed, 100rpm).

Fig.1

Fig.2A

Fig.2B

Fig.3A

Fig.3B

Fig.4A

Fig.4B

Fig.5

Fig.6

Fig.7