Progressive freeze-concentration: Improvement and applications

Osato Miyawaki

Department of Food Science, Ishikawa Prefectural University, 1-308 Nonoichi, Ishikawa 921-8836, Japan (osato@ishikawa-pu.ac.jp)

ABSTRACT

Progressive freeze-concentration (PFC) is a method, in which a single ice crystal is formed in the system to remove water from a solution. In this method, the system is much simpler as compared with the conventional method of suspension crystallization, in which many small ice crystals are formed. A small cylindrical test system for PFC was successfully applied for the high quality concentration of fruits (pear) flavour solution with high yields of flavour components. No incorporation of flavour components was observed into the ice phase. The concentration yields were compared among the three methods of concentration; evaporation, reverse osmosis, and PFC. PFC showed the highest concentration yield among the three. PFC was also applied for the concentration of apple, tomato, and water melon juices by using a tubular ice system for scale-up of PFC. In this case, some part of solute was incorporated into the ice phase because of the effect of high osmotic pressure of the samples used. The concentration yields for apple, tomato, and water melon juices were, 73.6, 91.2, and 80.3%, respectively, in about two-fold concentration process. In these cases, partial melting of ice after PFC was effective. By recovering the initial melt fractions with the higher solute concentration, the concentration yield could be improved to a necessary level.

Keywords: progressive freeze-concentration; partition coefficient; partial ice melting; concentration polarization theory; tubular ice system

INTRODUCTION

There are three methods for the concentration of liquid food: evaporation, reverse osmosis, and freeze concentration. Among these, freeze concentration is known to give the best quality [1]. The conventional method of freeze concentration is based on the suspension crystallization [2], in which many small ice crystals are formed. This system is very complex to require very high initial investment. On the contrary, the progressive freeze-concentration (PFC) is a method with a single ice crystal formed on the cooling plate. This method is expected to be much simpler in its system as compared with the conventional method based on the suspension crystallization.

In PFC, the partition coefficient of solute (K) between ice and liquid phase is very important. According to the concentration polarization theory, K was proved to be affected by the moving speed of ice front (u) and the mass transfer coefficient (k) at the ice-liquid interface [3]. At the infinitesimal u and/or the infinite k, the limiting partition coefficient, K_{lim}, is obtained. The K_{lim} was dependent on the osmotic pressure of the solution to be concentrated [4,5].

PFC is very flexible system and is applicable to various samples with wide ranged physical properties, even to emulsion and suspension. This is applicable not only to aqueous systems but also to nonaqueous systems. In its size, various systems are available from small cylindrical system to large tubular system [6]. This is operated in a repeated batch manner with 2-3 hr cycle so that a cleaning step is available between operation cycles.

In the present paper, PFC was applied for the high quality concentration of fruits (pear) flavour solution, apple juice, tomato juice, and water melon juice. When the osmotic pressure of the sample to be concentrated was low, a single step PFC was effective with a high concentration yield for solute components. When the osmotic pressure of the sample was high, some part of the solute was incorporated into the ice phase to reduce the yield. In this case, however, partial melting of ice was effective to improve the concentration yield.

MATERIALS & METHODS

Materials

A model solution of pear (La France) flavour components, apple juice, tomato juice, and water melon juice were used as samples to be concentrated.

Apparatus for progressive freeze-concentration

A test apparatus with a vertical cylindrical sample vessel (Fig. 1) was used for the small-scale PFC of 100 to 200 mL sample The sample vessel was plunged into a cooling bath (-15 ^{o}C) at a constant speed to control the ice crystal growth rate. The sample vessel was equipped with a stirrer to control the mass transfer at the ice-liquid interface. For the scale-up of PFC, a tubular ice system with 10 L scale was used (Fig.2). In this case, a circulation pump was used instead of stirring.

Evaporation and reverse osmosis

Rotary evaporator with reduced pressure operated at 50 ^{o}C and reverse osmosis system with a test vessel (C40-B, Nitto Denko) with a reverse osmosis membrane (NTR-70 SWC, Nitto Denko) were also used for the concentration of pear flavour solution.

Analytical method

The pear flavour solution was extracted with diethylether, which was analyzed chromatographically. For identification and quantification of the flavour components, GC/MS system (Focus DSQ 2, Thermo Fisher Scientific) and gas chromatograph (G-3900, Hitachi) were used with a capillary column (InertCap WAX, GL Science). In the concentration of apple juice, tomato juice, and water melon juice, the concentration in Brix was measured by a refractometer (APAL-1, Atago).

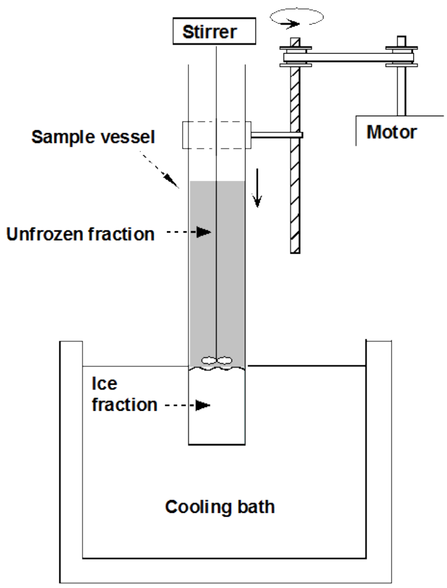

Figure 1. A small test apparatus for progressive freeze-concentration

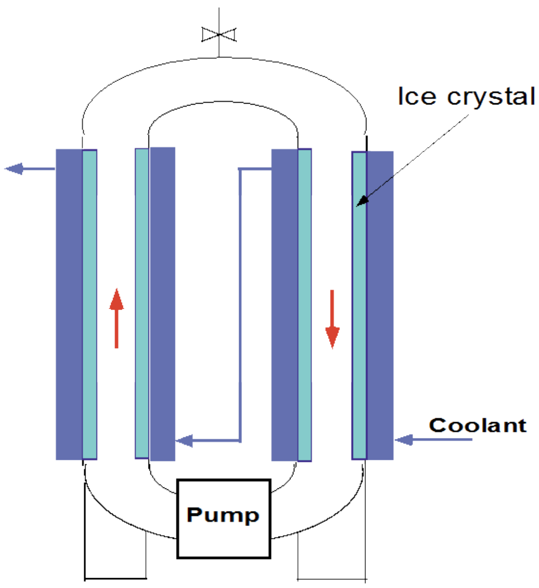

Figure 2. A tubular ice system for scale-up of progressive freeze-concentration.

RESULTS & DISCUSSION

Figure 3 shows a GC/MS chromatogram of the diethylether extract of the pear flavour model solution, which consisted of alcohols, aldehydes, and esters. In this chromatogram, methylbutanoate was an internal standard added. This solution was concentrated by about four-fold by the three concentration methods to compare the efficiency.

In Fig. 4, the concentration yields were compared for each flavour components among the three methods. The concentration yields for most flavour components in the evaporation method were less than 20% and those in the reverse osmosis were less than 60%. In PFC, the concentration yields for most flavours, except esters, were the highest among the three concentration methods to be 80 to 100%.

In the evaporation, most flavour components were lost in gas phase in the concentration process in spite of the reduced evaporation temperature down to 50 ^{o}C. In the reverse osmosis, the lost components were detected in the permeate although a tight RO membrane was used. In PFC, however, the lost components were not detected in the ice phase so that the lost components have been not incorporated into the ice phase. The relatively lower yields for esters might be related to the open-air structure of the cylindrical sample vessel with stirring.

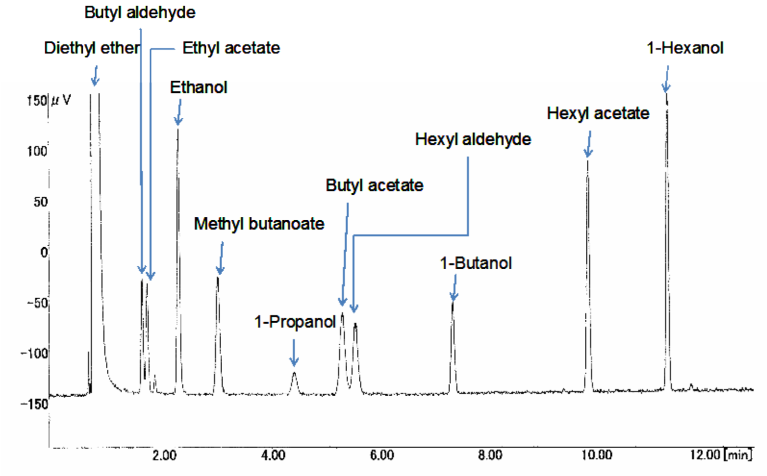

Figure 3. GC/MS chromatogram of pear flavour components.

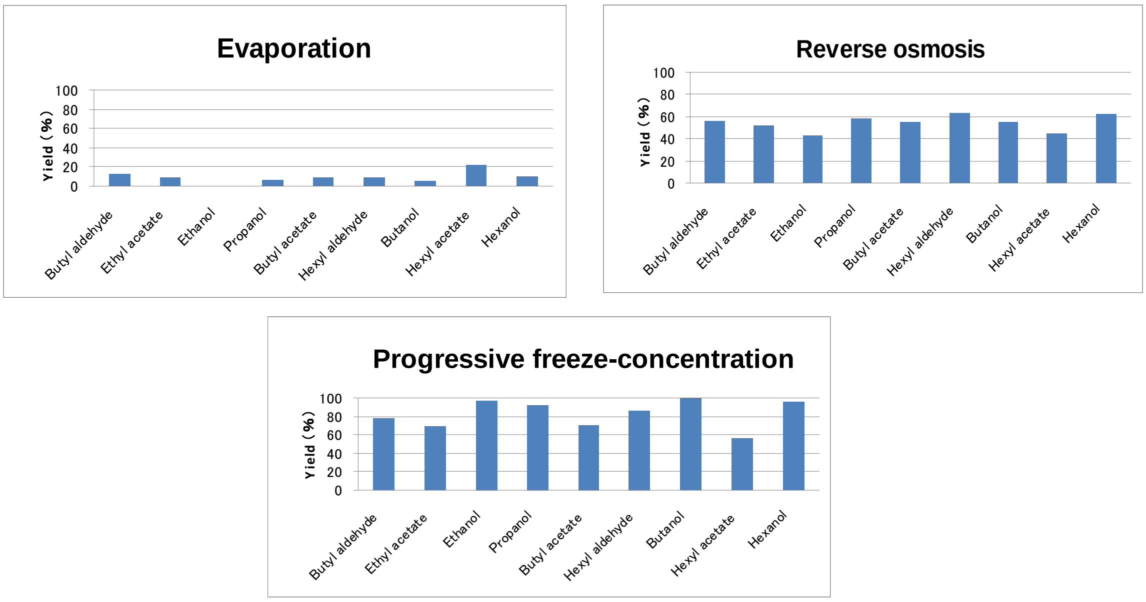

Figure 4. Comparison of concentration yield among the three methods for concentration of pear flavour components.

When the osmotic pressure of the solution was low, high concentration efficiency was obtained with a high yield by a single step PFC as shown above. With an increase in the osmotic pressure, however, concentration yield decreases because of the incorporation of solute components into the ice phase [4,5].

Apple juice, tomato juice, and water melon juice were freeze-concentrated by about two-fold by the tubular ice system. Results are summarized in Table 1. The concentration yield for apple, tomato, and water melon juices were 73.6, 91.2, and 80.3%, respectively. In these cases, the loss components were incorporated into the ice phase.

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

Sample		Volume (ml)	Concentration (Brix)	Yield (%)	Partition coefficient
Apple juice	Feed	10,000	12.1	100	
	Concentrate	4.101	21.3	73.6	
	Ice phase	5,899	5.3	26.4	0.249
Tomato juice	Feed	10,000	3.4	100	
	Concentrate	6,129	7.9	91.2	
	Ice phase	3,871	1.2	8.8	0.152
Water melon juice	Feed	10,000	9.2	100	
	Concentrate	4,194	18.1	80.3	
	Ice phase	5,806	3.2	19.7	0.177

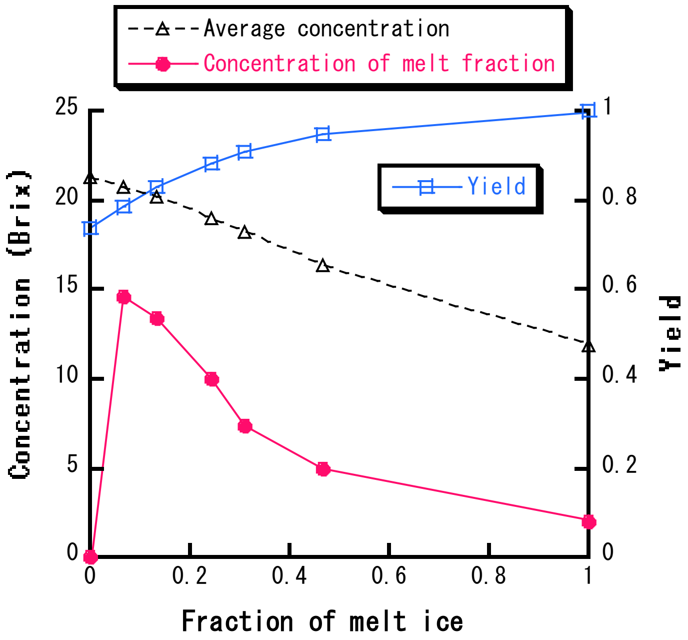

Figure 5. Partial melting of ice formed after progressive freeze-concentration of apple juice by tubular ice system.

The incorporation of solute into the ice phase has been supposed to be the weak point of PFC. To improve this, the partial melting of ice was applied. When the contaminated ice crystal was partially melted, the initial fractions of melt ice contained the higher amount of solutes. By recovering these concentrated fractions, the concentration yield of the process could be improved to a necessary level. According to this principle, partial melting of ice formed after the PFC of apple juice was carried out. Figure 5 shows the result. The concentration of the initial ice melt fractions were high and the concentration yield could be improved to 90% by recovering the initial 30% of the melt fractions. This shows the effectiveness of the partial melting of ice to improve the concentration yield in PFC.

CONCLUSION

PFC was proved to be effective for the concentration of solute for the solution with a low osmotic pressure. In this case, no incorporation of solute components into the ice phase was observed. For solutions with a high osmotic pressure, however, some part of solute components was incorporated into the ice phase to reduce the concentration yield. In this case, partial melting of ice was useful to improve the yield to a necessary level. The possible applications of PFC are summarized in Table 2.

Table 2. Possible application of progressive freeze-concentration.

１． High quality concentration of liquid food
Fruits and vegetable juice
Extracts of coffee, tea, seasoner, etc.
Milk products
２． Development of new food materials
Grape juice for ice-wine-like wine
Fruits juice flavors
Highly concentrate alcohol drinks
Concentration of proteins
３． Other applications
Freeze concentration crystallization
Waste water treatment with low temperature energy regenerator

REFERENCES

[1] Deshpande SS, Bolin HR, & Salunkhe DK. 1982. Freeze concentration of fruit juices. Food Technology, May, 68-82.

[2] Huige NJJ, & Thijssen HAC. 1972. Production of Large crystals by continuous ripening in a stirred tank. Journal of Crystal Growth, 13/14, 483-487.

[3] Miyawaki O., Liu L., & Nakamura K. 1998. Effective partition constant of solute between solid and liquid phases in progressive freeze-concentration. Journal of Food Science, 63(5), 756-758.

[4] Gu X., Suzuki T., & Miyawaki O. 2005. Limiting partition coefficient in progressive freeze-concentration, Journal of Food Science, 70(9), E-546-551.

[5] Gu X., Watanabe M., Suzuki T. & Miyawaki O. 2008. Limiting partition coefficient in tubular ice system for progressive freeze-concentration, Food Science and Technology Research, 14(3), 249-252.

[6] Miyawaki O., Liu L., Shirai Y., Sakashita S. & Kagitani K. 2005. Tubular ice system for scale-up of progressive freeze-concentration, Journal of Food Engineering, 69, 107-113.