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Influence of Ice Recrystallization on Rheological Characteristics of Ice Slurries and Physicochemical Properties of Concentrated Milk

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Abstract Freeze concentration of milk was carried out through the controlled recrystallization of ice in a multi-stage freeze concentrator. Rheological characteristics of ice slurries were analyzed to determine efficient concentration levels for the freeze concentration process. It was determined that efficient concentration level was 17% of total solids in the first and 27% in the second stage. Physicochemical properties were compared between freeze concentrated and evaporated milk. Freeze concentrated milk was more similar in color appearance to control milk than was evaporated milk. pH significantly decreased in evaporated milk than in freeze concentrated milk. pH of freeze concentrated milk resulted in similar value to control. These results indicated the advantages of freeze concentration as a non-thermal milk processing technology in terms of physicochemical properties. Consequently, we investigated the influence of ice recrystallization on the rheological characteristics of ice slurries and physicochemical properties of freeze concentrated milk.

Keywords: freeze concentration, recrysallization, milk, rheological properties

Introduction

In the dairy industry, concentrated milk has been widely used as intermediate materials or final products for consumers. The water content in milk must be reduced by 70% in order to obtain a concentrate, so there should be some operation to eliminate excess water (1). There are generally three methods for the concentration of liquid food: evaporation, reverse osmosis, and freeze concentration (2). Of these methods, the evaporation process is most widely used for the concentration of milk in the dairy industry. However, there are some problems due to thermal processing such as discoloration, heat-coagulation, and burnt flavor in the final products. Milk contains various nutritional components and biologically active substances necessary for both infants and adults (3). When milk is heated above 70°C, the whey protein denatures and interacts with other milk proteins (4). Therefore, freeze concentration is currently being studied as a non-thermal processing technology in the dairy industry.

In freeze concentration, water is separated from other liquids by crystallized ice at low temperatures. No heat-induced changes occur, thus resulting in high quality products (5). Freeze concentration is carried out in an enclosed system at below freezing temperature and possesses several unique advantages. These include low chemical deterioration, microbiological, and enzymatic activity, which originate in non-thermal processing. There is no loss of volatile aroma components, owing to the absence of liquid-vapor interfaces in the closed system. Freeze concentration also results in lower product losses (6). Qualitatively, freeze concentration has been known to be the best among the above three methods of concentration in giving the highest retention of flavors and thermally fragile compounds (2). It is possible to contain aroma components in the solution with no gas phase using this method, which is applicable to heat sensitive liquid solutions (6-8). Therefore, freeze concentration has been applied to produce concentrated fruit juices and products like coffee, tea, and dairy products (9). However, in the dairy industry, its' industrial application has been limited by low solute concentration of final product. According to Zhang and Hartel (10), freeze concentration in a multilayer freezer was only feasible for low-concentration (10-17%) skim milk.

One important prerequisite for freeze concentration is the flow property of ice slurries to separate liquid and solid phases. These rheological characteristics of ice slurries have a major influence on the efficiency of freeze concentration coupled with the filtration process. Ice slurries are a mixture of fine ice crystals, water, and solute additives (11). The crystal size in ice slurries can vary between 100 μm and 12 mm in diameter (12, 13). Ice slurries have very good thermophysical and transport properties almost like liquids and can be pumped through pipes or stored in tanks (14). However, there has been little research about the properties of ice slurries in relation to the freeze concentration process. In addition, a basic understanding of the physicochemical characteristics of freeze concentrated milk are required for industrial application. Therefore, this study was conducted to investigate the rheological characteristics of ice slurries and the basic qualitative aspects of freeze concentrated milk.

Materials and Methods

Sample preparation LTLT (low temperature long time, 63°C, 30 min) pasteurized whole milk having initial total solids of 13% was purchased from local markets and pre-cooled at 4°C for 12 hr. About 1,860 mL was then loaded into the concentrator for each freeze concentration process.

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Freeze concentration process Freeze concentration was carried out in a multi-stage freeze concentrator (Fig. 1), using the technique described by Park *et al.* (15). Ice crystals were formed on the inner wall of the stainless steel vessel (Ø135×200 mm) by circulating coolant from a cryostat (FP-80; Julabo, Seelbach, Germany). A teflon scraper continually rotated at 50-60 rpm in the center of the concentration vessel to remove ice crystals while maintaining a minimum distance of 1.5 mm from the inner wall. Ice crystals removed from the inner wall were collected in the central part of the vessel and recrystallized. Coolant temperature was varied to accelerate the recrystallization of ice, which is referred to heat and cold shock in this study. Initial freezing occurred at a sample temperature of -4°C coupled with nucleation and crystallization. After nucleation, coolant temperature was increased from -4 to a constant -2°C during the recrystallization process. Sample temperature was -0.3°C in the early stages and was slowly decreased to -1.8°C by the end of the recrystallization process. Temperature profiles of coolant and milk were collected with a K-type thermocouple and data logger (MV-100; YOKOGAWA, Tokyo, Japan). Ice crystals and milk concentrate were filtered using a stainless steel net (200 mesh) and a vacuum pump. After the first stage, concentrated milk was transferred to the second stage to increase solute concentration.

Evaporation process Evaporated milk was prepared to have the same total solids as freeze concentrated milk through the vacuum evaporator (R-205; Büchi, Bern, Swiss). During evaporation, the vapor temperature was maintained at 70°C under a vacuum state of 200 to 250 Torr to prevent major changes in milk components.

Total solids Total solids of filtered product were measured with an infrared vacuum drying unit manufactured in our laboratory. During infrared vacuum drying, vacuum was maintained at 0.02 Torr and infrared intensity was set to 100 W.

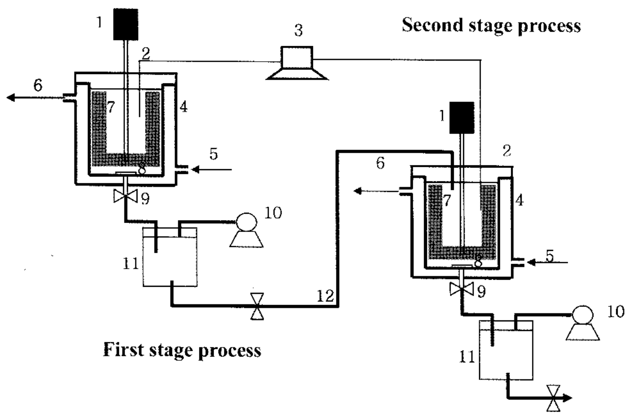

Fig. 1. Schematic diagram of the multi-stage freeze concentrator. 1. D.C. motor, 2. Thermocouple, 3. Data-logger, 4. Stainless steel vessel, 5. Coolant inlet, 6. Coolant outlet, 7. Teflon scraper, 8. 200 mesh, 9. Valve, 10. Vacuum pump, 11. Sample container after filtration, 12. Sample transportation pipe for the second stage process.

Rheology of ice slurries Rheology of ice slurries was analyzed according to ice slurry volume fraction and viscosity of concentrated liquid. Viscosity of ice slurries and their flow behavior index was calculated. Viscosity of concentrated milk was measured with a rotational viscometer (VISCO STAR-L; J.P. Selecta S.A., Abrela, Spain). Temperature of the sample was fixed at 5°C and spindle 1 rotated at 200 rpm.

Ice crystal size Ice crystal size was measured with a low-temperature stereo microscope system (CX40; OLYMPUS, Tokyo, Japan). After filtration, separated ice crystals were fixed on a cold tray connected to a cryostat (RBC-11; JEIO TECH, Seoul, Korea). Images of ice-crystals were transmitted to a computer and analyzed with the image analysis program (Image Tool 3.0; UTHSCA, Austin, TX, USA). For statistical analysis, more than 100 ice crystals were analyzed.

Colour measurement Colour values were compared between freeze concentrated and evaporated milk with a colorimeter (CR210; Minolta, Tokyo, Japan) after calibrating control values with fresh milk on a standard plate (X=97.83, Y=81.58, Z=91.51). L^*, a^*, and b^* values were measured as indicators of lightness (L^*), redness (a^*), and yellowness (b^*), respectively. ΔE value as total colour difference was calculated described in Eq. (1).

$$\Delta E\ \text{value} = \sqrt{(L^* - L^{*\prime}) + (a^* - a^{*\prime}) + (b^* - b^{*\prime})^2} \qquad \text{Eq. (1)}$$

L^*, a^*, b^*: each colour value of control, $L^{*\prime}$, $a^{*\prime}$, $b^{*\prime}$: each colour value concentrated milk.

Freezing Point (FP) FP of each type of concentrated milk was measured with a Beckman thermometer. After sampling of 50 mL concentrated milk in the aluminum container (∅ 30×60 mm), coolant was circulated through the heat exchanger with constant stirring of the sample to minimize supercooling. Sustention of mercury meniscus was determined as the freezing point which represented the freezing plateau for the phase transition.

pH The pH values between freeze concentrated and evaporated milk were compared using the glass electrode pH-meter (Model 440; Corning, Schiphol-Rijk, the Netherlands).

Statistical analysis The data obtained from three replications were analyzed by ANOVA using the SAS statistical program (V8, SAS Institute, Cary, NC, USA), and differences among the means were compared using Duncan's multiple range test. In ice crystal distribution, the Kolmogorov-Smirnov test was carried out to compare pairs of cumulative distribution at a confidence level of 95%.

Results and Discussions

Rheology of ice slurries Rheology of ice slurries was described with several parameters (Table 1). After filtration of liquid concentrate, ice slurry volume fraction (I_f) was calculated in the volume ratio of non-filtrated ice slurries

Table 1. Parameters in the flow property of freeze concentration

Total solids (%)	Process[1)]	I_f	μ_l (Pa·sec)	μ_s (Pa·sec)	F_i
13 (control)		0	0.010	0.010	100[a]
17	F-2H	0.420±0.009[c2)]	0.012	0.079±0.006[c]	12.784±0.988[a]
22	F-4H	0.610±0.004[a]	0.017	1.174±0.077[a]	0.854±0.056[b]
27	S-4H	0.540±0.012[b]	0.025	0.709±0.122[b]	1.439±0.246[b]

[1)]F-2H, 2 hr recrystallization in the first stage; F-4H, 4 hr recrystallization in the first stage; S-4H, 4 hr recrystallization in the second stage.
[2)]Means within same column with different superscript are different ($p<0.05$).

to filtrated liquid concentrate. The maximum value was observed as 0.61 at 22% solute concentration after 4 hr of recrystallization in the first stage. In the second stage concentration, I_f was lower after 4 hr of recrystallization than in the first stage of processing. The reduced water content in the second stage concentration appears to be the reason for the low I_f.

Viscosity of each liquid concentrate (μ_l) was measured with a rotational viscometer after filtration. Concentrated milk showed shear stress linearly proportional to the velocity gradient in the direction perpendicular to the plane of shear typical of Newtonian flow behavior. Similar results were observed in the work of Chang and Hartel (5) in which skim milk exhibited Newtonian behavior at solute concentrations less than 40%.

The direct measurement of viscosity (μ_s) of ice slurries in the freeze concentrator was not easy because of the subzero temperature. Some mathematical prediction model was needed to calculate the viscosity of ice slurries. Christensen and Kauffeld (16) presented a mathematical model (Eq. 2) from similar experimental conditions and requirements. The equation made it possible to predict the viscosity of ice slurries in our study.

$$\mu_s = \mu_l \{1+2.5\cdot I_f+10.05\cdot I_f^2+0.00273\cdot \exp(16.6\cdot I_f)\} \quad \text{Eq. (2)}$$

The maximum μ_s of 22% total solids was obtained as 1.174 Pa·sec after 4 hr of recrystallization in the first stage. However, the μ_s from 27% total solids after 4 hr of recrystallization in the second stage presented a lower value than that from the 22% solute concentration obtained in the first stage. This result originated from the excessive I_f after 4 hr of recrystallization in the first stage.

Flow behavior index (F_i) was calculated with Eq. (3), the inverse of μ_s (17).

$$F_i = 1/\mu_s \quad \text{Eq. (3)}$$

In this equation, a higher value means increased fluid flow behavior. The maximum value representing the highest flow behavior was 100 as obtained from control milk. The minimum F_i was observed as 0.854 in the 22% total solids recovered after 4 hr of recrystallization in the first stage. In our research, it was observed that F_i lower than 0.854 caused difficulties in separation of liquid concentrate from ice crystals during filtration. In addition, it resulted in significantly lower yields (<40%) in final products. Therefore, in our research, it was appropriate to maintain F_i values higher than 0.854 for technical and economical reasons. To maintain this range of F_i, it was desirable to prevent the freeze concentration from exceeding solute concentrations of 17% in the first stage and 27% in the second stage. This is especially important in the multi-stage freeze concentrator, where liquid concentrate should be transported from the first stage to the second stage process. At this time, a pressure drop occurs in relation with various parameters of ice slurries: volume fraction, viscosity, and flow behavior. In view of this, the rheology of ice slurries should be carefully considered in the freeze concentration process. Recently, there have been many studies on fluid dynamics in ice slurries. However, it is difficult to draw conclusions about the rheology and flow behavior of ice slurries due to divergent data and their interpretation in different experiments (18). These deviations might be caused by other factors related to the internal flow behavior of a non-Newtonian fluid. Such factors include the presence of recirculation zones caused by the shape of transportation mechanism (19). For Newtonian behavior in ice slurries, Egolf and Kaufell (20) demonstrated that I_f should be less than 0.15 to 0.20. From these previous authors' works, it is postulated that the fluid property of ice slurries showed a non-Newtonian behavior in the case of high ice fractions like those resulting from the freeze concentration process. Bellas *et al.* (14) reported that ice fraction growth caused a drop in pressure. This pressure drop in ice slurries could have a detrimental effect on flow behavior, transportation, and filtration efficiency in the multi-stage freeze concentrator. For optimum filtration efficiency, it was desirable to let the ice slurries have a Newtonian flow behavior with the range of I_f between 0 and 0.15 (11, 20). However, the low range of I_f needed for efficient filtration causes some problems in the concentration process. This is because I_f should exceed 0.40 to increase solute concentration according to our experimental results. Therefore, it is recommend to make homogeneous ice particles coupled with the appropriate level of F_i (>0.854) for good flow behavior. In our study, the proper concentration level was determined as 17% in the first stage. Total solid content of 27% in the second stage was based on the United States federal standards for concentrated milk, which require more than 25% solute concentration (21). In view of this, physicochemical analysis was conducted with concentrations of 17 and 27% total solids in our research.

Changes in ice crystal size Cumulative frequency and microscopic images of ice crystals at solute concentrations of 17 and 27% are shown in Fig. 2. The Kolmogorow-Smirnov test was carried out to identify the significant differences between the distributions of the two groups. In

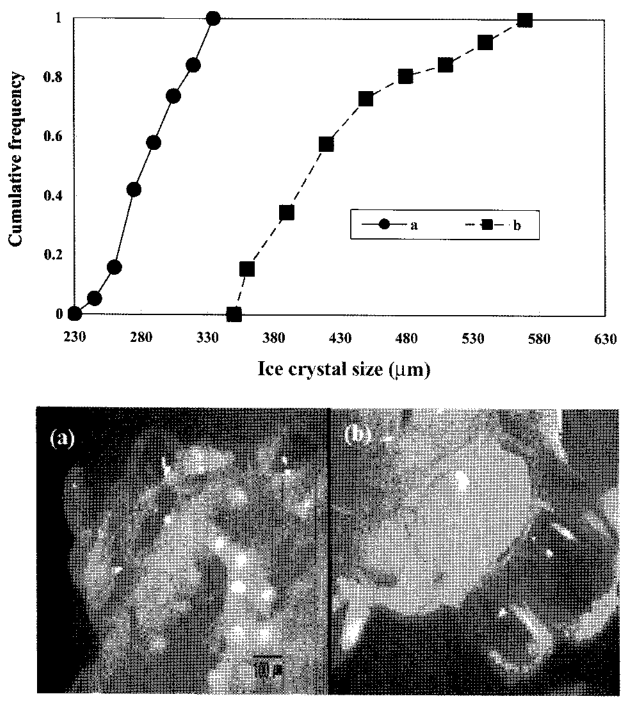

Fig. 2. Cumulative distribution and microscopic images of ice crystals after recrystallization process. (a) 17% solute concentration after 2 hr recrystallization in the first stage, (b) 27% solute concentration after 4 hr recrystallization in the second stage.

this test, *p* value of 0.0001 was obtained, indicating significant difference ($p<0.05$). Greater accumulation of large ice crystals was observed in 27% solute concentration after 4 hr of recrystallization in the second stage. The range of ice crystal size was from 360 to 600 μm, with most observed to be between 420 and 450 μm. The size range of ice crystals in milk with 17% total solids was from 245 to 350 μm, with most observed to be between 275 to 290 μm. Similar results were observed from the research of Min *et al.* (22) which greater accumulation of larger ice crystals in a sucrose matrix according to elapsed recrystallization time. Mean ice crystal size also expressed the significant difference in Duncan's multiple range test ($p<0.05$) and increased with increases in total solids and longer recrystallization time. Such increments in crystal size originate in water-vapor transport (migration) from smaller to large crystals (23) caused by different water-vapor pressure above crystals of different radii (22). In our research, this increase in ice crystal size resulted in increased solute concentrations through phase transition of water. Miyawaki *et al.* (2) reported that solute concentration increases with ice volume.

There are several kinds of ice recrystallization processes. Generally, they can be classified as two types. One is the static process (migratory, accretive, and iso-mass recrystallization) under constant temperature and pressure conditions. The other is dynamic (melt-refreeze and pressure-induced recrystallization) under conditions of fluctuating temperature and pressure. In this experiment, melt-refreeze recrystallization was conducted to increase solute concentration by heat and cold shock operation. It was important to maintain a low freezing rate for large ice crystal size. The work of Woient *et al.* (24) showed that the formation of large crystals occurred at slow freezing rates. Miyawaki *et al.* (2) proposed that a large single ice crystal, instead of many small ice crystals, is better for separating liquid solutions from ice crystals.

Microscopic images showed larger ice crystals in milk at 27% solute concentration than in 22% solutions concentration. All ice crystals were spherical and agglomerated. This spherical type of crystal was formed through the transition of dendrite into compact round crystals as determined by iso-mass recrystallization (22). In addition, the opaque state of ice crystals was significant, originating in the attachment of solute concentrates to surface and internal space of crystals. It could cause low yields of final products, decreasing the efficiency of the freeze concentration process. This phenomenon is especially significant in emulsified substances like milk with a high conjunction between hydrophilicity and hydrophobicity. Therefore, in this study, artificial melt refreeze recrystallization (heat and cold shock operation) was conducted to separate the concentrated solution from ice crystals. The limitations of concentration of solutes in milk was overcome with the multi-stage freeze concentrator and artificially-induced ice recrystallization process. Ice crystallization kinetics are being investigated in various solutions including liquid foods to obtain an optimum ice crystal size in freeze concentration (8, 17, 25-27). In the research of Huige and Thijssen (28), ice crystals with in 1 mm diameter were produced in the application of the Ostwald ripening effect. Regarding these phenomena, further experiments are required to develop an efficient freeze concentration process with the appropriate ice crystal size.

Changes in colour Table 2 describes the comparison of colour value between freeze concentrated and evaporated milk. Discoloration of milk was observed in all concentrated samples and was significant at higher concentrations. Increases in b* value in concentrated milk was the most significant. As for total colour difference, ΔE values were calculated applying Eq. (1). Higher ΔE values mean increased discoloration. The maximum ΔE value observed was 2.82 from evaporated milk with 27% total solids, whereas freeze concentrated milk with 27% total solids showed less discoloration and a lower ΔE value. Similar results were observed in milk with 17% total solids, with less discoloration occurring in freeze concentrated milk than in evaporated milk. This discoloration phenomenon is considered to be a consequence of lactose caramelization and Maillard's reaction due to thermal treatment in the evaporation process. Lactose caramelization in milk can result in a product with a bitter, unpleasant, and burned taste in insufficiently controlled thermal processing (21). Previous reports have shown that fluid milks with visual properties characteristic of whole milk have the highest appeal for consumers (29). In particular, L^* value in milk has been demonstrated to have the most positive influence on consumer appeal (30). In this study, freeze concentrated milk had L^* values more similar to controls than did evaporated milk. From our experimental results, freeze concentration induced less discoloration of milk, yielding a product with an appearance similar to that of non-

Table 2. Comparison of color value between freeze concentrated and evaporated milk

Color value[2)]	Total solids[1)] (%) 13	17		27	
	Control	FC	Eva	FC	Eva
L^*	92.67±0.12[c3)]	92.45±0.04[d]	93.28±0.08[a]	91.45±0.08[e]	92.97±0.10[b]
a^*	-3.12±0.04[a]	-3.10±0.02[a]	-3.31±0.03[c]	-3.19±0.02[b]	-3.96±0.02[d]
b^*	8.95±0.02[e]	9.60±0.05[d]	10.04±0.16[c]	10.63±0.08[b]	11.62±0.01[a]
ΔE		0.70±0.04[d]	1.22±0.09[c]	2.08±0.14[b]	2.82±0.13[a]

[1)]FC, Freeze concentrated milk; Eva, Evaporated milk.
[2)]L^*: whiteness, a^*: redness, b^*: yellowness, ΔE: total discoloration.
[3)]Means within same row with different superscript are different (p<0.05).

thermal treated fresh milk. Therefore, freeze concentration is better than conventional thermal concentration processes for preserving the original colour and appearance of milk.

Changes in viscosity Figure 3 describes changes in viscosity of freeze concentrated and evaporated milk according to increments in solute density. All samples showed Newtonian behavior, with shear stress linearly proportional to the velocity gradient in a direction perpendicular to the plane of shear. These results were in accordance with the work of Chang and Hartel (5) which showed that fluids with less than 25% total solids could be regarded as Newtonian fluids, including freeze concentrated skim milk. Viscosity of control milk represented 10 mPa·sec. Viscosity significantly increased according to solute concentration in both freeze concentrated and evaporated milk (p<0.05). Rheological properties of food suspensions also depend on concentration and temperature (31). At 27% total solids, freeze concentrated milk showed a significantly increased value of 25 mPa·sec and a value of 27 mPa·sec was seen in evaporated milk (p<0.05). However, it was difficult to recognize much difference between freeze concentrated and evaporated milk. Concentration of milk causes proportional increases in viscosity (32) and similar results were measured with a rotational viscometer in our research. Chang and Hartel (5) observed similar numerical results in their study of viscosity in concentrated skim milk. Increased viscosity could result in reduced flow rates, higher pressure drops, and decreased turbulence. In such methods as evaporation, reverse osmosis, and ultra filtration, the extent of concentration may well be limited by viscosity considerations (33). Therefore, there needs to be further understanding about the relationships between viscosity, concentration, and flow behavior during freeze concentration processes.

Changes in freezing point Freezing points of freeze concentrated and evaporated milk are shown in Fig. 4. The freezing point of each type of concentrated milk significantly decreased with increases in total solids (p< 0.05). At a concentration of 17% total solids, freeze concentrated milk had a freezing point of -0.787 and -0.763°C was the freezing point of evaporated milk. Chen *et al.* (34) reported that the freezing point of whole milk showed a depression in due to concentration. This change in the freezing point of concentrated milk should be adequately considered in multi-stage freeze concentration. It is necessary to maintain the sample temperature near the freezing point to induce large ice crystal formation and the appropriate I_f. Ice formation from aqueous solution flow is much more complex than ice formation from water flow

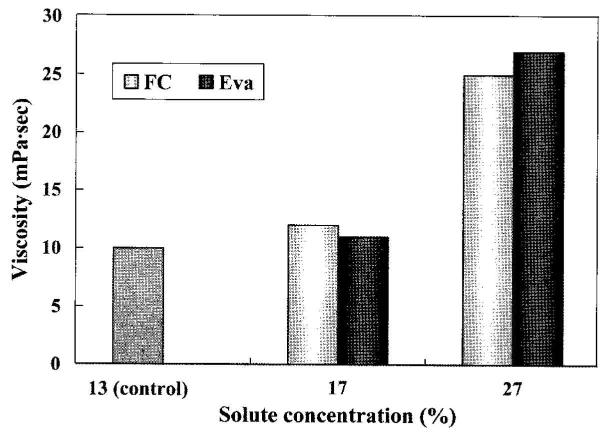

Fig. 3. Comparison of viscosity between freeze concentrated and evaporated milk. FC: Freeze concentrated milk, Eva: Evaporated milk.

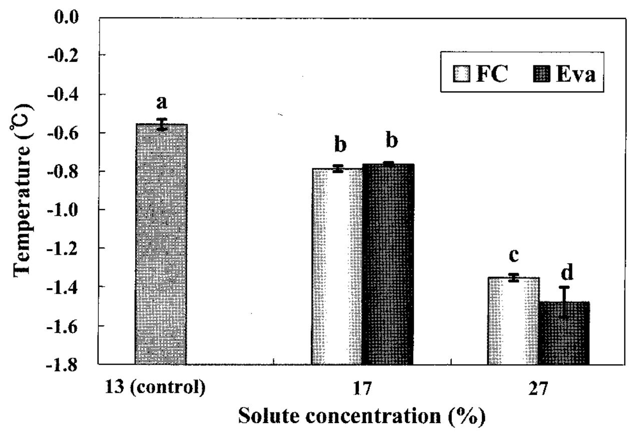

Fig. 4. Comparison of FP between freeze concentrated and evaporated milk. FC: Freeze concentrated milk, Eva: Evaporated milk. [a-d]Means in each bar with different superscript are different (p<0.05).

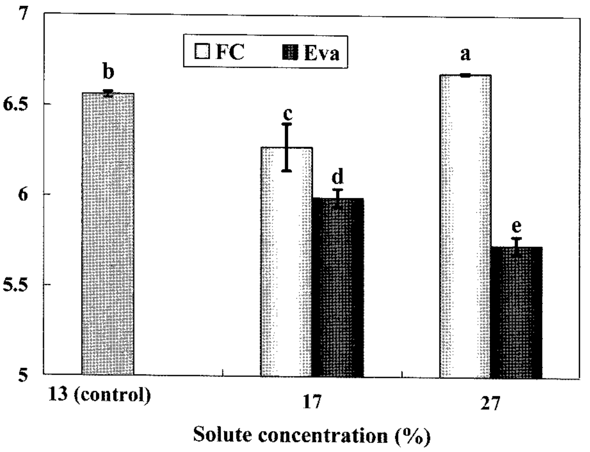

Fig. 5. Comparison of pH between freeze concentrated and evaporated milk. FC: Freeze concentrated milk, Eva: Evaporated milk. [a-e]Means in each bar with different superscript are different (p<0.05).

due to the effect of mass transfer during phase change (35). Therefore, there should be careful consideration of freezing points in the freeze concentration process.

Changes in pH Figure 5 describes the differences in pH between freeze concentrated and evaporated milk. The pH value of the control milk was 6.56 for fresh milk. Evaporated milk showed a significantly lower pH value (p <0.05) than that of control or freeze concentrated milk. At total solids concentration of 27%, the pH value of evaporated milk was 5.73, whereas freeze concentrated milk had a pH value of 6.68 similar to that of the control. Heat treatment causes this lowering of pH (<6.2) resulting in the coagulation and chemical cross links in the form of increased colloidal phosphate and lactose isomerism with organic acids (32). In the evaporated process of milk, the pH decreased, reducing protein charge and therefore facilitating association reactions (36). Greater levels of α-lactoglobulin and β-lactalbumin in association with casein micelle have been observed in heated milk adjusted to a more acidic pH (37-39). On the other hand, pH changes in freeze concentrated milk were not as significant as those of evaporated milk. Therefore, our research shows that freeze concentration can provide concentrated milk with chemical properties similar to those of fresh milk in terms of pH value.

Acknowledgments

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