DEVELOPMENT OF
PROGRESSIVE FREEZE-CONCENTRATION AS A NEW
METHOD FOR HIGH-QUALITY CONCENTRATION OF LIQUID
FOOD

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For the degree of Doctor of Bioresources and Environmental Science

Development of Progressive Freeze-concentration as a New Method for
High-Quality Concentration of Liquid Food

By

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INTRODUCTION

Liquid food concentration is a major unit operation in food industry. Concentration of liquid food removes a major part of water, which leads to increased microbial stability, reduction in bulk by weight and volume. The reduction of bulk weight and volume permits economy in packaging, transportation and distribution of the final product. On the other hand there is a growing demand for liquid food with high sensory and nutritional quality. Therefore liquid food concentration without deteriorating the original quality is a challenge as described below.

Mainly there are three liquid food concentration methods available. Those are evaporative concentration, membrane concentration and freeze concentration. Among these, the evaporative concentration is the oldest, best developed, and economically most favorable liquid concentration method which is widely used up to date. But the quality of the concentrated product by this method is very poor with loss of flavors and nutrients, colour degradation and a difference in taste due to thermal effects. Many developments have been made in this technology such as TASTE (Thermally accelerated short time evaporators), centrifugal evaporator, serum concentration process and process with aroma recovery to improve the quality of final concentrate product (Rameteke et al., 1993). However to this date this method produces concentrates with a lower quality compared to other concentration methods and easily distinguished from fresh juice.

Membrane concentration is a better alternative for evaporative concentration. The commonly used membrane method for removing water from liquid food is reverse osmosis (RO). Due to the possibility of operation at room temperature, this method causes lower thermal damage with increased aroma retention and requires less energy consumption. The limitations of this method are membrane fouling and difficulty in cleaning, frequent replacement of expensive membrane and inability to reach high concentrations like in evaporation because of osmotic pressure limitation. To improve the performance of RO, many research works have been carried out in membrane development and membrane configuration. In order to overcome the limitations of achieving high concentration levels, many new membrane processes such as direct osmosis, membrane distillation (MD) and osmotic distillation (OD) are at developing stage (Jiao et al., 2004). It has been reported that MD and OD could concentrate up to a 60% of dry matter. Another study reveals, orange and passion fruit juice were concentrated up to three-fold using OD pilot plant and the loss of flavor were about 32% and 39% respectively (Shaw et al., 2001).

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 unwanted chemical, physical and biological changes that happen in other types of processing. There are two types of freeze concentration methods available. They

are suspension crystallization and progressive freeze concentration (PFC) as shown in Fig1.A and Fig.1.B. In suspension freeze concentration liquids get concentrated by removing water by attaching water molecules into growing ice crystals which are suspended in solution to be concentrated. In PFC, water will be removed by attaching to them into a moving single ice front, which is in contact with the concentrating solution (Matthews and Coggeshall, 1959, Shapiro, 1961, Miyawaki et al., 1998).
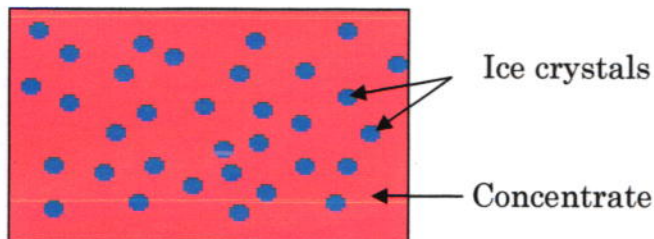
Fig 1.A Suspension Crystallization   Fig 1.B Progressive Freeze-Concentration
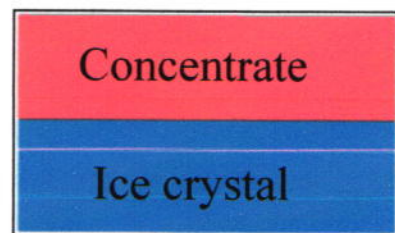
The commercially available freeze-concentration method is the suspension crystallization. This method requires a complicated system including surface-scraper heat-exchanger for making seed ice, re-crystallization vessel for ice crystal growth which happens by Ostwald ripening mechanism (Huige and Thijssen, 1972) and a washing tower for separating ice crystals from concentrated mother solution. Using this system, the final concentrations that could be obtained varies between 45 and 55 ° Bx with a pure ice crystals having a solute inclusion less than 100ppm (Sanchez et al., 2009). Despite of this performance, complexity of this system along with high capital cost has resulted in limited use of this method for liquid food concentration.

Due to the ease of separation of concentrated solution, PFC requires a simple system and a relatively cheap method than suspension crystallization. A falling film reactor has been developed for the scaling up of PFC (Fleshland, 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, ice crystal grows on a vertically placed cooling plate on which the solution to be concentrated flows as a falling film. The limited liquid flow rate on the cooling surface results in poor mass transfer between the ice and the liquid phases. Poor mass transfer rate will results in poor separation efficiency of the solute from ice phase as described in 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 compounds. Retention of flavor compounds is a major positive point in freeze concentration. 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 to increase the production scale of PFC which provides a good mass transfer and a controlled heat transfer in a closed, simple system (Miyawaki et al., 2005).This system is expected to give the higher separation efficiency and a high-quality for the concentrated products especially in the retention of volatile flavor compounds.

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The major drawback in PFC systems is the decrease in yield with an increase in the concentration of sample, due to the incorporation of solute into the ice phase. Many researchers have investigated on obtaining high concentrated fractions by controlled melting, thawing or sweating of solute incorporated ice (Nakagawa et al., 2010a, Nakagawa et al., 2010b, Moreno et al., 2014, Aider and Ounis, 2012, Aider and de Halleux, 2008, Moreno et al., 2013, Rich et al., 2012, Mandri et al., 2011, and Miyawaki et al., 2012). Vacuum assisted freeze concentration (Petzold et al., 2013) and centrifugal freeze concentration (Petzold and Aguilera, 2013) were explored as a one step configuration for separating concentrated solution from the ice matrix. Even though those laboratory scale experiments were possible for concentration of sucrose solutions, practical application for real liquid food could be complicated. The solute incorporated ice produced in PFC has partially melted under normal room temperature by Miyawaki et al., (2012). They have found that initial melted fractions have high concentrations and by recovering of those fractions, the total yield of the PFC can be favorably improved. Since samples with high solute concentrations give lower yields in PFC (Gu et al., 2005); partial melting of solute incorporated ice has been proposed as a method of improving total yield by solute recovery.

Table.1 Comparison of available concentration methods

Method	Driving Force	Energy consumption	Cost	Quality	Remarks
Evaporation	Heat	540 cal/g-w	Low	Low	Multiple operation
Reverse Osmosis	Pressure	~0	Medium	Intermediate	Membrane cost and maintenance
Freeze-concentration					
Suspension crystallization	Low temperature	80 cal/g-w	High	High	Continuous, large scale operation
Progressive freeze-concentration	Low temperature	80 cal/g-w	Medium	High	Batch operation, High flexibility

Table 1 shows the comparison among the available liquid food concentration methods in terms of driving force, energy consumption, cost and quality. Driving force for evaporation is supplying heat whereas that for freeze concentration is removing the heat. For reverse osmosis, supplying a pressure higher than the osmotic pressure is the driving force. Among them, to remove a 1g of water, evaporation consumes the highest energy while reverse osmosis consumes the minimal energy. Freeze concentrated products will have the best quality following reverse osmosis and evaporation. Due to the complexity of the suspension system, it is only available in large scale continuous operation. However progressive freeze-concentration unit is available as a batch operation, therefore it has a high flexibility for a range of operating scales.

The use of combination of two or more concentration techniques for concentration of liquid

food has given better results, than using single concentration technique. Specially there are many examples of integrated membrane processes which use combined membrane concentration methods where one membrane process improves the performance of the other one (Jiao et al., 2004). An integrated membrane process for producing apple juice and apple juice aroma concentrates was proposed by Alvarez et al. (2000). It consisted of integrated enzyme membrane reactor to clarify the raw juice, reverse osmosis to pre-concentrate the juice, pervaporation to recover and concentrate aroma compounds and with a final evaporation step to concentrate apple juice up to 72 brix. Cassano et al. (2003) proposed an integrated membrane process for the production of high quality fruit juices. In this process ultra-filteration process firstly separated the juice into the serum and pulp. And then the serum/clarified juice was concentrated up to 60 brix by using reverse osmosis and osmotic distillation. The pulp was added to the osmotic distilled concentrate after pasteurization. A similar system was also used by Galaverna et al. (2008) for the concentration of blood orange juice up to 60 brix. Melon juice was concentrated up to 55 brix by using microfilteration and osmotic evaporation along with enzymatic treatment as a pre treatment step (Vaillant et al., 2005). In future depending on the characteristics of the liquid food, tubular ice system could be used as a progressive freeze-concentration stage in integrated concentration process.

The objective of this study is to develop progressive freeze-concentration method as a practical method for the concentration of liquid food with high quality. This is the least developed method among the other concentration methods which needs more examination for its actual applications. It`s simple operation along with the flexibility are promising features of this method as a commercial scale high quality liquid food concentration method.

The structure of the thesis is as follows. In Chapter 1 the theoretical considerations in PFC is explained. The relevance of theoretically derived equations with the experimental results in ice phase solute distribution is presented in the same chapter. Chapter 2 is about the development of tubular ice system for scale-up of PFC. Details about the design and operation along with the improvements done in existing tubular system is described. Yield improvement by partial melting of solute incorporated ice and the design of the new partial melting vessel are present in the Chapter 3. Evaluation of flavor components retention in three types of concentration methods and ability of maintaining same flavor profile after concentrate-reduction up to original concentration are discussed in Chapter 4. Chapter 5 is about the details of new products that are developed using progressive freeze-concentration.

CHAPTER 1

THEORETICAL CONSIDERATIONS IN PROGRESSIVE FREEZE CONCENTRATION

1.1 Introduction

In progressive freeze-concentration, the solute in mother solution is separated at the ice-liquid interface. The solute inclusion in ice phase adversely affects the efficiency of the concentration process. The degree of solute inclusion is explained by effective partition coefficient which is strongly dependent on the ice growth rate and the mass transfer at the ice liquid interface. To analyze the effect of operating conditions on separation efficiency, a concentration polarization model has been successfully applied (Miyawaki et al., 1998). According to this model, the limiting partition coefficient of solute at the ice-liquid interface has been found to be an important design parameter in progressive freeze-concentration (Pradistsuwana et al., 2003)

Lab scale cylindrical test apparatus was used for progressive freeze-concentration of sucrose solutions under different operating conditions. From the concentration polarization model the limiting partition coefficient for each initial sucrose concentrations were found. Another set of experiments were performed using the same apparatus with sucrose solutions and the ice formed in the process was cut in to 3 equal parts. The amount of solute inclusion in each ice fraction was measured and the liquid volume and concentration which was in equilibrium with each ice fraction was calculated. From these data and using the theoretically derived equation, the effective partition coefficients for each sucrose concentrations were calculated.

1.2 Theory

The effective partition coefficient of solute between the ice and liquid phase in progressive freeze concentration was measured using Eq.1 (Liu et al., 1997).

$$K = C_s / C_L \qquad\qquad (1.1)$$

where, C_s and C_L are solute concentrations in ice and bulk liquid phase, respectively.

Fig.1.1 describes the concentration polarization model, which happens at the moving ice front in progressive freeze-concentration. As the ice phase grows at a speed of u into the liquid phase, a solute flux of uCs from the liquid to solid phase exists when the x-axis is fixed on the ice front to the solid phase. There is a solute repulsion from the forming ice crystal which form by pure water and only part of pure solute get entrapped in between forming dendritic ice structure (Watanabe et al., 2013). Due to this action the solute concentration at the very interface between ice and liquid is higher than that in bulk solution.
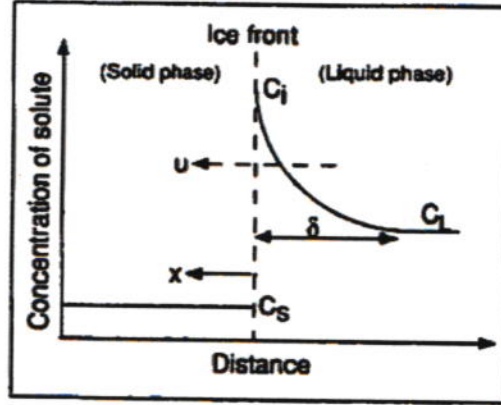
Fig.1.1 Concentration polarization at the ice front of progressive freeze-concentration

According to the concentration polarization model, the following equation is obtained from the mass balance equation of solute in the boundary layer near the ice-liquid interface in the solution phase (Miyawaki *et al.*, 1998),

$$-D(dC/dx) + uC = uC_S \qquad (1.2)$$

Where D is the diffusion coefficient of solute, C is the solute concentration in the boundary layer, and u is the advance rate of ice front.

Eq.(1.2) is combined with the following boundary conditions.

$C = C_i$ at $x = 0$ (in the liquid phase)

$C = C_L$ at $x = -\delta$

And after integration gives,

$$ln[(C_i - C_S)/(C_L - C_S)] = u\delta/D \qquad (1.3)$$

The limiting partition coefficient of solute between ice and liquid phase at the ice liquid interface is defined as follows.

$$K_0 = C_s/C_i \qquad (1.4)$$

where C_i is the solute concentration in the solution phase at the very interface between ice and liquid.

From Eq.(1.1), (1.3) and (1.4) the following equation can be derived for the effective partition coefficient.

$$K = K_0 / [K_0 + (1 - K_0) \exp(-u/k)] \qquad (1.5)$$

Where k is the mass transfer coefficient at the boundary layer defined by

$$k = D/\delta \qquad (1.6)$$

The mass transfer coefficient is expected to be related to the stirring speed N, by the following equation (Miyawaki *et al.*, 1998),

$$k = aN^{0.2} \qquad (1.7)$$

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Finally combining these relationships and mathematical simplification along with the experimental data, Eq. 1.5 can be arranged as follows (Pradistsuwana et al., 2003).

$$ln(1/K - 1) = ln(1/K_0 - 1) - (1/a)(u/N^{0.2})$$ (1.8)

According to Eq. 1.8, a linear dependence of $ln(1/K-1)$ is expected with $u/N^{0.2}$. The limiting partition coefficient, K_0 can be obtained from the extrapolation of the linear plot to $u/N^{0.2} \to 0$, which corresponds the infinitesimal ice growth rate and/or the infinite mass transfer rate at the ice-liquid interface (Gu $et\ al.$, 2005).

The following equation is obtained from the mass balance of the solute, at the moment when the solution volume is V_L in the process of freeze-concentration (Liu $et\ al.$, 1997).

$$C_L V_L = -C_S dV_L + (C_L + dC_L)(V_L + dV_L)$$ (1.9)

From Eq.1 and Eq.2:

$$(dC_L/C_L)/(dV_L/V_L) = K - 1$$ (1.10)

When the effective partition coefficient, K is constant during the concentration process, Eq. 1.10 can be integrated and get following equation:

$$(1-K)\ ln(V_L/V_0) = ln(C_0/C_L)$$ (1.11)

Where, V_0 and C_0 are initial volume of Solution and initial solute concentration in the liquid phase. Then Eq. 1.11 can be rearranged as follows:

$$C_L/C_0 = (V_L/V_0)^{K-1}$$ (1.12)

From Eq.1.1 and Eq. 1.12, the following expression can be obtained.

$$C_S/C_0 = K\ (V_0/V_L)^{1-K}$$ (1.13)

According to this, from the ratios of C_S/C_0 and V_0/V_L, the effective partition coefficient K, which is constant throughout the process of progressive freeze concentration, can be found.

1.3 Experimental method

As shown in Figure 1.2, a small cylindrical test apparatus was used for the progressive freeze concentration (Gu $et\ al.$, 2005). Two types of cylindrical sample vessels were used in this study. One vessel consist of a plastic side with a stainless steel bottom (49mm dia, 168mm height, 3mm thick) and the other one is a fully stainless steel vessel (47mm dia, 198mm height, 1.4mm thick). The vessel was plunged into a cooling bath (BB 400, Yamato Scientific, Tokyo, Japan) at a constant speed. The advance rate of ice front was calculated from the thickness of ice and the duration of the time of the experiment. The sample vessel was equipped with a stirrer (SM-102, As One, Osaka, Japan) and a 4- blade propeller (4cm in diameter) for stirring the solution at the ice liquid interface.

Sucrose solutions of various concentrations were used as samples to be concentrated. Sucrose was obtained from Kanto Chemicals (Tokyo, Japan). The concentration of sucrose solutions was determined using a refractometer (APAL-1, AS ONE, Japan).

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Sucrose solutions with concentration of 3%, 10%, 20% and 30% were progressive freeze concentrated using the stainless steel vessel. Pure water of 1ml was added to the bottom of the vessel to provide seed ice crystals to stop initial super cooling. The sample volume was 150ml in all the experiments. A fully stainless steel vessel used because effective heat transfer from the side surface is necessary to ensure a constant ice crystal growth rate during long time operation. Before being added to the vessel, the sample solution was precooled to the freezing point to prevent melting of seed ice. All experiments were carried out with stirring speed of 1000 rpm at the ice-liquid interface and a moving speed of ice front of 1cm/hr for 5h. The cooling bath temperature was -20 ° C for all the solutions, except for the 3% solution sample, for which the cooling bath temperature was -15 ° C. After concentration experiment, the single ice crystal formed was separated from concentrated solution and was cut by a saw in to three fractions of roughly equal amount. The volumes and the concentration of solute in three ice fractions and concentrated solution were measured after melting the ice.
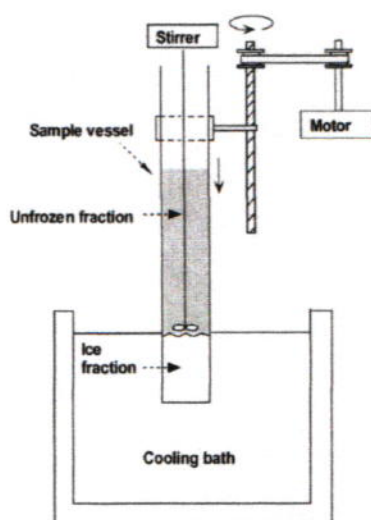
Fig. 1.2 Small cylindrical test apparatus for progressive freeze-concentration

Sucrose solutions of 5%, 15% and 25% concentrations were progressive freeze concentrated at various operating conditions using the plastic sample vessel. In this vessel, the heat transfer from the side surface is negligible, so a strict uni-dimensional ice crystal growth was expected. The stirring rate at the ice liquid interface was varied from 300rpm to 1300rpm. The moving speed of ice front was varied from 0.35cm/hr to 2.0cm/hr. The cooling bath temperature was set at -15 ° C for all the moving speeds and for lowest moving speed which was 0.35cm/hr, experiments were repeated for cooling bath temperature of -10 ° C . Before starting the freeze concentration experiment, 1ml of pure water was added to the bottom of the vessel to provide seed ice crystals to prevent initial super cooling (Liu et al., 1997). The sample solution of 150 ml was precooled to the freezing point in order to avoid melting of seed ice crystal before it transfers into the sample vessel. The concentration processes were continued until 1cm thick ice crystal was formed in the sample vessel, then the concentrated solution was separated and ice layer was allowed to melt. The volume and the sucrose concentrations of melted ice and concentrated solution were

measured and the exact thickness of the ice crystal was determined from the volume of the melted ice.

1.4 Progressive freeze-concentration of sucrose solutions and analysis of solute distribution in ice phase

Progressive freeze-concentration of various sucrose solutions was carried out with the same operating conditions of ice crystal growth rate at 1cm/h and stirring rate at 1000rpm.

Table 1.1 summarizes the results. In the freeze concentration process with volumetric concentration ratios, V_0/V_L, between 2.5 to 3.5, concentration ratios, C_L/C_0, of 1.5 to 2.9 were obtained. In this table, total volume of ice formed and concentrated liquid is little lower than that of initial solution mainly because of the loss in the ice cutting process. When the initial sucrose concentration was 3%, a concentrated solution of 8.7% was obtained with a yield of 82.2%. With an increase in solute concentration, the yield decreased to 58.6% for the 30% sucrose solution, although the final concentration for this solution was as high as 45%.

<p align="center">Table 1.1 Progressive freeze-concentrations of sucrose solutions</p>

Initial solute conc. C_0(wt%)	Final volume V_L(ml)	Volume ratio V_0/V_L	Final liq. conc. C_L(wt%)	Conc. ratio C_0/C_L	Total ice volume V_S(ml)	Conc. in ice phase C_S(wt%)	Yield (%)
3	42.5	3.53	8.7	2.9	99.2	0.745	82.2
10	54.5	2.75	20.2	2.02	89.0	3.66	73.4
20	61	2.46	32.2	1.61	85.2	10.82	65.5
30	59	2.54	44.7	1.49	88.8	18.93	58.6

*) Initial volume of solution before freeze concentration, V_0, was kept constant at 150 ml.

Table 1.2 shows how the solute concentration varies in the ice phase during the concentration process. The bottom fraction of the ice represents the initial ice fraction formed at the beginning of the concentration process, the middle fraction represents the middle stage of the concentration and the top ice fraction represents the last stage of concentration. With the progress in the concentration process, the solute concentration in the liquid phase increases from the bottom to the top, and the amount of solution incorporated into the solid ice phase increases gradually. This causes a higher solute concentration in the top ice fraction compared with the bottom fraction.

From the concentration and the volume of each ice fraction, the solute concentration in the solution phase, C_L, at the end of ice crystal growth of each ice fraction can be calculated by the mass balance equation. Thus C_L/C_0 was obtained and compared with V_0/V_L according to Eq.1.13. Figure 1.3 shows the results. Straight lines are obtained in the log-log plot between C_L/C_0 and V_0/V_L. This was rather unexpected because the effective partition constant, K, was supposed to increase experimentally with the

concentration process although constancy was assumed in the derivation of Eq.1.13. The limiting partition coefficient, K_0, is solute-concentration dependent (Gu *et al.*, 2005) so that K is also concentration-dependent according to the concentration polarization theory (Miyawaki *et al.*, 1998). Therefore, the plot in Fig.1.3 was expected to be a curved line but straight lines were obtained for each condition. From the slope of the plot in Fig.1.3, K values were obtained to be 0.150, 0.270, 0.437, 0.521 for 3%, 10%, 20%, 30% sucrose solutions, respectively.

Table 1.2 Concentration distribution of solute in solid phase in progressive freeze-concentration

C_0(wt%)	V_S(ml)	Ice location	Volume of ice fraction (ml)	C_S(wt%)
3	99.15	Bottom	34.5	0.310
		Middle	38.4	0.620
		Top	26.3	1.24
10	88.95	Bottom	37.9	2.83
		Middle	27.1	3.25
		Top	24.0	5.45
20	85.2	Bottom	34.1	8.39
		Middle	28.2	10.79
		Top	22.9	14.48
30	88.8	Bottom	25.8	15.85
		Middle	31.8	17.47
		Top	31.2	22.96
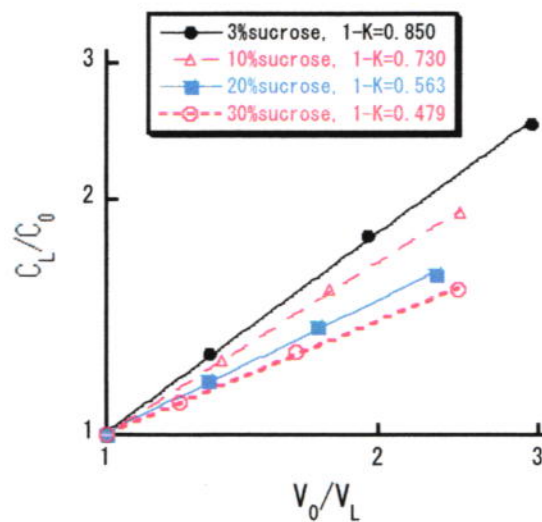
Fig.1.3 Concentration process in progressive freeze-concentration of sucrose solutions as determined by solid phase analysis

1.5 Limiting and effective partition coefficient by concentration polarization model

The effective partition coefficient, K, was experimentally measured for 5%, 15% and 25% sucrose solutions by forming a small amount of ice crystal for different combinations of ice growth rates, u and stirring rates, N. From Eq.1.8, a linear relationship is expected between $u/N^{0.2}$ and $ln(1/K-1)$. Figure 1.4 shows the results for a 5% sucrose solution. Although data are little scattering mainly because of the difficulty in controlling the clearance between the stirrer and the ice surface, a linear line was obtained statistically. Extrapolation of this linear line to $u/N^{0.2} \rightarrow 0$ allowed the limiting partition coefficient, K_0, to be obtained. Thus obtained K_0 values were 0.131, 0.227, 0.363, respectively, for 5%, 15%, and 25% sucrose solutions (Table 1.3). In a previous study, K_0 has been obtained for various salt solutions and was found to correlate well to the osmotic pressure of the solutions (Gu *et al.*, 2005). In Table 1.3, the osmotic pressure is shown so that K_0 values obtained here are compared with the literature value for salts. Then it turned out that K_0 values obtained for sucrose are much higher than those for salts. There are many differences between salts and sugars in molecular structure, size, and charge, which might have caused the difference in the affinity between solute and ice. In the literature, the difference in K_0 between salts and glucose has been discussed (Gu *et al.*, 2005).

From the limiting partition coefficient, K_0, obtained, the effective partition coefficient, K, was calculated by using Eq.1.5 and Eq.1.7. As shown in Table 1.3, both K and K_0 increased with an increase in solute concentration. However, there was a difference between K and K_0 with the former being much larger than the latter. This reflects the limiting effect of the operating conditions of the advance rate of ice front and the stirring rate on K.
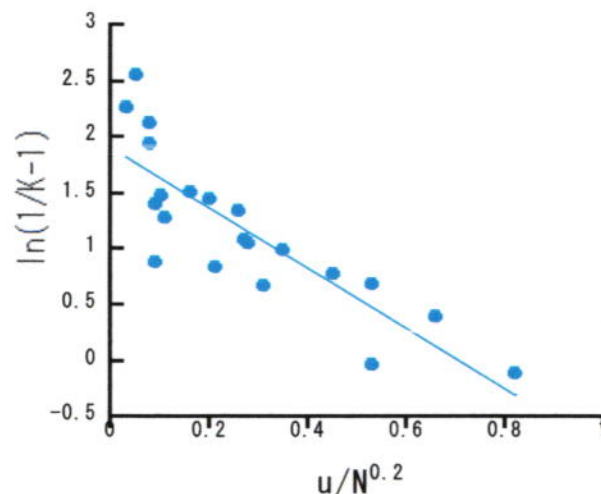
Fig.1.4 Determination of limiting partition coefficient in progressive freeze-concentration for 5% sucrose solution

Table 1.3 Limiting partition coefficients for sucrose in progressive freeze-concentration

Sucrose conc. (wt %)	Limiting Partition Coeff. (K_0)	Parameter a in Eq.(7)	Correlation coefficient	Effective partition coeff. (K)	Osmotic pressure (MPa)	K_0 for salts[*]
5%	0.131	0.372	0.845	0.228	0.388	0.02
15%	0.227	0.350	0.812	0.376	1.36	0.09
25%	0.363	0.457	0.695	0.497	2.69	0.16

*) Estimated from   Gu *et al.*(2005).

1.6 Comparison of effective partition coefficients obtained from ice-phase analysis and concentration polarization model

The effective partition coefficient, K, is practically very important because this parameter determines the amount of solute to be incorporated into the ice phase, which directly affects the yield in progressive freeze-concentration. The K values obtained from the ice phase analysis and the concentration polarization theory are compared in Fig.1.5 showing a good agreement between the two. The K from the ice phase analysis is an average value in the freeze-concentration process so that this was expected to be higher than that from the concentration polarization theory in principle. In practice, however, a good agreement was observed between the two.
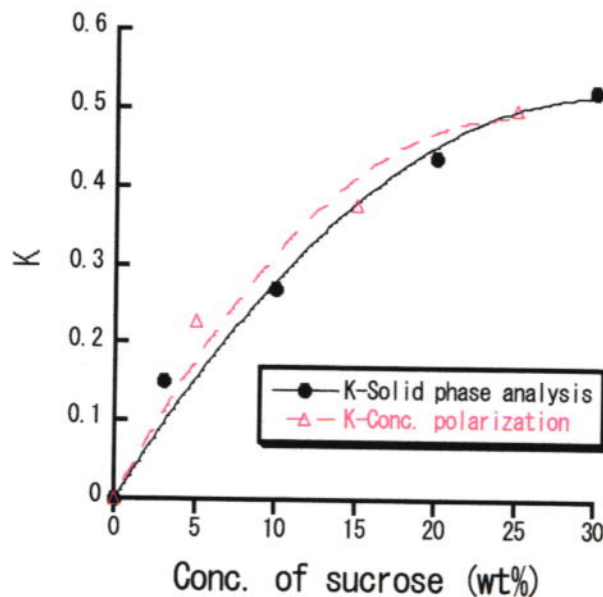
Fig.1.5. Comparison of effective partition coefficients determined from ice phase analysis and concentration polarization theory in progressive freeze-concentration of sucrose solution.

1.7 Conclusions

Solute distribution analysis of the ice phase was effectively carried out for progressive freeze-concentration of sucrose solutions with concentration varied from 3% to 30%. The solute concentration in the ice phase was shown to increase with the progress in the concentration process. From the solute concentration in the solid phase, the corresponding liquid phase concentration in the concentration process was calculated. From this, an effective partition coefficient, K, was obtained for progressive freeze-concentration. The K was assumed to be constant during the concentration process, which was proved experimentally.

K was also obtained from the concentration polarization model. To this purpose, the limiting partition coefficient, K_0, was obtained by measuring K at various operating conditions of the advance rate of ice front and the stirring rate. The K_0 obtained for sucrose was much higher than those for salts in the literature. K was also determined from concentration polarization theory. Thus obtained K agreed well with that obtained from the ice phase analysis. K values from the two methods increased with an increase in solute concentration of sucrose, which corresponds to the higher incorporation rate of solute into the ice phase in progressive freeze-concentration.

CHAPTER 2

SCALE UP OF PRGRESSIVE FREEZE-CONCENTRATION BY TUBULAR ICE SYSTEM

2.1 Introduction

Beside the advantages of progressive freeze-concentration over suspension freeze-concentration, progressive freeze-concentration has not yet developed up to commercial scale applications. A falling film reactor has developed as a scale up system for progressive freeze-concentration (Fleshland, 1995). However it's design provides poor mass transfer between the ice and liquid while having free space which could leads loss of volatile components. A closed tubular ice system with circulating flow was developed as a closed system which provides good mass transfer efficiency between ice and liquid (Miyawaki et al., 2005).

This tubular ice system was used to concentrate variety of liquid food. The operating conditions were adjusted according to the osmotic pressure of the solution and final required concentration level of the liquid food. The effectiveness and efficiency of concentration have assessed for solutions with low osmotic pressure, medium osmotic pressure and high osmotic pressure.

2.2 Batch type tubular ice system with circulating flow
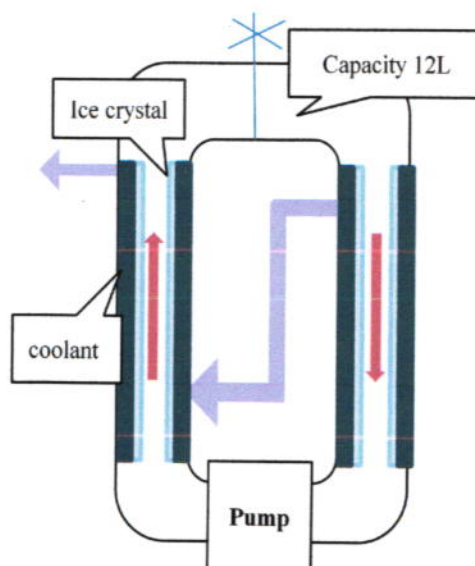
Fig 2.1 Schematic diagram of tubular ice system

Fig 2.1 shows the schematic diagram of the tubular ice system with circulating flow (MFC-10, Mayekawa, Tokyo). This system was composed of jacketed straight cylindrical tube (59.5 mm in diameter,

1800 mm x2 in length), bent tubes at the top and the bottom, 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 straight tube to cool down the tube to form ice layer inside. The total capacity of this system can be easily increased by increasing surface area by adding more tubes into the system. The system has designed with a minimum length of bent tubes, so that heat transfer from the environment is minimized. The connection between the straight and bent tubes part can be detachable to take out tubular ice crystal formed inside the straight tubes (Fig 2.2).
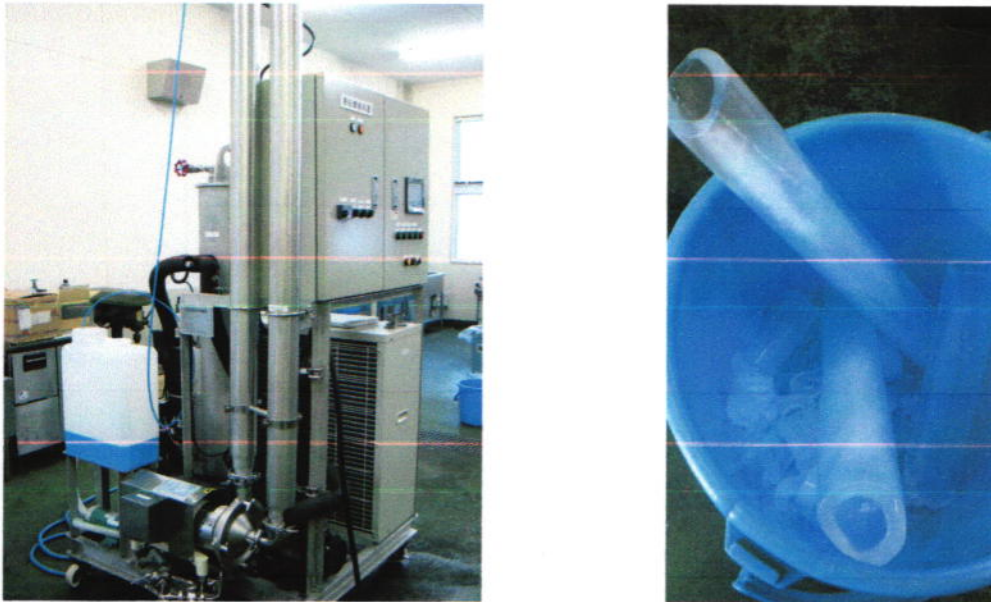
Fig 2.2 Tubular ice system (left) and the ice produced in the system (right)

2.3 Operational procedure of the tubular ice system

The operational procedure of the tubular system mainly depends on the initial osmotic pressure of the liquid food that used to concentrate. For solution with high osmotic pressure with high freezing point depression, the effect of super-cooling leads to high solute incorporated ice and poor concentration. However for solutions with low osmotic pressure the effect of super-cooling is not significant. Therefore, for high osmotic pressure solutions, before starting freeze concentration, pure water was introduced into the system by a feed pump to form a seed ice lining on the cooling surface. The volume inflation of 8.5% happens during the phase change of liquid phase to solid phase forming ice in progressive freeze-concentration. At the top of the system there was a small drain connected to a fine tube, through which the increased water volume flow out from the system. The volume of formed ice can be estimated from this overflow volume of water. After the formation of seed ice lining, the pure water initially introduced was removed and the system was filled with a sample solution to start progressive freeze-concentration. When seed ice lining was used, the sample solution must precooled close to the freezing temperature before being introduced into the system to avoid melting of the seed ice crystal.

For effective concentration, ice crystal growth should happen at a slow rate with a possible high mass transfer rate (Gu et al., 2008). The temperature program of the coolant and the circulation rate inside the tube change accordingly during the concentration. The circulation rate was controlled by changing the pumping speed. Initially there was a relatively bigger surface area available for liquid flow rate inside the tubes and efficient heat transfer from the cooling surface due to direct contact or through a thin seed ice layer. Therefore generally at the begging high circulation flow rate (higher pumping speed) and a relatively low surface cooling temperature were employed. With the progress in freeze-concentration, the ice layer thickness gradually increases while reducing the available cross sectional area for liquid flow. On the other hand ice crystal is not a good heat conductor to remove heat from the liquid during ice formation and freezing point depression also increases with the increase in concentration. Therefore the circulation speed should be gradually reduced while gradually increasing the cooling rate with the progress of freeze-concentration. After the concentration process, concentrated solution was removed from a bottom valve, and the jacketed tubes started to heat up to remove the ice crystal formed inside the tubes.

2.4 Applications of tubular ice system for concentration of liquid foods

Tubular ice system was used for concentration of a variety of liquid food. Mainly they can be categorized according to their initial osmotic pressure as low osmotic pressure solutions, medium osmotic pressure solutions and high osmotic pressure solutions (Table 2.1). To decide the suitable operating condition for tubular system, it is important to measure the freezing point depression of these solutions.

2.4.1 Freezing point depression measurement

The freezing point depressions of the solutions were measured from the melting curve (Miyawaki et al., 1997). About 3ml of sample was places in a plastic tube (15mm in diameter) which was equipped inside with a thermister (0.01 $°$ C in accuracy), was frozen completely at -20 $°$ C and then warmed at room temperature. The sample tube was stirred with a vortex mixer and the change in the temperature of the sample was recorded. The temperature which takes considerable time (than usual) for temperature increase was recorded as freezing point of the sample. By using freezing point (T) value corresponding water activity (A_w) was found using Hildebrand and Scott's equation (2.1) and then the corresponding osmotic pressure (π) of the solution was calculated by substituting water activity in equation (2.2).

$$ln\, A_w = -\Delta H_f(T_fT)/RT_fT + \Delta C_f/R\{[(T_f-T)/T]\, ln\, (T_f/T)\} \qquad (2.1)$$

Where, ΔH_f– latent heat of water

T_f– freezing point of water

ΔC_f– change of specific heat of water

R – gas constant

$$\pi = - RT/V_w \ln A_w \qquad\qquad (2.2)$$

Where, R – gas constant

T – Room temperature

V_w – molar volume of water

The liquid solutions used for concentration in tubular ice system and their freezing points with corresponding osmotic pressures are shown in Table 2.1.

Table 2.1 Freezing point and osmotic pressure of solutions

	Name	Freezing point (°C)	Osmotic pressure (atm)
Low osmotic pressure solutions	Peach condensate	-0.054	0.710258
	Pear (La-France) condensate	-0.04	0.526114
	Kaga stem tea	-0.04	0.526114
Medium osmotic pressure solutions	Apple juice	-1.518	19.97891
	Watermelon juice	-0.799	10.51262
High osmotic pressure solutions	Apple syrup	-3.885	51.18349
	Sake (Genshu)	-8.373	110.5139

2.4.2 Temperature and pumping speed program

Fig. 2.3 shows the temperature programs used in tubular ice system for concentration of the liquid food solutions presented in Table 2.1. Low osmotic pressure solutions which have the lowest freezing point depressions were operated at a temperature range about 0 ° C to -20 ° C. The freezing point of these solutions were around 0 ° C. At this temperature, the effect of super-cooling was not so strong for making impure ice crystals. Therefore, seed ice lining was not prepared before concentration of the solutions. The medium osmotic pressure solutions were operated at a temperature range about -5 ° C to -25 ° C. Their freezing points were about -1 ° C, and the effect of super-cooling might have an influence for making impure ice. Therefore, seed ice lining was used. Sake (Genshu) was the solution with the highest freezing point depression (-8 ° C) and the osmotic pressure was as high as 110.5 atm. The most severe cooling program (about -10 ° C to -35 ° C) was used in this case along with a good seed ice lining.

Fig 2.3, Fig 2.4 and Fig 2.5 show the temperature and pumping speed program for a low osmotic pressure solution (Kaga stem tea), medium osmotic pressure solution (Watermelon juice) and high osmotic pressure solution (Sake-Genshu). For formation of ice crystal in progressive freeze-concentration, speed of circulation of solution is also an important factor along with the temperature program. It is required to provide a good mass transfer between liquid and ice phase while allowing the ice crystal growth at a acceptable purity, since the concentration proceed with the ice crystal

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growth. If the requirement is to obtain a high concentration level, beside the ice purity, speed of circulation should slow down allowing ice crystal growth. For Kaga stem tea and watermelon juice, with which initial ice lining were not applied, concentration started at a relatively lower speed (35Hz and 40Hz) since high pumping speed delays the initial ice crystal growth. Ice crystal formation can be observed by observing the overflow solution from the tubular system. Once initial ice was formed pump speed increases up to 45Hz and then gradually decreased with the progress of concentration. Such an initial slow pumping was not used in high osmotic pressure solution, since the seed ice lining was used initially and concentration progresses by growing ice. However, for Sake (Genshu), due to its very high freezing point depression (-8 ° C) it was difficult to make ice even the seed ice lining was used. Therefore, it was operated at mild pumping speeds (35Hz -20Hz) compared to other solutions.
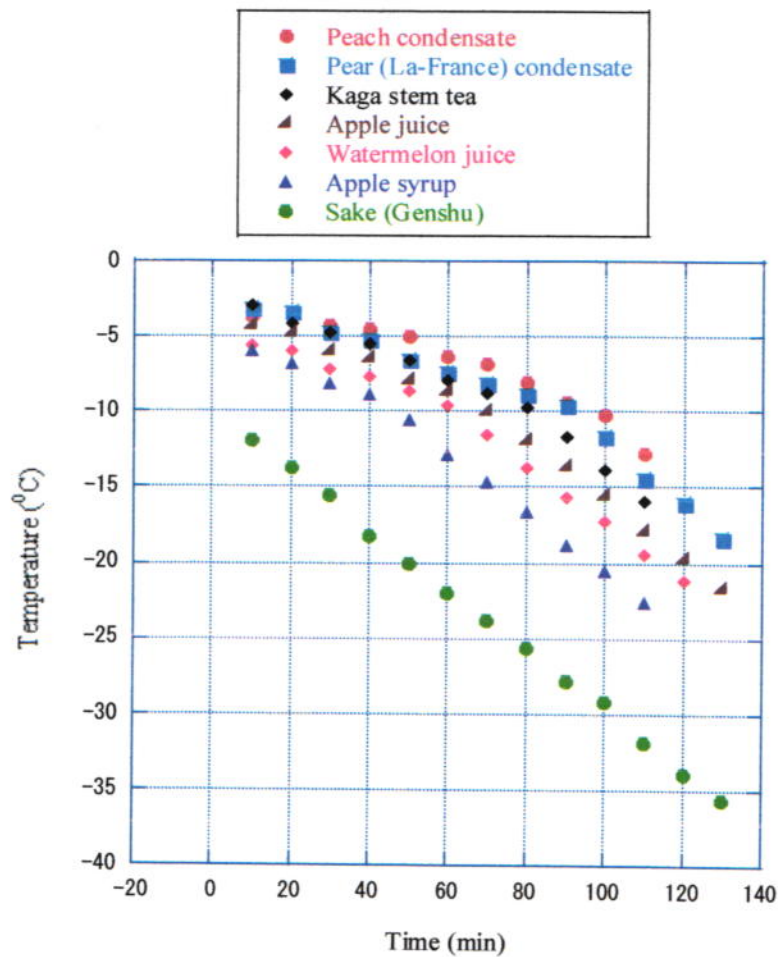
Fig. 2.3 Temperature program of tubular ice system for variety of liquid foods
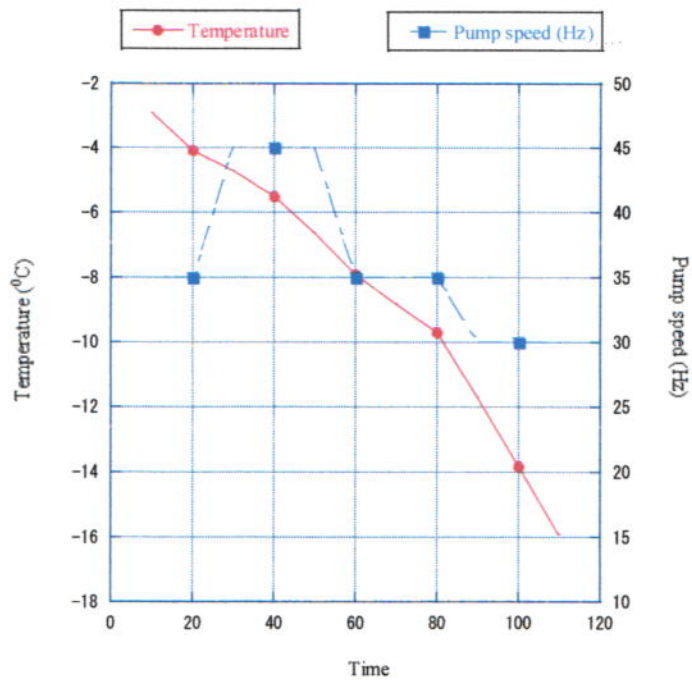
Fig 2.4 Temperature and pumping speed program for Kaga stem Tea
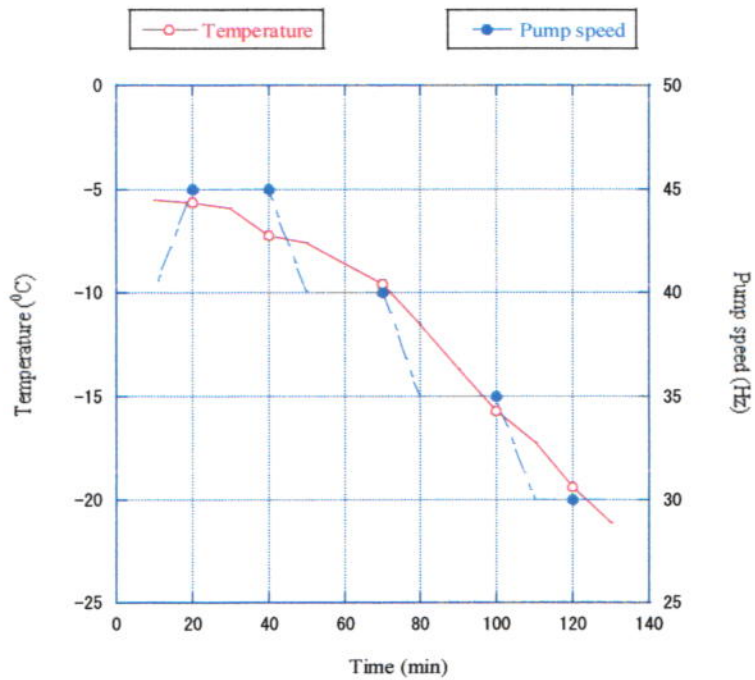
Fig 2.5 Temperature and pumping speed program for watermelon juice

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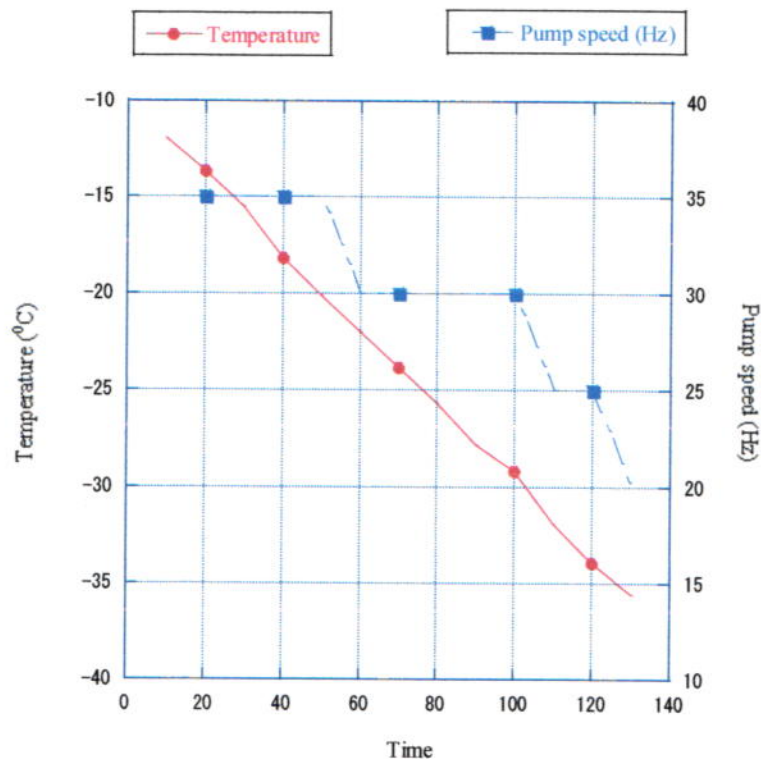
Fig 2.6 Temperature and pumping speed program for sake (Genshu)

2.4.3 Concentration of Kaga stem tea, watermelon juice and sake (Genshu) by tubular ice system

Table 2.2 shows the results obtained for the concentration of Kaga stem tea, watermelon juice and Sake (Genshu). As it was inaccurate to evaluate concentration of Kaga stem tea based on brix value, concentration was evaluated based on absorbance at 271nm. Kaga stem tea was efficiently concentrated achieving a highest yield of 93%. This means that this concentration method was very effective for concentration of low osmotic pressure solutions. Watermelon was concentrated from initial brix value of 8.3% to final brix value of 19.1% with a yield of 65%. Despite of the relative low yield, watermelon juice was concentrated by 2.3 times (based on brix) preserving the original color quality of the juice. Among the other concentrations, concentration of sake (Genshu) with a very high osmotic pressure (110.514 atm) was the most difficult concentration with a lowest yield About 35%. Concentration of a alcoholic solution under a low temperature preserve it's original flavor components while increasing it's alcoholic content and other heat sensitive soluble components. Therefore this concentrated sake (Genshu) was a unique alcoholic product which could not be obtained from any other concentration process.

With an increase in osmotic pressure of solution, the yield achieved in progressive freeze-concentration decreased. Therefore, it is important to find out techniques which could use to improve the yield of concentration of solutions with high osmotic pressure.

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Table 2.2 Concentration of Kaga stem tea, watermelon juice and sake (Genshu) by tubular ice system

		Kaga stem tea	Watermelon juice	Sake (Genshu)
Original	Volume (ml)	12180	12180	12180
	Brix (%)	0.9	8.3	10.7
	Osmotic pressure (atm)	0.526	10.513	110.514
Concentrate	Volume (ml)	3260	3450	2300
	Brix (%)	2.8	19.1	20
Ice	Volume (ml)	8920	8732	9880
	Brix (%)	0	3.9	6.8
Volume based concentration ratio		3.74	3.53	5.30
Brix based concentration ratio		2.91*	2.30	1.87
Yield (%)		93.03*	65.45	35.30

* Calculations were done using absorbance (at 271nm) based concentration

2.5 Conclusion

The production scale of progressive freeze concentration was increased by batch type, closed tubular ice system. In this system ice crystal grows inside of a tube which being cooled by a coolant from the outside surface of the tubes. This was a compact, simple system where the total capacity can be easily increased by increasing the surface area by adding more tubes into the system. Ice crystal growth rate and mass transfer rate, which cause the separation efficiency of solutes from ice, were controlled by the cooling rate and the circulation speed of the solution inside the tubes. This system was very efficient for the concentration of low osmotic pressure solutions and the yield decreased with an increase in the initial osmotic pressure of the solution.

CHAPTER 3

YIELD IMPROVEMENT IN PRGRESSIVE FREEZE-CONCENTRATION BY PARTIAL ICE
MELTING

3.1 Introduction

The major drawback in progressive freeze-concentration system is the decrease in yield with the increase of concentration of the sample, because of the incorporation of solute into the ice phase. Mechanism of solute incorporation into ice phase in progressive freeze-concentration has investigated by Watanabe et al., (2013). According to their report low moving speed of ice front and high mixing at the ice liquid interface makes less space among ice dendrites for solute inclusion compared to high moving speed of ice front and slow mixing. However for high concentrated solutions with high osmotic pressure, solute entrapment into ice dendrites is inevitable with increasing solution`s concentration during the progress of concentration (Gu et al., 2005). Therefore obtaining a highly concentrated product with a high yield is difficult in progressive freeze-concentration. To improve this, the partial ice- melting has been reported to be effective (Miyawaki et al., 2012).

It has been known from a long time that, initially melted snow releases ion enriched water into the natural environment (Johannessen and Henriksen, 1978, Davies et al., 1982). This is the same phenomena with the melting of solute incorporated ice. Many researchers have investigated on obtaining high concentrated fractions by controlled melting, thawing or sweating of solute incorporated ice (Mandri et al., 2011, Moreno et al., 2014, Nakagawa et al., 2010a, Nakagawa et al., 2010b, Rich et al., 2012). Some authors have tried microwave assisted thawing to increase the thawing speed by increasing the mobility of unfrozen solute. However thawing of frozen skim milk by microwave-assisted thawing has resulted in partial denaturation of some peptides even it has increased the thawing speed for both skim milk (Aider and Ounis, 2012) and maple sap (Aider and de Halleux, 2008). The shortest thawing time with the highest solute recovery has obtained for coffee brews by using microwave thawing along with vacuum separation (Moreno et al., 2013). However there was no quality analysis done in order to find out about flavor loss, which was highly possible with a vacuum system. The solute incorporated ice produced in vertical progressive freeze-concentration test apparatus and tubular ice system was partially melted under normal room temperature by Miyawaki et al., (2012). They have found that initial melted fractions have the higher concentrations than the later fractions and by recovering of those with the higher concentration fractions, the total yield of the progressive freeze-concentration can be favorably improved. Since samples with high solute concentrations give lower yields in progressive freeze-concentration (Gunathilake et al., 2013) partial melting of solute incorporated ice has proposed as a method of improving total yield by solute recovery.

In this chapter, the effectiveness of partial melting process of solute incorporated ice produce in progressive freeze-concentration was further improved by controlling the melting temperature with mixing of ice. A simple partial melting vessel was designed and the optimum operating conditions were found using ice of 10% sucrose. Ice produced by tubular ice system during concentration of various liquid food were partially melted using the partial melting vessel. The total yield improvement by recovering high concentrated fractions was evaluated based on soluble solids except in pear juice flavor condensate, where the flavor component `butyl acetate` was assessed in each melted fractions.

3.2 Recovery of solute by partial melting of ice produced in progressive freeze-concentration
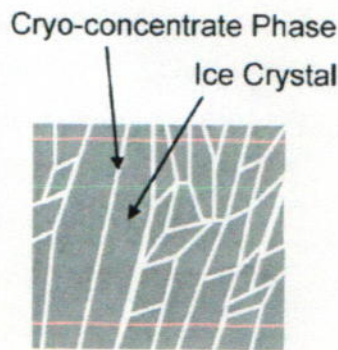
Fig. 3.1 Cryo-concentration phase of solute (Nakagawa et al., 2010)

During freezing of a solution, crystallization happens only for water molecules, and solutes molecules do not get crystallized. Instead of being crystallized, solutes get cryo-concentrated between ice dendrites as shown in Fig. 3.1 (Nakagawa et al., 2010). During melting of ice, these cryo-concentrated solutes come out through the channels formed in between ice crystals as a result of melting. The melting of ice should happen at a slow rate so that the cryo-concentrated solutes will not get diluted too much with melted ice, before it dripped down as a concentrated fraction. Therefore, there should be a balance between controlled heat and mass transfer for recovering solutes at a high concentration.

Concentration decreases gradually in later factions
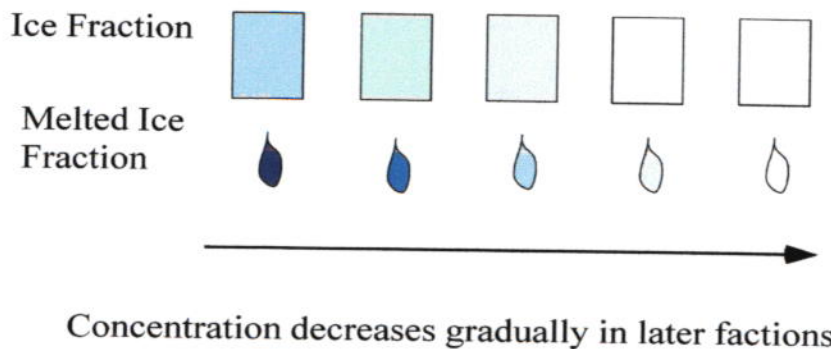
Fig. 3.2 Partial melting of solute incorporated ice

Fig. 3.2 shows the nature of partial melting of solute incorporated ice. When the ice formed in progressive freeze-concentration process is allowed to melt, the initial melted ice fractions contains the higher amount of solute giving a concentrated fractions and concentrations gradually decrease in later fractions. By recovering these concentrated fractions from solute incorporated ice, the major drawback of progressive freeze-concentration can be eliminated to achieve the high yield for concentration of high osmotic pressure solution.

3.3 Partial melting vessel
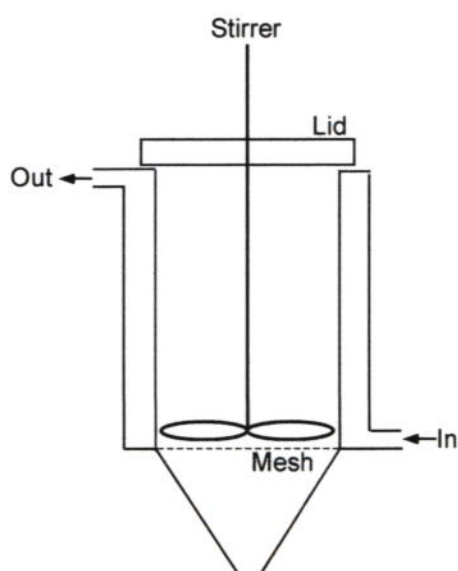
Fig. 3.3 Partial melting vessel

A partial melting vessel (Fig. 3.3) was used for partially melting of ice formed in progressive freeze-concentration process with controlling the vessel temperature and mixing the ice. The vessel is a jacketed vessel which was cooled down to a certain temperature by a circulation type cooler (TRL 108 H, Thomas, USA). The ice was mixed (SM-102, As one, Osaka) in an anti-clock wise direction using a 4-blade, paddles blade stirrer (10cm in diameter). This vessel was designed to provide controlled slow melting and good mixing of ice, so that cryo-concentrated solutes can be collected at a high concentration.

3.4 Optimum operating conditions for partial melting vessel

Cube ice made from 10% sucrose solution (Kanto Kagaku, Tokyo, Japan) was used to find the optimum temperature and mixing speed for partial melting of ice using the partial melting vessel. The temperature range of 0°C, 2°C, 10°C and 20°C was used with the mixing speeds of 0rpm (No mixing), 50rpm, 100rpm and 200rpm. Ice of total melted volume about 550ml was used in this experiment. The melted ice fractions were separated when the melted volume about 50-100ml was collected. The time for

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which each fraction took for melting was recorded. The brix and volume of each fraction was measured. The optimum conditions for partial melting vessel were evaluated in terms of speed of ice melting, maximum achievable concentration of the initial fractions and maximum yield.

Fig. 3.4 shows the speed of ice melting at different vessel temperatures from 0 ° C to 20 ° C. With an increase in the vessel temperature, the melting speed increased. Fig 3.5 shows the concentration of each fraction collected in each operating temperature with a stirring speed of 100rpm and Fig 3.6 shows the increase in yield after collecting each fraction. According to Fig 3.5 and 3.6, vessel temperature of 0 ° C gave the highest concentrated fraction with the highest yield. The highest initial fraction was as high as 19% brix. This is almost 2 times of original concentration. By melting 40% of ice fraction gives a higher concentration than 12% brix while achieving a high yield more than 60% (which corresponds to recovery of more than 60% solute). Only to obtain first three highly concentrated fractions, it takes about 75mins. Therefore even the lowest vessel temperature takes longer time for ice melting, it gives the highest concentration fractions which satisfy the objective of using partial melting vessel.
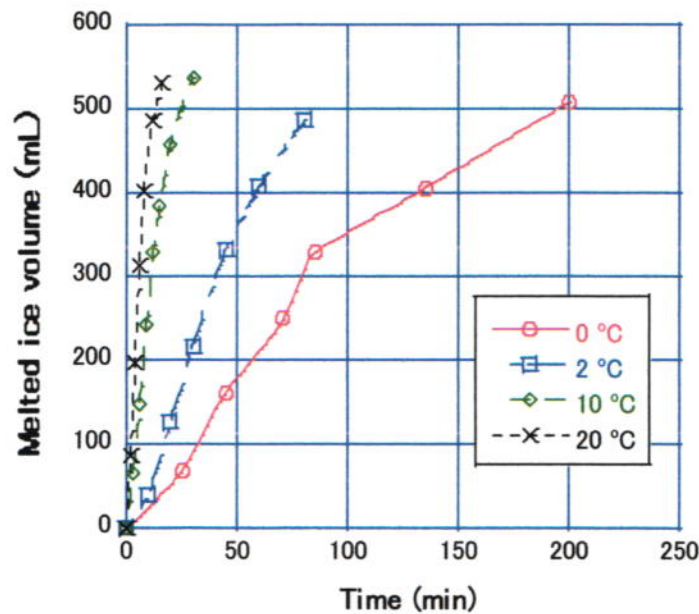
Fig.3.4 Speed of melting ice of 10% Sucrose with different vessel temperatures (Stirring speed was maintained at 100rpm in all the temperatures)
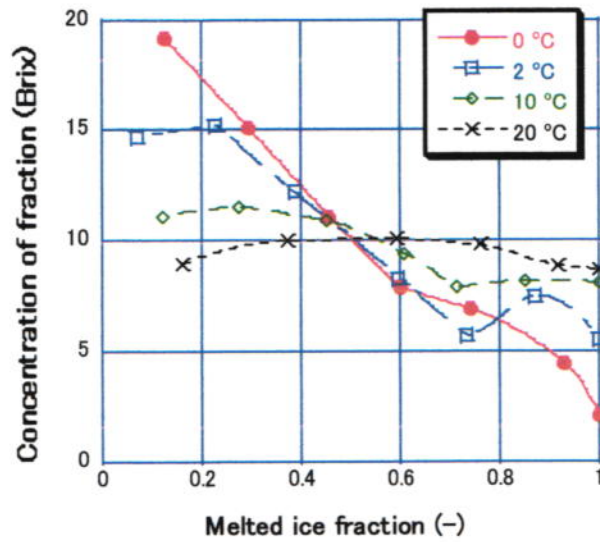
Fig.3.5 Achieving maximum concentrated fractions under different vessel temperatures for ice of 10% sucrose (stirring speed was maintained at 100rpm in all the vessel temperatures)
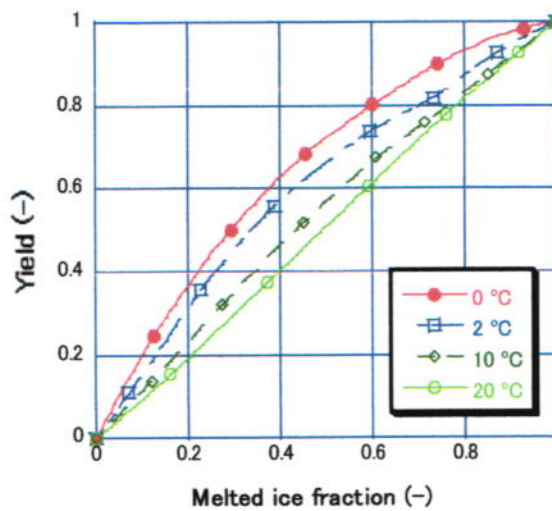
Fig.3.6 Achieving maximum yield under different vessel temperatures for ice of 10% Sucrose (stirring speed was maintained at 100rpm in all the vessel temperatures)

Fig 3.7 shows the speed of ice melting for different mixing speeds. According to it, by mixing ice, speed of melting has greatly increased. Mixing improves both mass transfer and heat transfer which is equally important in partial melting. However for initial fractions there is not much difference in required time for stirring at 50rpm, 100rpm and 200rpm. Fig. 3.8 shows the concentrations of melted fractions collected during the operation with different mixing speeds and with a vessel temperature at 2°C. According to this, maximum mixing speed of 200rpm gives highest initial concentration of 16% brix which is 1.6 times of initial concentration. By melting 50% of ice at this operating condition gives a

concentrated fraction higher than 12% brix. Fig 3.9 shows the increase in yield for melted fractions operating with different mixing speeds and the highest yield was also achieved for the highest mixing speed of 200rpm. More than 70% of solute can be recovered by melting 50% of ice, which corresponds to the melted fraction with concentration higher than 12% brix.
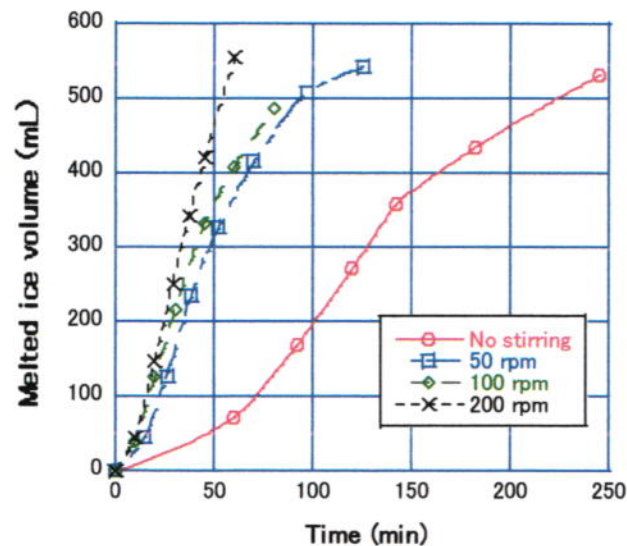
Fig.3.7 Speed of melting ice of 10% Sucrose with different stirring speeds (Vessel temperature was maintained at 2 ° C in all the speeds)
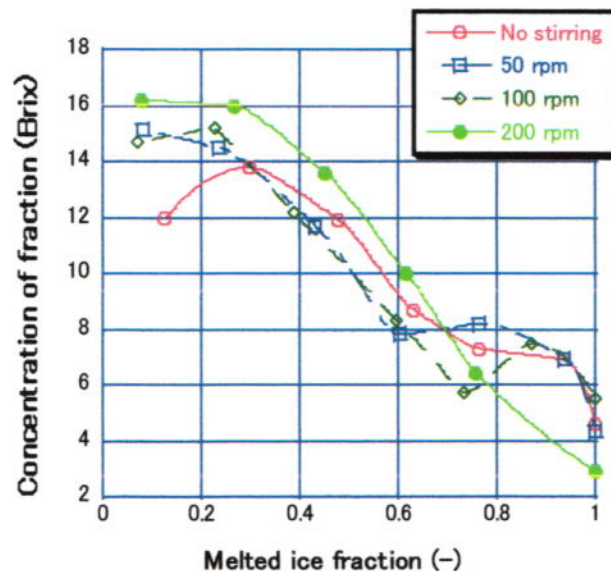
Fig.3.8 Achieving maximum concentrated fractions under different stirring speeds for ice of 10% Sucrose (vessel temperature was maintained at 2 ° C in all the stirring speeds)
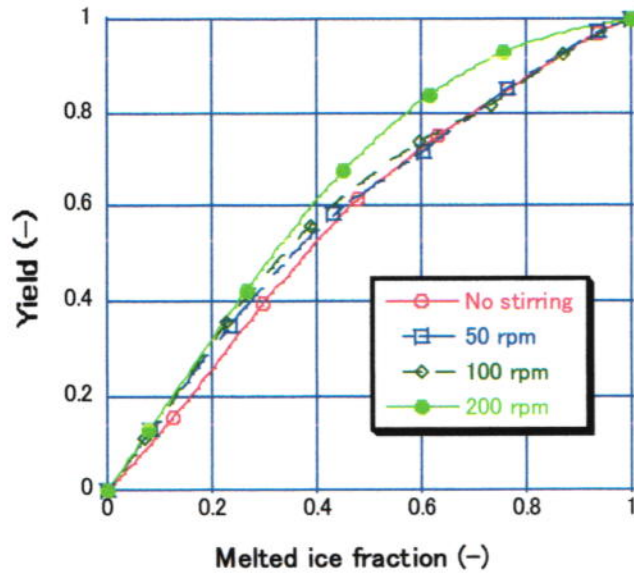
Fig.3.9 Achieving maximum yield under different stirring speeds for ice of 10% Sucrose (vessel temperature was maintained at 2 ° C in all the stirring speed)

According to these results, it is clear that the melting temperature and mixing of ice plays an important role in partial ice-melting. However low vessel temperature is the most important parameter, even it takes much time. It is important to understand the kinetic balance of droplet growth rate and the solute mass transfer rate (Nakagawa et al., 2010a). Low vessel temperature results in slow droplet growth rate which allows sufficient time for unfrozen cryo-concentrated solute to diffuse from the ice crystal. Mixing helps to collect those droplets and remove as a concentrated fraction from the partial melting vessel. For the ice of 10% sucrose solution, the freezing point depression is -0.625 ^{0}C (Weast, 1974). Therefore lowest temperature which was 0 ^{0}C provides the slightly higher temperature for the slow melting. Fast mixing helps to provide the fast collection of concentrated solute which results in efficient dripped down.

Even though these experiments revealed that the fastest mixing gives the best result, the influence of mixing speed for retention of volatile flavor components has not investigated. Since progressive freeze-concentration will be developed as a high quality concentration method, it is important to consider about the total quality of the processed product.

3.5 Application of partial melting vessel for solute incorporated ice produced in progressive freeze-concentration

Table 3.1 shows the results of concentration of various liquid foods by tubular ice system. Since it was inappropriate to quantify concentration of pear juice flavor condensate based on brix, the concentration was evaluated based on the relative peak area of flavor component butyl acetate. For all the

other solutions` concentrations, brix based concentration was used. As shown in Table 3.1, pear juice flavor condensate, the solution with lowest osmotic pressure had the highest yield with the least solute incorporated ice. Watermelon juice, Japanese pear juice and apple juice were solutions with intermediate osmotic pressure. They resulted in more solute incorporation with ice with the lesser yield. Apple syrup, which was the highest concentrated solution (27.9 % brix) with the highest osmotic pressure, resulted in highest solute incorporation with ice (16.2% brix of total ice) with the lowest yield. A part of ice produced in tubular ice system, after concentration of these solutions was used to melt by partial melting vessel. Except pear juice flavor condensate, for all the other solutions, the brix values of each melted ice fraction were measured. The identification of flavor components of pear juice flavor condensate was done by GC-MS (Focus DSQ II, Thermo Scientific Japan, Yokohama) and flavor components quantification was done by GC (G3900, Hitachi, Tokyo) using SPME method (50/30um, DVB/CAR/PDMS (Grey), Supelco Analytical, PA, USA).

Table 3.1 Yield obtained in progressive freeze concentration of various liquid food by tubular ice system

Sample	Initial Conc. (Brix)		Volume (ml)	Final Conc. (Brix)	Volume based Conc. ratio	Brix based Conc. ratio	Yield
Watermelon juice	8.3	Concentrate	3450	19.1	3.53	2.30	0.654
		Ice	8732	3.9			
Japanese pear juice	12.1	Concentrate	3350	26.1	3.64	2.16	0.662
		Ice	8832	5.3			
Apple juice	13.7	Concentrate	3500	25.5	3.48	1.86	0.638
		Ice	8682	6.2			
Apple syrup	27.9	Concentrate	4000	43.6	3.05	1.56	0.570
		Ice	8182	16.2			
Pear juice flavor condensate*	1	Concentrate	3320	2.36	3.67	2.36	0.87
		Ice	8862	0.23			

* Concentration based on flavor component `butyl acetate` concentration

By partial melting of 30% of ice from watermelon juice, the total yield of the concentration process was improved up to 85% from the initial yield of 65% (Fig. 3.10). The brix value of the 30% melted ice fraction could be high as 4.5% brix. As in Fig 3.11, the total yield of concentration of Japanese pear juice was improved to about 85% from initial yield of 66% by melting 40% of ice. The melted ice fraction concentration could be higher than 6% brix. The similar yield improvement was observed in the melting of ice from apple juice (Fig. 3.12). By melting 40% of ice the yield improved from 64% to 89%.

Watermelon juice, Japanese pear juice and apple juice were the solutions with medium osmotic pressure showed a similar yield improvement in partial melting of ice.
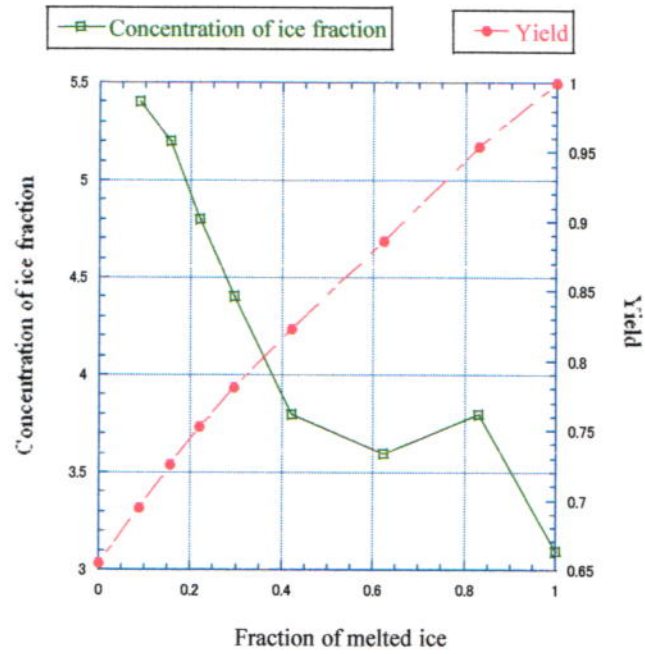
Fig. 3.10 Yield improvement by partial melting of ice of watermelon juice using partial melting vessel operating at 2°C and 100rpm
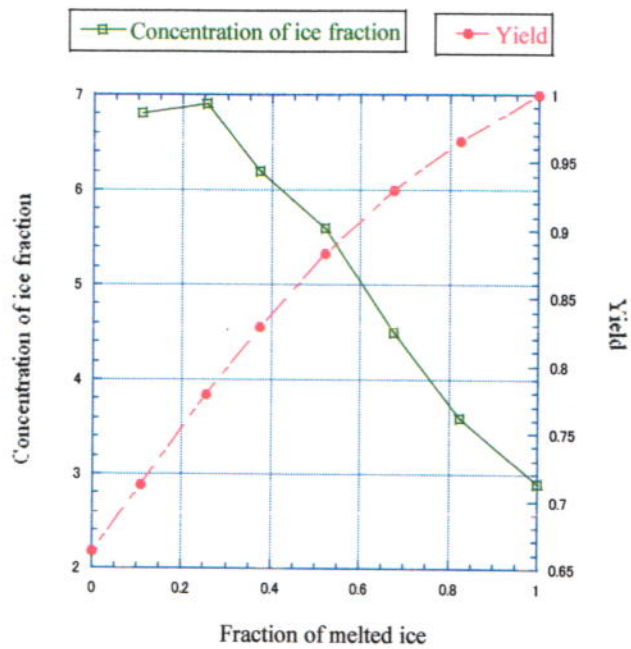
Fig. 3.11 Yield improvement by partial melting of ice of Japanese pear juice using partial melting vessel operating at 2°C and 100rpm
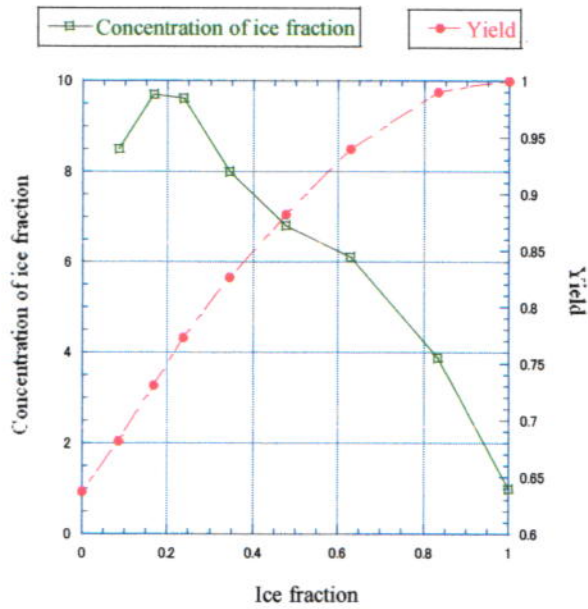
Fig. 3.12 Yield improvement by partial melting of ice of apple juice using partial melting vessel operating at 0°C and 100rpm
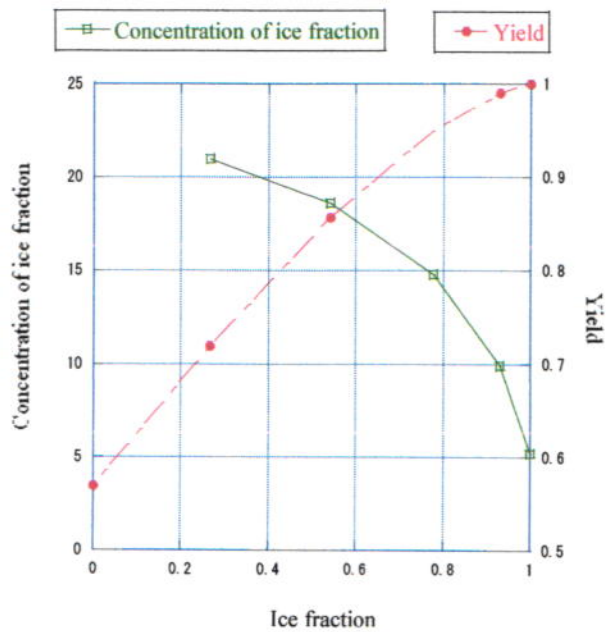
Fig. 3.13 Yield improvement by partial melting of ice of apple syrup using partial melting vessel operating at 0°C and 100rpm

Since the ice from apple syrup was with high solute incorporation, because of the high osmotic pressure of original solution, the partial ice-melting was most effective in the yield improvement.

As shown in Fig.3.13, melting of 40% of ice resulted in the highly concentrated fraction about 20% brix to improve the yield from 60% to 80%. The apple syrup is a waste from osmotic dehydration of apples. Due to the contamination with apple extract which cause browning reactions at high temperature, this solution cannot be concentrated by evaporative concentration. Reverse osmosis concentration is also not a suitable option due to very high initial concentration. Therefore the progressive freeze-concentration along with partial melting seems the only available method to re-concentrate this syrup.

Fig 3.14 shows the yield improvement of flavor component butyl acetate in pear juice flavor condensate. Even for a very low contaminated ice as in this case, the first initial fractions contain substantially high flavor concentration which is effective to improve the yield.
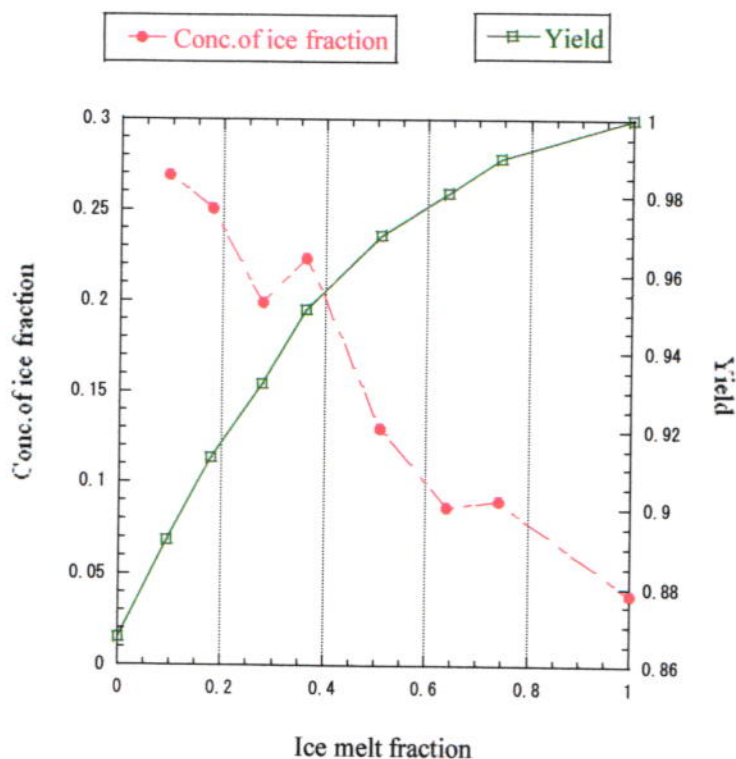
Fig. 3.14   Yield improvement based on butyl acetate flavor component of pear juice flavor condensate by partial melting of ice using partial melting vessel operating at 0°C and 200rpm

3.6 Conclusion

The main drawback of obtaining the lower yield for highly concentrated solution in PFC was minimized by partially melting of solute incorporated ice. A simple partial melting vessel was used to melt ice by controlling vessel temperature and mixing of ice. In the melting of ice from 10% sucrose the lowest vessel temperature (0 ° C) and fastest mixing speed (200rpm) gave the best results. Further studies should be necessary to find the influence of mixing speed on retention of flavor which is the major

advantage in freeze concentration. This vessel was used for partial melting of the ice produced in tubular ice system for watermelon juice, Japanese pear juice, apple juice, apple syrup and pear juice flavor condensate. For the ice from watermelon juice, Japanese pear juice and apple juice, the yield was increased up to 85% by recovering ice fraction about 30-40%. For apple syrup which was the highest in concentration, partial melting found to be very effective. Melting 40% of ice resulted in high concentrated fraction of more than 20% brix with a yield increase up to 80%. For pear juice flavor condensate, the amount of flavor recovery was quantified with flavor component `butyl acetate` as an index. The initial melted fractions showed relatively higher flavor concentration although the osmotic pressure was minimal in this case. The partial ice-melting vessel is very useful with its simple operation mechanism to improve in the yield in progressive freeze-concentration. This technique will play a key role in the practical application of progressive freeze-concentration.

CHAPTER 4

FLAVOR RETENTION IN CONCENTRATION PROCESS OF LIQUID FOOD

4.1 Introduction

One of the major factors concerning the quality of the concentrated liquid food is the retention of the original flavor same with the natural liquid food. Flavor deterioration happens in many stages of product life cycle of liquid food such as pretreatment, concentration, sterilization and storage until it is consumed by the end user. However there is an increasing consumer demand for natural foods with natural nutrients, flavors and aroma. Therefore it is a technological challenge to produce such liquid food in order to meet the current demands.

The most widely use, and highly explored method of concentration is evaporation (Evp). Despite of its technological maturity, evaporation removes major part of flavors and destroys heat sensitive components like nutrients and colors while consuming high energy for phase transition of water. Therefore it is the least attractive option for high quality liquid food concentration. There are many developments have been done in order improve the quality of evaporation with aroma recovery, however with such a system the cost of production become comparable to freeze-concentration along with the inferior quality product to that of a product of freeze concentration (Ramatake et al., 1993).

Reverse osmosis (RO) is a more attractive option, since it operates at room temperature causing relatively minimal thermal damage and consuming lower energy cost. The main disadvantage of RO is the limitation of concentration up to relatively low levels of dissolved solids about 22-33% brix (Jiao et al., 2004). Membrane distillation and osmotic distillation/evaporation does not have this limitation. However for membrane distillation, the requirement to heat the feed stream to maintain the water vapor pressure gradient provides condition which leads to significant loss of organic volatiles and for osmotic distillation, organic volatiles flux depends on the pore size of the membranes (Barbe et al., 1998). Another group has investigated on volatile components retention of orange and passionfruit juice after concentration by osmotic evaporation (Shaw et al., 2001). They have reported a loss of 32% of volatile components in orange and about 39% in passionfruit along with a significant difference between the initial juice and reconstituted concentrate in sensory evaluations. Osmotic evaporation was also used for concentration of roselle extract, grape and apple juice and losses of volatile aroma compounds of 1-27%, 6-31% and 12-46% were observed in each solution respectively (Cisse et al., 2011). Another cause for the volatile component loss for membrane distillation and osmotic distillation/evaporation could be due to the low evaporative capacity with a long time of treatment (Jiao et al., 2004).

Among the methods of liquid food concentration, freeze concentration is the best method in

terms of preserving the original characteristics of the liquid food (Deshpande *et al.*, 1982, Ramteke *et al*, 1993). Andes berry has concentrated using a progressive freeze concentration method (PFC) by Ramous and others and according to their finding concentrated pulp could not be differentiated with the original pulp (Ramous *et al.*, 2005). However there is not much published literature for the comparison of the flavor retention of the three main concentration methods.

Coffee is a brewed beverage and one of the most popular drinks in the world. Sensory properties of the extracted coffee play an important role in quality and acceptability of coffee drinks. Therefore after extraction or brewing coffee, post treatments like concentration should preserve the original quality of the coffee. In this study coffee extract was concentrated using progressive freeze concentration, reverse osmosis and vacuum evaporation and their flavor compounds were analyzed qualitatively and quantitatively. These results were used to evaluate the best mode of concentration for coffee extract. Consumers prefer to buy food flavored with natural flavors, other than artificial flavors. La-France pear has an attractive, unique pleasant flavor. La-France pear flavor condensate was collected during the evaporation of La-France pear juice. This flavor solution was also concentrated using the above three methods. Same as coffee extract, flavor compounds were analyzed quantitatively and qualitative to find out the best method of concentration.

4.2 Experimental method

Coffee extract was prepared by extracting 1 part of coffee powder with 5 parts of water at 90 ° C for 30 min and filtrated firstly with a 200mesh filter and then by a paper filter. Pear (La France) juice flavor condensate was a by-product in vacuum concentration of pear juice and was gifted by Kakoh Fruits and Flavors, Tokyo.

A small cylindrical test apparatus was used for the progressive freeze-concentration of coffee extract. A stainless steel cylindrical sample vessel (96mm in diameter, 270mm in height) was used. The vessel was plunged into a cooling bath (NCB 3200, Tokyo Rikakikai, Tokyo)at a constant speed. Temperature of the cooling bath was kept at -15 ° C. The sample vessel was equipped with a 6- blade turbine type (8cm in diameter) stirrer(SM-102, As One, Osaka) for stirring the solution at the ice liquid interface. A tubular ice system with circulating flow (MFC-10, Mayekawa, Tokyo) was used for the concentration of pear juice flavor condensate. This system was composed of jacketed cylindrical tube (59.5 mm in diameter, 1800 mm x2 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.

A reverse osmosis test cell (C40B, Nitto Denko, Osaka) was used for the concentration by reverse osmosis. The membrane used was a flat sheet membrane (NTR 70 SWC (NaCl rejection, 99.6%),

Nitto Denko, Osaka). Applied pressure was 3 MPa and the solution in the test cell was stirred near the membrane with a magnetic stirrer.

A rotary evaporator (RE 200, Yamato Scientific, Tokyo) was used with an aspirator (Gas-1, As One, Osaka) and a cooling unit (TRL 108H, Thomas, USA).Sample was kept at 50 ° C in a water bath (BM 200, Yamato Scientific, Tokyo).

The tentative concentration analysis for samples before concentration, concentrates, ice formed after PFC, permeate in RO, and condensates after Evp were carried out by a refractometer (APAL-1, As One, Osaka).

The solid phase micro extraction (SPME) was used for the flavor extraction. A 10ml sample, mixed with 40ppm methyl butanoate as an internal standard, was transferred in a 20 ml screw-cap vial and heated up to 45 ° C for 5mins 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 15min. 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 desorption of flavor component for 3mins.

Flavor components of the samples were identified by GC/MS (Focus DSQ II, Thermo Scientific Japan, Yokohama) and quantified 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 .

4.3 Concentration of coffee extract

Table 4.1 shows the results obtained for the concentration of coffee extracts using the three concentration methods. Volume-based concentration levels were 4.7, 4.2, and 1.9 fold, respectively, for PFC, RO, and Evp and accordingly, the Brix-based concentration increased from 4.0 Brix to 12.1, 19.4, and 10.3 Brix, respectively. The Brix-based concentration levels were3.03, 4.85, and 2.58 fold, respectively, for PFC, RO, and Evp.

Table 4.1 Concentration of coffee extract by progressive freeze-concentration (PFC), reverse osmosis (RO), and vacuum evaporation (Evp).

		PFC	RO	Evp
Original	Volume (ml)	700	300	300
	Concentration (%Brix)	4.0	4.0	4.0
Concentrate	Volume (ml)	148	71	156
	Concentration (%Brix)	12.1	19.4	10.3
Ice/Permeate/Condensate	Volume (ml)	545	221	118
	Concentration (%Brix)	1.5	0	0.5
Concentration ratio – Volume based		4.73	4.23	1.92
Concentration ratio – Brix based		3.03	4.85	2.58

4.4 Flavor analysis in concentration of coffee extract

Fig. 4.1 shows the GC chromatogram of head-space analysis for the original coffee extract, its concentrate by PFC, and the ice formed in PFC. Nine major peaks were observed for the coffee extract. The chemical components of the peaks were identified by GC/MS as listed in Table 2. Coffee flavor contained many heterocyclic compounds which seem to generate in the roasting process. In PFC, the chromatograms show quite similar profiles before and after concentration. In this case, the similar profile was observed also for the ice phase. This incorporation of solute into ice phase causes the loss to reduce the yield but this seems to happen without changing the flavor profile.
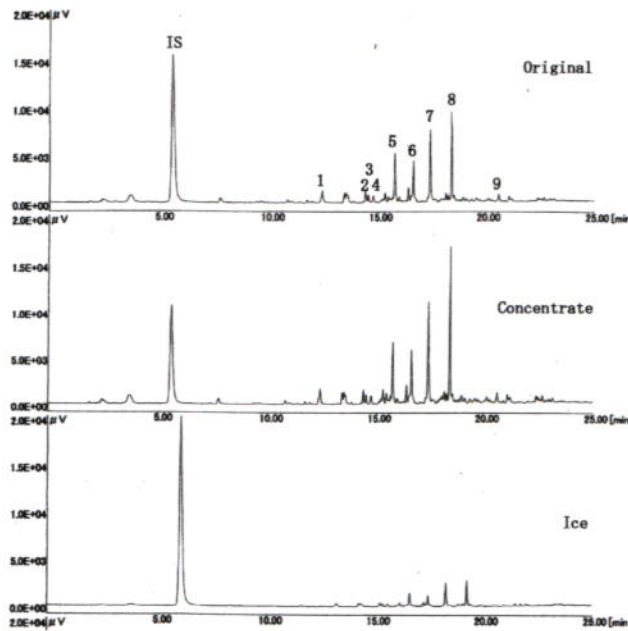
Fig. 4.1 GC chromatograms for original solution, concentrate, and ice in progressive freeze-concentration of coffee extract.

Table 4.2 Identification of peaks in GC chromatogram of coffee extract in Fig.4.1.

Peak No	Flavor component	Retention time (min)
IS	methyl butanoate	5.58
1	methyl pyrazine	12.44
2	2-ethyl-6-methylpyrazine	14.43
3	2-ethyl-5-methylpyrazine	14.56
4	2-ethyl-3-methylpyrazine	14.79
5	furfural	15.79
6	2-furfuryl acetate	16.66
7	5-metyl-2-furaldehyde	17.43
8	2-furfurylalcohol	18.43
9	1-furfurylpyrrole	20.63

Fig. 4.2 shows the GC chromatogram for RO concentration of coffee extract. In this case, the flavor profile in the concentrate seems not much different from that for the original. In the chromatogram for permeate, small peaks were observed for the components which passed through the membrane. In Fig. 4.3, the GC chromatogram for Evp concentration of coffee is shown. In this case, most flavors were lost from the concentrate, except 2-furfurylalcohol, and some were transferred into condensate.

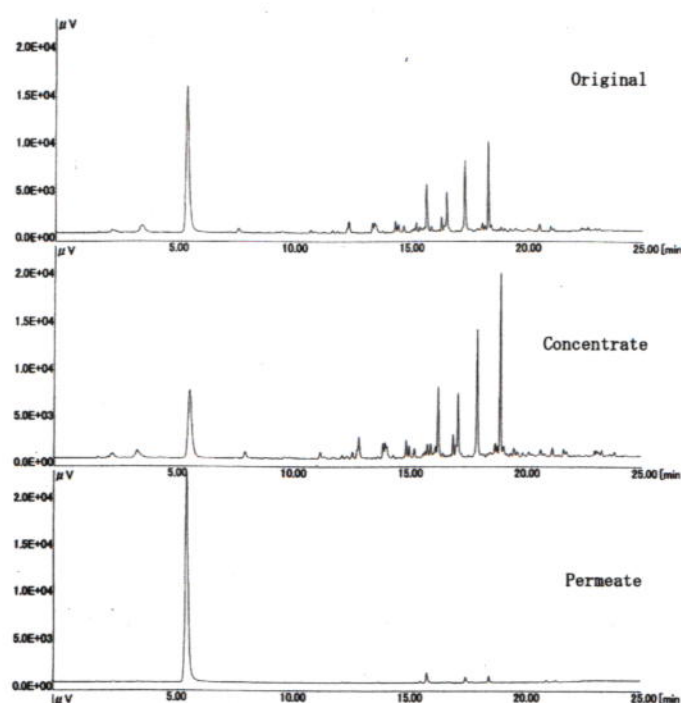Fig. 4.2 GC chromatograms for original solution, concentrate, and permeation concentration of coffee extract by reverse osmosis.

cTable 4.3 summarizes the relative concentration ratio for all the flavor components compared with the original solution for the three concentration methods. Among the concentrates, the concentration ratio was quite low for Evp showing the poorest quality for this method even if this was done at a reduced temperature at 50 ℃. Concentration ratios in PFC and RO were much different among components because the flavor analysis by the head-space SPME does not necessary reflects the concentration profile in the solution.

On the contrary, the difference in flavor distributions among ice, permeate, and condensate was interesting. In Evp, most of flavor components lost or transferred into the condensate. In RO, permeation ratios were much different among components. In PFC, the loss of flavors into ice phase was at around 20% and was larger than RO but the flavor distribution in the ice phase was not much different from the original sample. This means that the incorporation of components into the ice phase in PFC is nonselective. This corresponds to the mechanism of the solute incorporation into ice phase, in which solutes are non-selectively incorporated into the space between the dendrite ice-crystal structures (Watanabe et al., 2013). This non-selectivity in the incorporation of solute into ice phase supports the effectiveness of the partial ice-melting technique to improve the yield in PFC (Miyawaki et al., 2012). In this method, the incorporated components into ice phase are recovered by the partial melting of ice to improve the yield. The present result suggests that the quality of the recovered product by the partial ice-melting is expected to be not much different from the original.

After concentration, the concentrates obtained were diluted with water for reconstitution based on the brix-based concentration ratio. The flavor profiles are also shown for the reconstituted products in Table 4.3. Based on this, a radar chart is drawn as shown in Fig.4.4, which clearly shows the difference in flavor profile balance among the three concentration methods. As compared with the original solution, PFC shows the better flavor-profile balance than RO reflecting the difference in the selectivity in the concentration mechanism while Evp showed the poorest result.
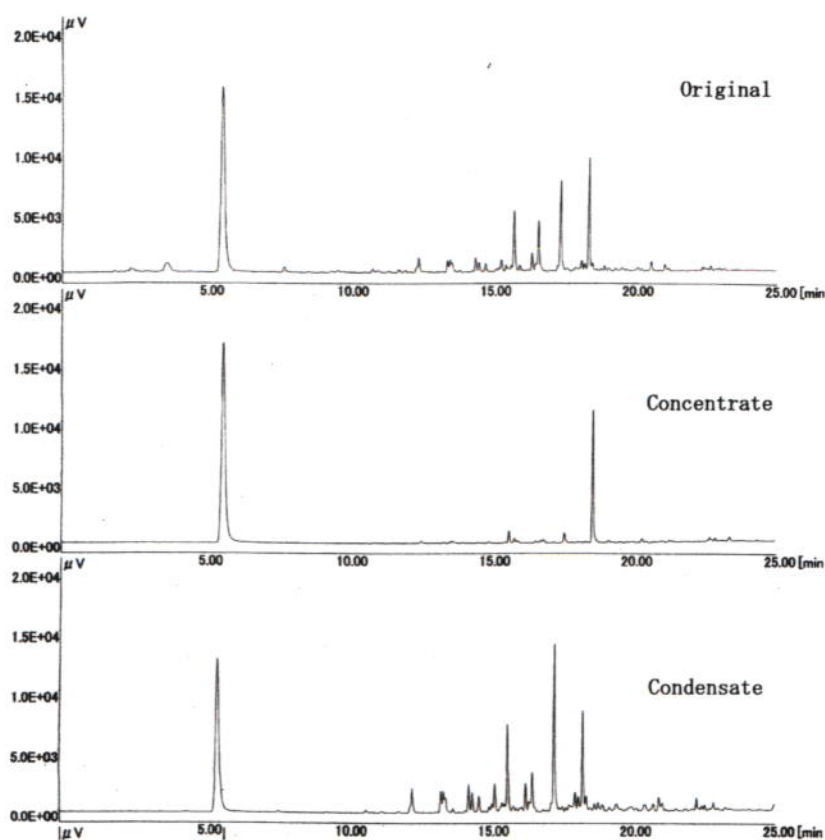
Fig. 4.3 GC chromatograms for original solution, concentrate, and condensate in vacuum evaporation of coffee extract at 50 ℃.

Table 4. 3 Comparison of concentration ratio among the three methods in concentration of coffee extract

Peak No.	Progressive freeze-conc. (PFC)			Reverse osmosis(RO)			Evaporation(Evp)		
	Conc	Ice	Reconst.	Conc	Permeate	Reconst.	Conc.	Condensate	Reconst.
1	2 .098	0.235	0.769	3.276	0.000	0.664	0.107	1.964	0.034
2	1.968	0.260	0.752	2.829	0.000	0.670	0.000	2.579	0.000
3	1.948	0.271	0.779	2.922	0.000	0.669	0.077	2.797	0.000
4	1.981	0.312	0.795	2.736	0.000	0.728	0.021	2.663	0.000
5	1.961	0.242	0.814	2.779	0.199	0.591	0.200	1.862	0.066
6	2.252	0.248	0.913	5.143	0.004	0.619	0.056	1.103	0.034
7	2.275	0.293	0.753	3.611	0.072	0.725	0.132	2.258	0.055
8	2.679	0.247	0.821	3.828	0.063	0.752	1.247	1.084	0.443
9	2.522	0.300	0.728	2.494	0.200	0.565	0.075	1.541	0.038
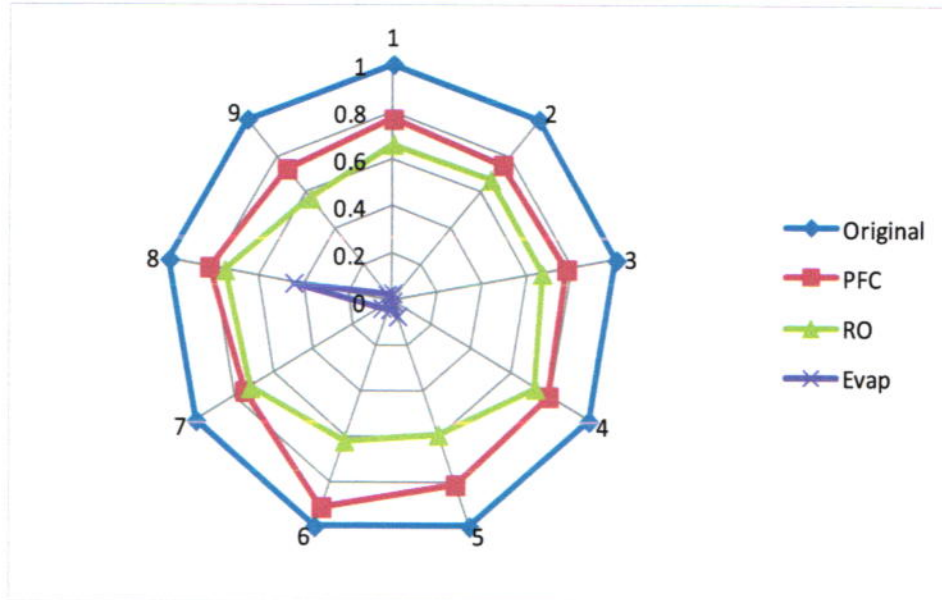
Fig. 4.4 Comparison of flavor profiles for reconstituted product of concentrate after concentration of coffee extract by progressive freeze-concentration (PFC), reverse osmosis (RO), and vacuum evaporation (Evp).

4.5 Concentration of pear juice flavor condensate

Table 4.4 shows the results obtained for the concentration of LaFrance pear flavor condensate using the three concentration methods. Volume-based concentration levels were 3.67, 4.62, and 4.95 fold, respectively, for PFC, RO, and Evp. Accordingly, the Brix-based concentration increased from 1.0 to 2.7 Brix for PFC and to 3.5 Brix for RO but this decreased to 0.8 for Evp. This suggests that the major components were lost from the concentrate in Evp.

Table 4.4 Concentration of pear (LaFrance) juice flavor condensate by progressive freeze-concentration (PFC), reverse osmosis (RO), and vacuum evaporation (Evp).

		PFC	RO	Evp
Original	Volume (ml)	12180	300	500
	Concentration (%Brix)	1.0	1.0	1.0
Concentrate	Volume (ml)	3320	65	101
	Concentration (%Brix)	2.7	3.5	0.8
Ice/Permeate/Condensate	Volume (ml)	8862	227	370
	Concentration (%Brix)	0.4	0.5	1.0
Concentration ratio – Volume based		3.67	4.62	4.95
Concentration ratio – Brix based		2.7	3.5	-

4.6 Flavor analysis in concentration of pear juice flavor condensate

Figure 4.5 shows the GC chromatogram of head-space analysis for the original pear juice flavor condensate, its concentrate by PFC, and the ice formed in PFC. Twelve major peaks were observed for the pear juice flavor condensate, the chemical component of which were identified by GC/MS as listed in Table 4.5. The major components in pear condensate were low-molecular alcohols and esters, which are much different from those in the coffee extract. In PFC, the chromatograms showed quite similar profiles before and after concentration. In this case, the similar profile was observed also for the ice phase. This incorporation of solute into the ice phase causes the loss to reduce the yield but this loss can be recovered by applying the partial ice-melting technique.

Fig. 4.6 shows the GC chromatogram for RO concentration of pear juice flavor condensate. In this case, the flavor profile in the concentrate was much different from that for the original. In the chromatogram for permeate, small peaks were observed for the components which passed through the membrane. In Fig.4.7, the GC chromatogram for Evp concentration of pear juice flavor condensate is shown. In this case, almost all the flavors were lost from the concentrate so that the reconstitution from the concentrate was not carried out.

Fig.4.5 GC chromatograms for original solution, concentrate, and ice in progressive freeze-concentration of pear (La France) juice flavor condensate.

Table 4.5 Identification of peaks in GC chromatogram of pear (LaFrance) juice flavor condensate in Fig. 4.5.

Peak No.	Flavor component	Retention time (min)
1	ethyl acetate	3.25
2	ethanol	4.32
IS*	methyl butanoate	5.28
3	butyl acetate	7.59
4	1-butanol	9.34
5	pentyl acetate	9.72
6	2-methil-1-butanol	10.52
7	hexyl acetate	11.83
8	1-hexanol	13.20
9	3,4,5-trimethyl-4-heptanol	14.13
10	3,7-dimethyl-1,6-octadien-3-ol	15.96
11	1-octanol	16.13
12	allyl methyl sulfide	17.36

*) Internal standard
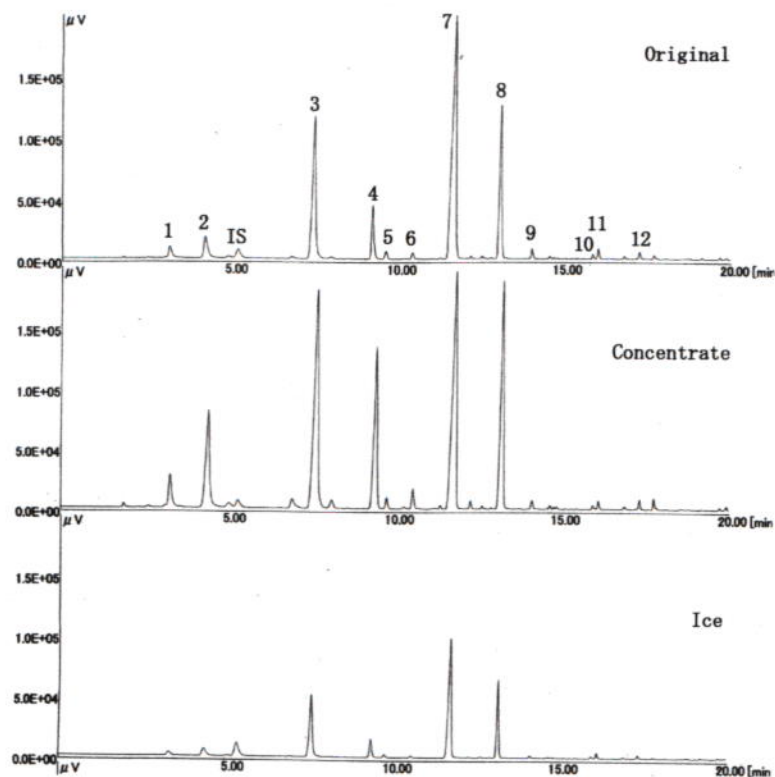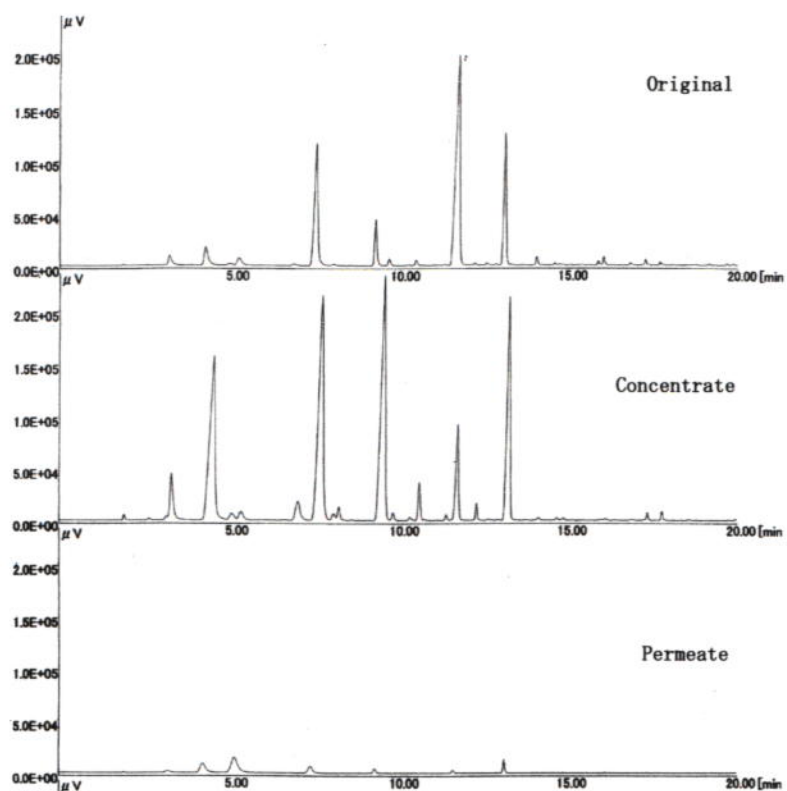

Fig. 4.6 GC chromatograms for original solution, concentrate, and permeate in concentration of pear (La France) juice flavor condensate by reverse osmosis.

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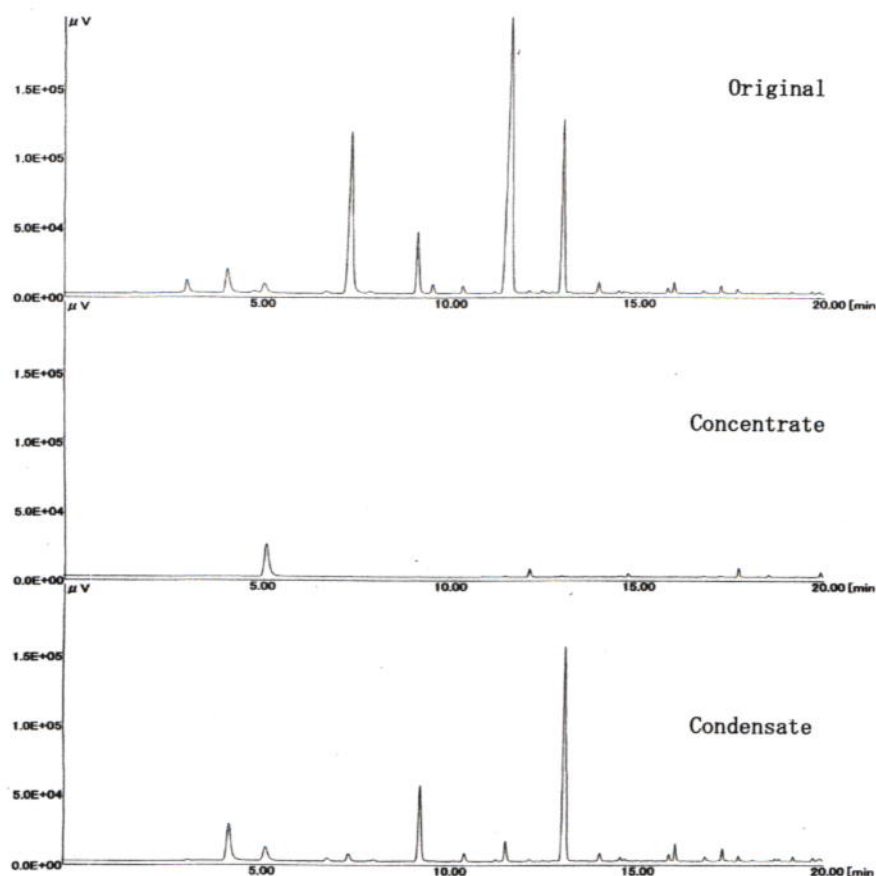
Fig. 4.7 Chromatogram for original solution, concentrate, and condensate in vacuum evaporation of pear (La France) juice flavor condensate at 50 ^{0}C

Table 4.6 summarizes the relative concentration ratio for all the flavor components compared with the original solution for the three methods in the concentration of pear juice flavor condensate. Among the concentrates, the concentration ratio was quite low for Evp showing that almost all the components were lost. Concentration ratios in PFC and RO were much different among components because the flavor analysis by the head-space SPME does not necessary reflects the concentration distribution in the solution. As for the difference in distributions among the ice, permeate, and condensate, the substantial part of the flavor components lost from the concentrate was trapped in the condensate in Evp. In RO, all the components, more or less, permeated through the membrane although the permeation ratios were different among components.

Table 4.6 Comparison of concentration ratio among the three methods in concentration of pear juice flavor condensate.

Peak No.	Progressive freeze-conc. (PFC)			Reverse osmosis(RO)			Evaporation(Evp)	
	Conc	Ice	Reconst.	Conc	Permeate	Reconst.	Conc.	Condensate
1	3.614	0.199	0.968	1.882	0.179	0.395	0.000	0.037
2	5.939	0.204	1.353	2.632	0.410	1.713	0.005	0.853
3	2.374	0.226	1.096	1.010	0.071	0.292	0.000	0.027
4	5.406	0.203	1.171	3.006	0.095	1.285	0.001	0.784
5	1.635	0.208	0.932	0.580	0.049	0.203	0.000	0.000
6	3.916	0.205	1.098	2.116	0.018	1.014	0.000	0.573
7	1.201	0.199	1.068	0.381	0.065	0.191	0.000	0.000
8	2.276	0.239	0.933	1.001	0.077	0.751	0.001	0.837
9	1.059	0.128	0.824	0.462	0.024	0.481	0.005	0.309
10	0.954	0.266	0.654	0.512	0.022	0.453	0.000	0.821
11	1.092	0.316	0.792	0.562	0.100	0.516	0.000	0.834
12	1.490	0.212	0.946	1.378	0.106	1.119	0.018	0.956

In the literature, permeation of apple aroma compounds (Alverez, 1998), alcohols, esters, and aldehydes (Pozderovic, 2006AB; 2007) through RO membrane has been investigated and the alcohols and esters with the lower molecular weight were reported to permeate easily through RO membranes. In PFC, the loss of flavors into ice phase, roughly at about 20%, was larger than RO but the flavor distribution in the ice phase was unchanged compared with the original sample as was the case with coffee extract. In the literature, good flavor retention was also reported in the concentration of Andes berry juice by PFC (Ramos et al., 2005).

The flavor profiles for the reconstituted products after concentration and dilution are also shown for PFC and RO in Table 6. Based on this, a radar chart is drawn as shown in Fig.4.8, which clearly shows the difference in the flavor profile balance between PFC and RO. In PFC, the flavor balance is closer to the original solution but in RO some components were lost substantially. These components are ethyl acetate, butyl acetate, pentyl acetate, and hexyl acetate, all of which are esters. Because of this, flavor distribution balance was completely changed in RO. As the permeation ratios of these compounds through the membrane are not necessarily high (Table 4.6), these compound might have lost also by the adsorption on the membrane and apparatus in addition to the permeation through the membrane. In Table 4.6 and Fig.4.8, concentrations of some components after reconstitution are apparently higher than those in the original solution. This might have happened because of the large change in flavor profile balance

especially for RO and indirect nature of SPME analysis for solution analysis.

Fig. 4.8 Comparison of flavor profiles for reconstituted product of concentrate after concentration of pear (La France) juice flavor condensate by progressive freeze-concentration (PFC) and reverse osmosis (RO).

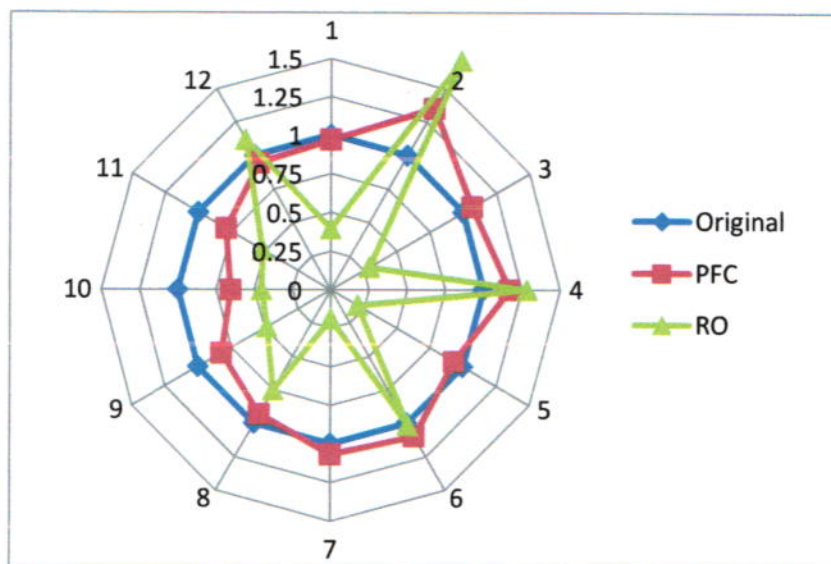4.7 Conclusion

Concentration of coffee extract and pear (La France) juice flavor condensate was carried out by PFC, RO, and Evp and the results were compared in terms of the flavor retention. PFC showed the best quality after concentration and reconstitution showing the closest flavor distribution balance to the original solution before concentration. RO showed the intermediate quality among the three. In this case, some of the low-molecular flavors were lost mainly because of the permeation through the membrane. In Evp, most of the flavors were lost and some were transferred to the condensate showing the poorest quality although it was operated at the reduced pressure with a boiling point at 50 ^{0}C. These differences seemed to originate from the differences in the mechanism of separation of solute from the solution among the three. In PFC, separation and concentration are nonselective among the components while these are highly selective in RO and Evp. Although the yield might be lower for PFC than RO because of the loss by the incorporation of solutes into the ice phase, the loss is expected to be recovered by applying the partial ice-melting technique.

CHAPTER 5

NEW PRODUCT DEVELOPMENT USING PROGREESIVE FREEZE-CONCENTRATION OF LIQUID FOOD

5.1 Introduction

Due to low temperature operation, freeze-concentrated products have superior qualities which could not be obtained from other liquid food concentration methods. The scaled up tubular ice system for progressive freeze-concentration has a main advantage over suspension system by being a batch type, flexible system for a wide range of operating scales. By using these unique features of tubular ice system for progressive freeze-concentration, the concentrated products were identified as new food product and a raw material for making new products which does not exist in the present liquid food market.

Kaga stem tea is a special kind of a tea that is only available in Hokuriku area of Japan. This tea was concentrated using tubular ice system and the quality of the product was assessed in order to check it's suitability to use as a Kaga stem tea flavor solution. Sake-Genshu, which is a high alcoholic, intermediate product in sake manufacturing was concentrated using tubular ice system. The quality of the product was evaluated as a high alcoholic beverage. Varity of fruit juices were concentrated using tubular ice system and the concentrated product was used as a raw material for wine making. The specialty of the wine made out of progressively freeze-concentrated juice was compared with the commercially available wine.

5.2 Concentration of Kaga stem tea

Thickly extracted Kaga stem tea supplied by Kobayashiya Chaho Co. Ltd. was concentrated using tubular ice system. The concentrations were measured in terms of absorbance measured at 271mn (UV/VIS Spectrophotometer, JASCO, V-560). The results obtained for concentration of Kaga stem tea is shown in Table 5.1.

Table 5.1 Concentration of Kaga stem tea

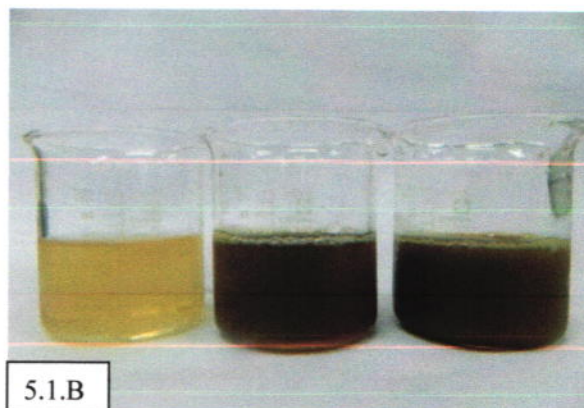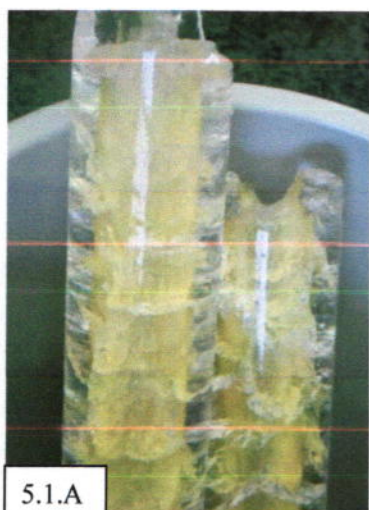|	Vol (ml)	Absorbance (at 271nm)	xDilution	Yield %
Original	12180	0.596	120	
Conc	3260	0.694	300	93.03
Ice	8920	0.57	10	6.97
Vol based concentration ratio	3.736			
Abs based conc.ratio	2.911			

Fig 5.1.A. Tubular ice produced in Kaga stem tea concentration, 5.1.B. Melted ice, original solution and concentrate of Kaga stem tea

Being a low osmotic pressure solution, Kaga stem tea was efficiently concentrated with a yield of 93% with a less contaminated ice (As shown in Fig 5.1 A & B). In order to evaluate the efficiency of flavor retention, favor components were identified by GC/MS (Focus DSQ II, Thermo Scientific Japan, Yokohama) and quantified by GC (G3900, Hitachi, Tokyo) using SPME method. The identified flavor components and their relative concentrations compared with the original solution in concentrate, ice and reconstituted concentrate are presented in Table 5.2.

Table 5.2 Flavor component as a ratio to the original solution for Kaga stem tea in concentrate, ice and reconstituted concentrate

	Flavor component name	Concentrate	Ice	Reconstituted concentrate
1	1H-Pyrrole,1-ethyl	3.151	0.000	1.108
2	Acetic acid,hexyl ester	3.166	0.000	1.163
3	Pyrazine, 2,5-dimethyl-	2.806	0.000	1.160
4	Pyrazine, 2-ethyl-6-methyl	3.322	0.000	1.243
5	Pyrazine, 2-ethyl-5-methyl	3.048	0.282	1.140
6	Pyrazine, 2-ethyl-3-methyl	2.708	0.382	1.154
7	Pyrazine, 3-ethyl-2,5-dimethyl	2.335	0.000	1.081
8	1,6-Octadien-3ol,3,7-dimethyl	2.117	0.062	0.890
9	1H-Pyrrole-2-carboxaldehyde,1-ethyl	3.048	0.000	1.211
10	Benzenamine,4-methoxy-2-methyl	2.976	0.000	1.239

As show in Table 5.2, most of the flavor components were heterocyclic compounds which could have produced during roasting of tea stems. Almost all the flavor components have efficiently concentrated in concentrate having a very high concentration ratio close to 3. The reconstituted concentrate also shows almost uniform flavor profile with a concentration ratio close to 1. Therefore this concentration method is a very efficient concentration method for concentration Kaga stem tea, where this concentrated solution could use as a Kaga stem tea flavor solution for making Kaga stem tea flavored desserts.

5.3 Concentration of Japanese sake

Sake (Genshu) was an intermediate product of `Seishu` with a high alcoholic (17.5%) content. This was concentrated using tubular ice system (Table 5.3). This solution was the highest osmotic pressure solution that was used in the tubular ice system. This was successfully concentrated by increasing its alcoholic content up to 28.9% (Table 5.4) even though with a lower yield. As shown in Table 5.4, all the quality related parameters of sake were favorably increased in concentrated solution. Therefore during the concentration all the solutes have increased in their quantity while preserving the quality of the sake.

Table 5.3 Concentration of Sake-Genshu

	Vol(ml)	Brix based concentration (%)
Original	12180	10.7
Concentrate	2300	20.0
Ice	9880	6.8
Concentration ratio	5.30	1.87

Table 5.4 Changing of quality of sake after progressive freeze-concentration

	Alcohol (%)	Nihon shu-do (Dryness)	Acidity (ml)	Amino acid content (ml)
Original	17.5	+2.2	1.7	1.0
Concentrate	28.9	+1.4	2.8	1.6
Ice	9.5	+2.9	0.9	0.6

The important flavor components of sake (Genshu) before and after concentration are shown in Table 5.5. Same as with the sake quality related parameters, all the flavor components have concentrated effectively. It is impossible to concentrate an alcoholic solution preserving all these quality related parameters using any other method. Therefore this high alcoholic sake is a unique new product which could be produced by progressive freeze-concentration using the tubular ice system.

Table 5.5 Important flavor components (mg/L) of sake (Genshu) before and after concentration

	AcOEt	n-PrOH	i-BuOH	AcOi-Am	i-AmOH	CaprOEt
Original	93	102	64	1.52	137	0.22
Concentrate	198	233	122	2.21	188	0.39
Ice	16	46	32	0.21	99	N.D.

AcOEt: Ethyl acetate , n-PrOH:n-Propanol, i-BuOH:Iso butanol, AcOi-Am: Iso amyl acetate, i-AmOH:Iso amyl alcohol, CaprOEt: Ethyl caproate, N.D.: Not Detected

5.4 Wine making from progressively freeze-concentrated fruit juice

Wine can be made out of fruit juices which have high amount of sugar content. By increasing the sugar content of juices by concentration, wine with high alcoholic content can be made. Grape juice concentration from17.4% to 20% brix by osmotic evaporation and wine making using the concentrated juice was reported by Versari et al. (2004). The wine made from this concentrated juice had an improved quality with a full body, more structure and persistence.

By progressive freeze-concentration the amount of sugar content can be increased while preserving original quality of the fruit juice. Therefore theoretically wine can be made out of any progressively freeze-concentrated fruit juice. Table 5.6 shows the original soluble solid contents of some of the fruit juices and the increase in their soluble solid contents after progressive freeze concentration.

Table 5.6 Soluble solid contents of original fruit juices and progressively freeze concentrated fruit juices

	Original brix%	After concentration brix%
Strawberry	8.5	
Mandarin orange	12.0	
Cherry	15.2	
Water melon	8.3	19.1 → 30.2 (2 step concentration)
Japanese pear	11.3	26.1
Pineapple	13.4	
Grape （Japan）	18	26
Grape （Europe）	>20	
Peach	10.2	
Apple	13.7	25.5
Lemon	7.1	16 → 23 (2 step concentration)
Melon	10.3	

5.4.1 Apple wine from progressively freeze-concentrated apple juice

Apple wine was made from original apple juice (without concentration) and progressively freeze concentrated apple juice. A set of wine from original and concentrated apple juice was made using 1ml of yeast solution and from only concentrated apple juice wine was made using 3ml of yeast solution. The amount of alcoholic content in each wine was as follows. Wine made from concentrated apple juice with 3ml of yeast solution had a highest alcoholic content of 11.63%.

Alcohol contents in each wine sample;
- Original juice with 1 ml yeast   - 6.78%
- Concentrate juice with 1ml yeast   – 10.2%
- Concentrate juice with 3ml yeast   – 11.63%

Flavor component of original apple juice and above three wines were identified by GC/MS (Focus DSQ II, Thermo Scientific Japan, Yokohama) and quantified by GC (G3900, Hitachi, Tokyo) using SPME method. The results are shown in Table 5.7. All the major flavor components of the original juice have disappeared and new flavor components have appeared after the fermentation process. Ethanol content was the higher in wine made out of concentrated juice, since high amount of sugar in concentrated juice had converted into alcohols during fermentation process. All the other flavor components were having relatively smaller share in wine made from concentrated solution, since major portion of volatile components were accompanied by ethanol and SMPE method provide information only about the total

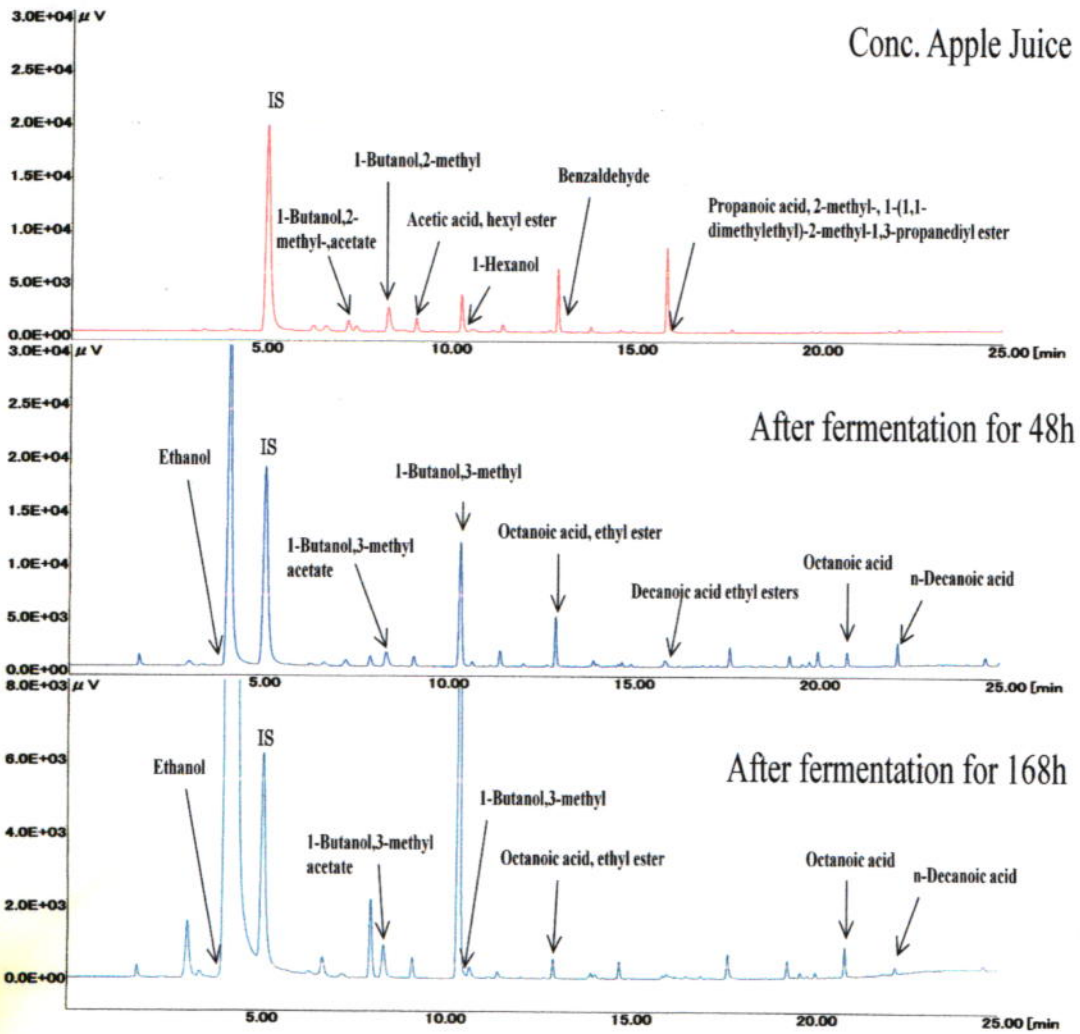flavor profile and not the actual quantity of each flavor components.

Fig. 5.2 Flavor pattern change during apple wine fermentation process

Table 5.7 Flavor pattern change during apple wine fermentation process

No		Original juice	Wine from original juice (with 1ml Yeast)	Wine from concentrated juice (with 1ml Yeast)	Wine from concentrated juice (with 3ml Yeast)
1	Ethanol	0	10.631	31.595	49.063
IS	Butanoic acid, methyl ester	1.000	1.000	1.000	1.000
2	1-Butanol, 2-methyl -, acetate	0.017	0	0	0
3	1-Butanol, 2-methyl	0.045	0	0	0
4	1-Butanol, 3-methyl-, acetate	0	0.116	0.132	0.105
5	Acetic acid, hexyl ester	0.018	0	0	0
6	1-Hexanol	0.051	0	0	0
7	1-Butanol, 3-methyl-	0	1.976	2.137	2.647
8	Hexanoic acid, ethyl ester	0	0.163	0.115	0.079
9	Benzaldehyde	0.072	0	0	0
10	Octanoic acid, ethyl ester	0.000	0.554	0.374	0.230
11	Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	0.125	0	0	0
12	Decanoic acid, ethyl ester	0	0.132	0.112	0.064
13	Ethyltrans-4-decenoate	0	0.107	0.080	0.043
14	Phenol, 2,4-bis(1,1-dimethylethyl)-	0.028	0	0	0
15	Octanoic acid	0	0.182	0.079	0.087
16	n-Decanoic acid	0	0.128	0.034	0.023

Another set of wine was made from concentrated apple juice using 3ml of yeast solution. During fermentation, wine samples were taken at different time intervals of 48hrs, 120hrs, 144hrs and 168hrs and kept frozen to stop fermentation process. These samples were later analyzed for flavor profile as shown in Fig. 5.2. It was interesting to see the appearing of peak of ethanol in 48hrs sample while disappearing peaks in original solution. In 168hrs sample, almost all the flavor components in original solution were disappeared and the peak of Ethanol was prominently increased. Fig. 5.3 is a comparison of flavor profile of commercially available apple wine (Cider wine) and wine made from progressively freeze-concentrated apple juice (New wine). New wine was having an alcoholic content almost 2 times higher than cider wine along with the other flavor components. However as described before, the accurate

amount of other flavor components cannot be quantified due to the limitation of the flavor analysis method.
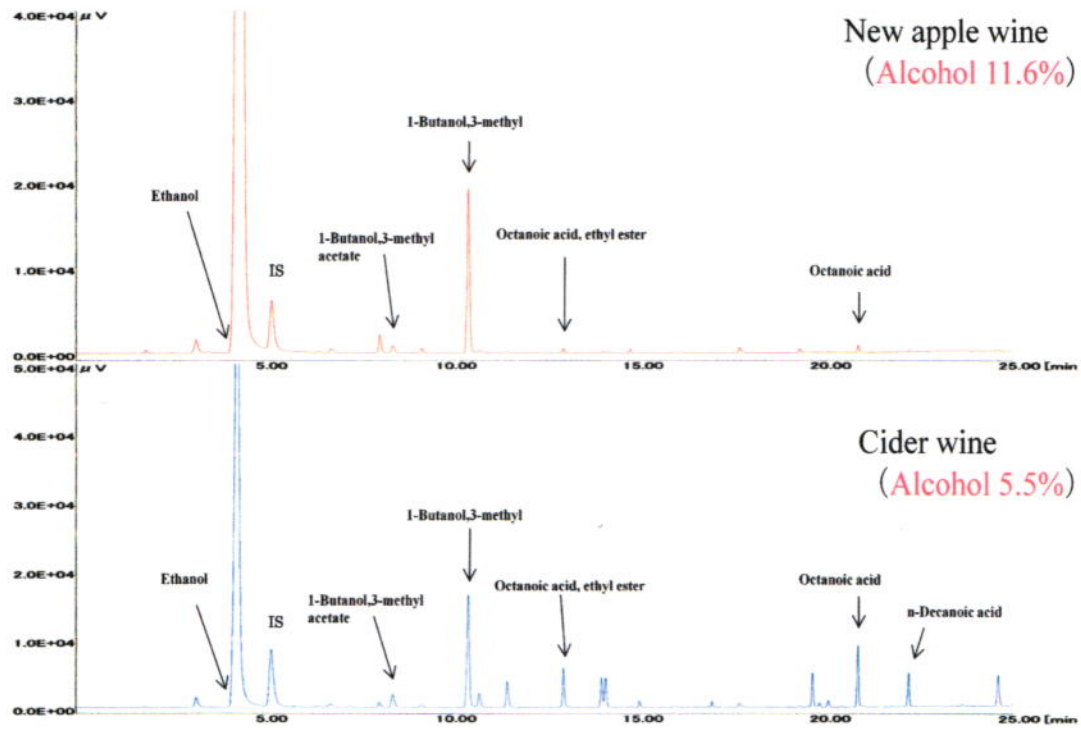

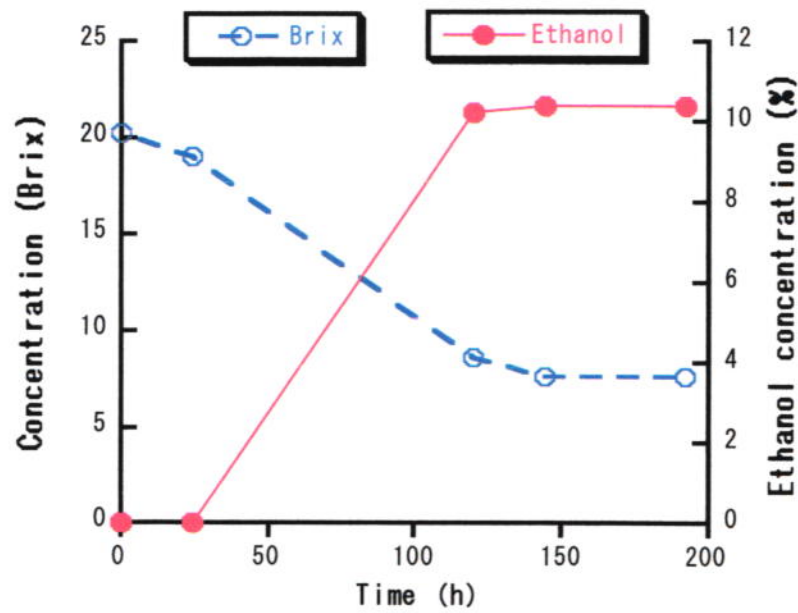Fig 5.3 Comparison of flavor profile between new apple wine and Cider wine

Fig. 5.4 Fermentation of progressively freeze-concentrated watermelon juice

Watermelon wine was produced by using progressive freeze-concentrated watermelon juice. Fig. 5.4 shows the change in soluble solid content and ethanol content with time during fermentation. Soluble solid content (brix) mainly represent the sugar content of the solution. Initially concentrated watermelon juice was having a high brix value of 20% and it gradually decreased about 10% brix during fermentation for 200hrs. During that time sugars had converted in to ethanol as shown in Fig. 5.4. Finally by using progressive freeze-concentrated water melon juice, a new wine having a high ethanol content about 10% and sugar content about 10% was possible to produce.

5.5 Conclusion

Tubular ice system of progressive freeze-concentration is a very flexible system and it can be used for a wide range of production scales. Due to it's flexibility along with the high-quality concentration preserving aroma and other components in original solution, the concentrated products can be used for development of new food products.

Using tubular ice system, Kaga stem tea was successfully concentrated achieving a high yield of 93%. Flavor analysis showed that most of the flavor components were effectively concentrated. Japanese sake (Genshu) was concentrated from 17.5% to 28.9% alcohol by tubular ice system. All the quality related parameters have successfully increased along with the flavor components. Apple juice was concentrated up to 25.5% Brix from initial 13.7% brix and this concentrated apple juice was fermented to produce apple wine. The apple wine obtained had an alcohol content of 11.63% whereas that for the commercially available apple wine (Cider wine) was 5.5%. This technique will be applicable to many other fruit juices and it is possible to make new wines such as watermelon wine which are not available in market.

SUMMARY AND CONCLUSIONS

Freeze-concentration is the best concentration method for high quality liquid food concentration due to its mild operation at low temperatures. The only commercially available freeze-concentration method is known as suspension crystallization method. Despite of the technological maturity, due to high investment cost and complicated operation the application of this method of concentration is limited. Progressive freeze-concentration is a much simpler and flexible freeze-concentration system compared to the conventional suspension system. Due to its simple and flexible operation, the scale-up tubular ice system for progressive-freeze concentration could offer a wide range of possible applications to a verity of liquid foods with different scale of operation. Therefore, following studies were done in order to develop this concentration method as a commercially viable high quality concentration method: (1) Behavior of solute inclusion in ice phase during progressive freeze-concentration and impact of operating conditions, (2) Application of tubular ice system for a variety of liquid food with optimum operating conditions, (3) Yield improvement by partial melting of ice produced in tubular ice system using a partial melting vessel, (4) Comparison of flavor retention among concentration methods, (5) Development of new food products using progressive freeze-concentration.

Chapter 1 discussed about the analysis of solute distribution in ice phase of progressive freeze-concentration. The solute inclusion in the ice phase was increased with the progress of the concentration process. From the solute concentration in the solid phase, the corresponding liquid phase concentration was calculated. From this, an effective partition coefficient, K, was obtained for progressive freeze-concentration. Theoretically, K was assumed to be constant during the concentration process and it was experimentally proved. K obtained from the concentration polarization model was agreed well with that obtained from the ice phase analysis. K values from the two methods increased with an increase in solute concentration of sucrose, which corresponds to the higher incorporation rate of solute into the ice phase in progressive freeze-concentration.

The scaling up of progressive freeze-concentration by tubular ice system was described in Chapter 2. Tubular ice system was a compact, simple system where the total capacity can be easily increased by adding more tubes into the system. The separation efficiency of solutes from ice was controlled by cooling rate of the tube and circulation speed of the solution inside the tube. The optimum operating conditions for the different solutions with different osmotic pressures were found.

The use of partial melting vessel for increasing the yield for high concentrated solution in progressive freeze-concentration was explained in Chapter 3. A simple partial melting vessel was used to melt ice produced in tubular ice system, by controlling vessel temperature and mixing ice. The optimum operating condition for melting ice of 10% sucrose was the lowest vessel temperature ($0\,^\circ$ C) and the fastest mixing speed (200rpm). By melting and recovering 30-40% of solute incorporated ice of

watermelon juice, Japanese pear juice and apple juice, yield was improved up to 85%. For apple syrup with the highest solute concentration, partial melting found to be very effective. By recovering the fractions with concentration higher than 20% brix, the yield improved from 60% up to 80%. The amount of flavor recovery for pear juice flavor condensate was quantified using flavor component of butyl acetate. The initial melted fractions gave relatively high flavor concentrations even the solute incorporation with ice was relatively low for low osmotic pressure solution. The above described partial melting vessel with simple operation could be easily applicable for future commercial scale application of progressive freeze-concentration method by tubular ice system.

Concentration of coffee extract and pear (La France) juice flavor condensate was carried out by progressive freeze-concentration (PFC), reverse osmosis (RO), and evaporation (Evp) in Chapter 4. The results in terms of the flavor retention in the three concentration methods were compared. PFC gave the best quality after concentration and reconstituted product showing the closest flavor distribution balance to the original solution before concentration. RO gave an intermediate quality product and the poorest quality product was observed in Evp. In RO, some of the low-molecular flavors were lost mainly because of the permeation through the membrane. Most of the flavors were lost in Evp and some were transferred to the condensate although it was operated at the reduced pressure with a boiling point at 50 ^{0}C. These differences were caused by the difference in the mechanism of separation of solute from the solution among the three. In PFC, separation and concentration are nonselective among the components while these are highly selective in RO and Evp.

Due to the unique features of tubular ice system and superior qualities of the concentrated products produced by tubular ice system, the concentrated products were identified as new food products and raw materials for making new products which do not exist in the present liquid food market. The details of these products are described in Chapter 5. Kaga stem tea was successfully concentrated as a Kaga stem tea flavoring ingredient. Japanese sake (Genshu) was concentrated from 17.5% to 28.9% in alcohol content. All the quality related parameters have successfully increased along with the flavor components. This was identified as a new, high alcoholic sake. Apple juice was concentrated up to 25.5% brix from initial 13.7% brix and this concentrated apple juice was fermented to produce apple wine. The apple wine obtained had an alcohol content of 11.63% whereas that for the commercially available apple wine (Cider wine) had only 5.5% alcohol. This technique will be applicable to many other fruit juices and it is possible to make new wines such as watermelon wine which are not available in market.

By using theoretical knowledge of progressive freeze-concentration, scaling up of progressive freeze-concentration was implemented as a closed tubular ice system with a circulating flow. An easy method to overcome the limitation of low yield for high concentrated solutions in progressive freeze-concentration was assessed using partial ice melting vessel. The superiority of progressive freeze concentrated products in terms of flavor components retention was revealed to support this method as a

high quality concentration method. New food products, which could not be obtained by using conventional concentration, were identified. All these findings proves progressive-freeze concentration as a novel high quality liquid food concentration method for commercial scale application using tubular ice system along with simple partial ice melting technique.

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