Food Sci. Biotechnol. Vol. 15, No. 2, pp. 196 ~ 201 (2006)

Food Science and Biotechnology

Effect of Ice Recrystallization on Freeze Concentration of Milk Solutes in a Lab-Scale Unit

Sung-Hee Park, Jee-Yeon Kim, Geun-Pyo Hong, Hae-Soo Kwak[1], and Sang-Gi Min*

Department of Food Science and Biotechnology of Animal Resources, Konkuk University, Seoul 143-701, Korea

[1]Department of Food Science and Technology, Sejong University, Seoul 143-747, Korea

Abstract Freeze concentration of milk was carried out thorough the controlled recrystallization of ice in a multi-stage freeze concentrator. Artificial temperature control was used to induce ice recrystallization via a heat and cold shock process. In each stage of freeze concentration, the recrystallization time was fixed at 1, 2, 4, and 8 hr to compare the solute concentrate, yield, Brix, ice crystal size, and freezing point at each experimental condition. Higher concentrations of milk solids were seen with increased durations of recrystallization time, and a maximum total solids in the final product of 32.7% was obtained with a ripening time of 8 hr in a second stage process. Milk solid yield decreased according to the solute concentration and recrystallization time. The results of Brix and ice crystal size showed a positive correlation with recrystallizaiton time. These results suggest the possibility of freeze concentration being of practical use in the dairy industry.

Keywords: recrystallization, freeze concentration, milk, yield

Introduction

In the dairy industry, the concentration process has been widely used to extend the shelf life, facilitate transportation, and make processed dairy products like condensed milk and powered milk. Generally, there are three basic methods in the concentration process that can be used: the removal of water as vapor by evaporation, removal of water by reverse osmosis, and removal of solid water (ice) by freeze concentration (1).

However, concentration can cause major physicochemical, structural, and nutritional modifications to the milk if conventional thermal processing is involved (2). Milk contains various nutritional components and biologically active substances necessary for both infants and adults (3). Therefore, non-thermal processing technology is required to preserve the quality of concentrated milk in the dairy industry, and freeze concentration is being studied as one such option.

The basis of freeze concentration is to concentrate an aqueous solution by removing ice crystals produced in the solution (4, 5). It's application in the dairy industry, however, has been limited by low solute concentrate in final product (10-17%) (6). This problem is due to the special properties of emulsion in milk. It is difficult to separate the solute concentrate from ice slurries in an emulsified state, and so there should be some operation coupled with recrystallization process. Ice recrystallization processes which are of two general types. One is a static process (migratory, accretive, and iso-mass recrystallsation) involving constant temperature and pressure, and the other is dynamic (melt-refreeze and pressure-induced recrystallization) in using fluctuations in temperature and pressure. In this study, a dynamic melt-refreeze recrystallization process was used to increase milk solute concentration via artificial temperature fluctuation. This artificial variation of temperature induces the separation of solute captured in ice crystal. In addition, it produces larger ice crystals for easier separation. In this study, the physical separation of ice crystals was accomplished using mesh filtration, so it was important to maintain an appropriate ice crystal size for the filtration process. In filtration process, changes in viscosity should be carefully considered with varying temperature. Rheological properties of food suspensions also depended on concentration and temperature (7). Widehem and Cochet (8) indicated that separation efficiency strongly depends on ice crystal size and shape. Economic efficiency of freeze concentration depends largely on ice crystals in the frozen matrix with regard to yield of final products (9-13).

Nevertheless, there has been relatively little research on the freeze concentration of milk involving the recrystallization of ice which is an important factor in freeze concentration. Further studies are necessary to increase the efficiency of the freeze concentration with regard to solute yield and operation time. Consequently, this study was conducted to develop an efficient freeze concentration process through carefully controlled ice recrystallization.

Materials and Methods

Sample preparation Low temperature long time (LTLT, 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 1860 mL was then loaded into the concentrator for each freeze concentration process.

Freeze concentration process Freeze concentration was carried out using the multi-stage freeze concentrator described in Fig. 1. Ice crystals were formed on the inner wall of the stainless steel vessel (Ø135×200 mm) by

---

*Corresponding author: Tel: 82-2-450-3680; Fax: 82-2-455-1044
E-mail: foodeng301@paran.com

Received July 15, 2005; accepted December 4, 2005

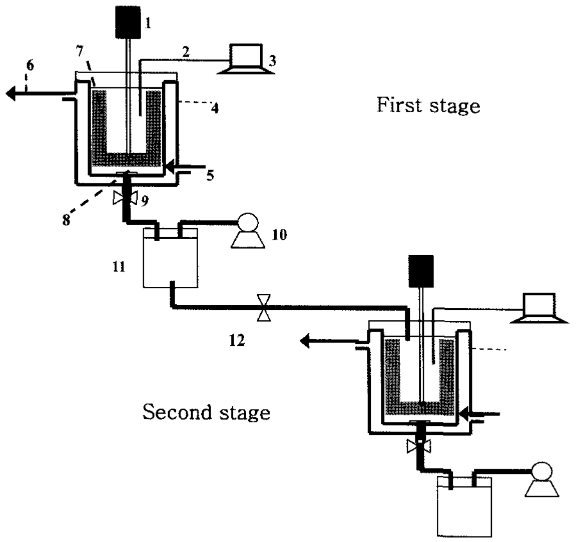


Fig. 1. Schematic diagram of the multi-stage freeze concentrator. 1. D.C. motor, 2. Thermocouple, 3. Data-logger, 4. Stainless steel vessel, 5. Coolant inlet, 6. Coolant outlet, 7. Teflon scrapper, 8. 200 mesh, 9. Valve, 10. Vacuum pump, 11. Filtrated sample container, 12. Sample transportation pipe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

circulating coolant from a cryostat (FP-80; Julabo, Seelbach, Germany). A teflon scrapper continually rotated at 50-60 rpm in the center of 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 for specific time periods (1, 2, 4, and 8 hr). Coolant temperature was varied to accelerate the recrystallization of ice in a process referred to as 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 increased from -4 to -2°C and maintained constant during the recrystallization process. Sample temperature was -0.3°C in the early stages and 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). After each recrystallization process (1, 2, 4, and 8 hr), ice crystals and milk concentrate were filtrated using stainless steel net (200 mesh) and vacuum pump. After first stage, concentrated milk was transferred to second stage process and recrystallized for specific time periods (1, 2, 4, and 8 hr).

Ice crystal size Ice crystal size was measured with a low temperature stereo microscope (CX40; OLYMPUS, Tokyo, Japan). Ice crystals removed by filtration 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 an image analysis program (Image Tool 3.0; UTHSCSA, Austin, TX, USA). For statistical analysis, more than 100 ice crystals were analyzed.

Total solids Total solids in each concentrated sample were measured using an infrared vacuum drying unit manufactured in our laboratory at a vacuum pressure of 0.02 Torr with an infrared intensity of 100 W.

Yield Yield of the concentrated milk was calculated by the mass ratio of final product to initial sample.

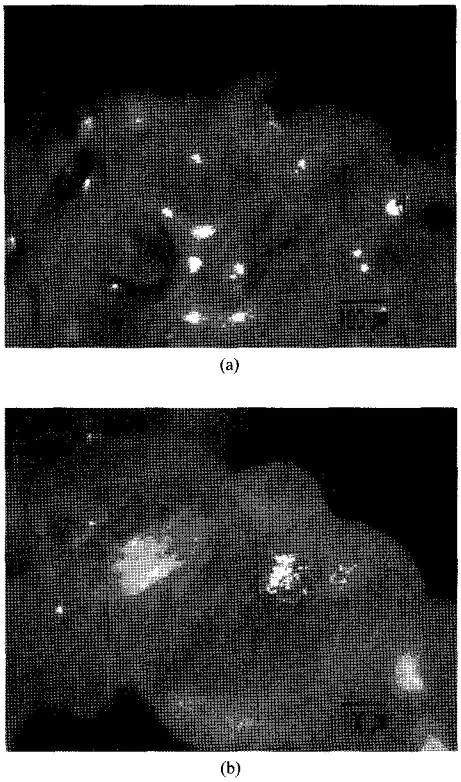
Brix Brix of freeze concentrated milk was measured with a refractometer (REF103; Greers Ferry Glass Works, Quitman, AR, USA). In this experiment, Brix measurement was used as a rapid prediction of total solids increment in the middle of the freeze concentration process.

Freezing Point (FP) FP of concentrated milk was measured with a Beckman thermometer. After sampling of 50 mL concentrated milk in the aluminum container (Ø30 ×60 mm), coolant was circulated through the heat exchanger with constant stirring of the sample to minimize supercooling. Sustention of the mercury meniscus was used as the freezing point which represented the freezing plateau for phase transition.

Statistical analysis Triplicate experimental results were evaluated statistically using the *Nalimov* Data Analysis Program (simplified *t-test*) for homogeneity of variance, and the Duncans Multiple *Range Test* was conducted to compare the significant differences among the means of respective experimental conditions using *SAS* statistics software (V8, SAS Institute, Cary, NC, USA) at the confidence level of 95%.

Results and Discussions

Changes in ice crystal size Ice crystal size continually increased during the course of recrystallization course (Fig. 2 and 3, $p<0.05$). Microscopic images of ice crystals after 1 and 8 hr recrystallization are shown in Fig. 2. Significant growth of ice crystals due to recrystallization time was observed. In this study, most of ice crystals exhibited a spherical shape and agglomerated form and this phenomenon increased with recrystallization time. Min *et al.* (9) showed that the transition of dendrites into compact round crystals depends on the process of iso-mass recrystallization, during which structures with a low thermodynamic potential form. This spherical crystal shape is likely due to the high sucrose concentration of the matix (9, 14-15), and similar results were obtained in our research. In addition, we observed an opaque state of ice crystals in this study. This originated in the attachment of solute concentrates like fat, casein, whey protein, and lactose to the surface and internal space of ice crystals. This could be a problem with regard to the yield of final products resulting in the low economical efficiency of the freeze concentration process. For this reason, a process of washing the ice crystals is commonly used in conjunction with the freeze concentration process (16-17). However, this method was not used in our study because the temperature difference between ice and the washing-water could cause melting of the ice crystals. We determined that the washing process would not be effective in the freeze concentration of milk solutes as emulsion.


(a)

(b)

Fig. 2. Microscopic images of ice crystal after (a) 1 hr and (b) 8 hr recrystallization in the first-stage process.

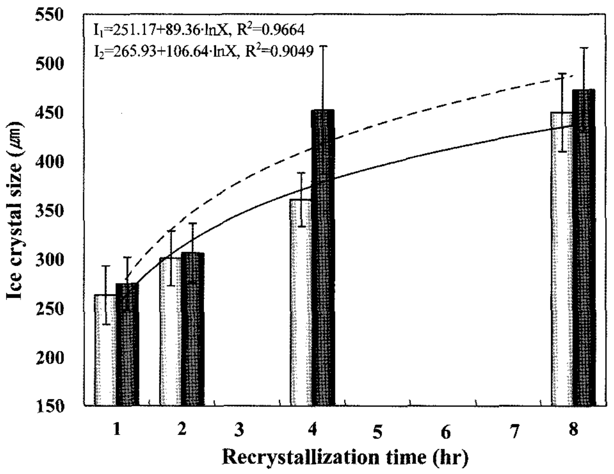


Fig. 3. Changes in ice crystal size of first stage (white bars) and second stage (dark bars) due to recrystallization time.
—— ; first stage (calculated), - - - ; second stage (calculated).
I_1: Ice crystal size (μm) in the first stage process, I_2: Ice crystal size (μm) in the second stage process, X: Time (hr).

In this emulsion state, it is difficult to isolate the solute concentrates on the surface and in the internal space of ice crystals. Therefore, in this study, we used a double stage process involving melt-refreeze recrystallization instead of a washing process.

Crystal size analysis revealed that ice crystal size increased from 264 to 450 μm in diameter as the duration of recrystallization time increased from 1 to 8 hr in the first stage process (Fig. 3, p<0.05). Similar results were observed in the second stage with ice crystal sizes ranging from 275 to 473 μm during recrystallization. These results were numerically modeled using logarithmic regression described in Fig. 3. There was a high correlation between ice crystal size and recrystallization as shown by the high R^2 values. Regarding ice crystal growth rate, more rapid growth of ice crystals was observed in the beginning of recrystalliza-tion process and these results were in accordance with the studies of Hartel and Espinel (12) which reported ice crystals that initially grew rapidly in the early stages of the freeze concentration process.

During the freeze concentration of waste water, the ice crystal weight increased with processing time (18). Many researchers have investigated ice crystallization kinetics in various solutions including liquid foods to obtain an optimum ice crystal size in the freeze concentration process (15, 19-22). As reported by Huige and Thijssen (23), ice crystals with a 1 mm diameter were produced by the application of the Ostwald ripening effect. In the recrystallization process, changes in ice crystal size were examined by Smith and Schwartzberg (24). Nowadays, the Ostwald ripening is widely used in the freeze concentration process (21).

In this study, there was a direct correlation between ice crystal size and total solids, yield such that larger ice crystal size resulted in higher solute concentration. Alternating heat and cold shock in our experiment had the greatest effect on ice crystal size during artificially induced recrystallization. In addition, caution was taken to maintain a rate of low freezing for the generation of large ice crystal sizes due to the reports of Min *et al.* (9) and Woinet *et al.* (25) which showed that low freezing rates lead to large ice crystal sizes. Therefore, we predicted that alternating heat and cold shock would promote the separation of ice slurry and solid components thus increasing the efficiency of the freeze concentration process. Careful temperature variation near the freezing point of the sample was also considered to be an important factor for accelerating the solute concentration during the freeze concentration process. Further studies involving the heat and cold shock process are necessary to increase the efficiency of the freeze concentration process with regard to ice crystal size.

Changes in total solids and yield Figure 4 and 5 represent the influence of recrystallization time on total solids and yield in each stage of freeze concentration, respectively. The solute concentrate as total solids in both stages significantly increased with recrystallization time (p<0.05). Solute concentrate increased from 13 to 27.7% as the duration of recrystallization time increased from 1 to 8 hr in the first stage of recrystallization. In the second stage, solute concentrate increased from 20.3 to 32.7% during the same period. Similar trends were reported in the research of Wideham and Cochet (8) which showed increased concentration in sucrose solution with crystallization time. As reported by Zhang and Hartel (6), solute concentrate increased with each column stages in the multilayer freeze concentrator. The resulting total solids and yield in each stage showed a close correlation with recrystallization time as indicated by high R^2 values. The

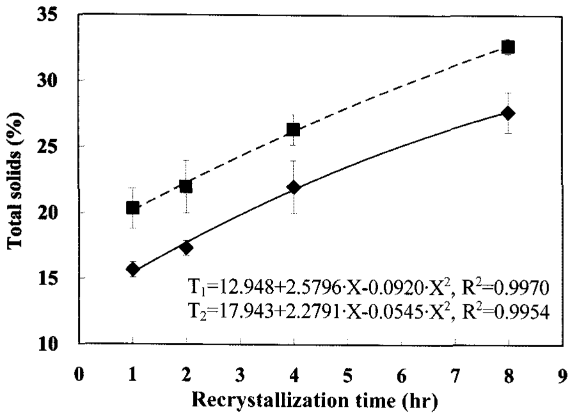


Fig. 4. Evolution of total solids in freeze concentrated milk due to recrystallization time.

◆ ; first stage (measured), ■ ; second stage (measured).

—— ; first stage (calculated), - - - ; second stage (calculated).

T_1: Total solids (%) in the first stage process, T_2: Total solids (%) in the second stage process, X: Time (hr).

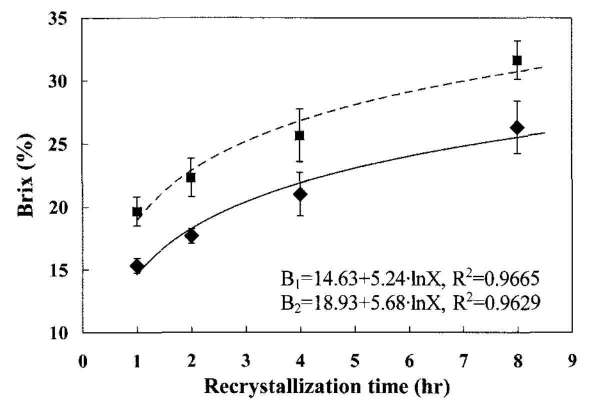


Fig. 6. Changes in Brix due to recrystallization time.

◆ ; first stage (measured), ■ ; second stage (measured)

—— ; first stage (calculated), - - - ; second stage (calculated).

B_1: Brix (%) in the first stage process, B_2: Brix (%) in the second stage process, X: Time (hr).

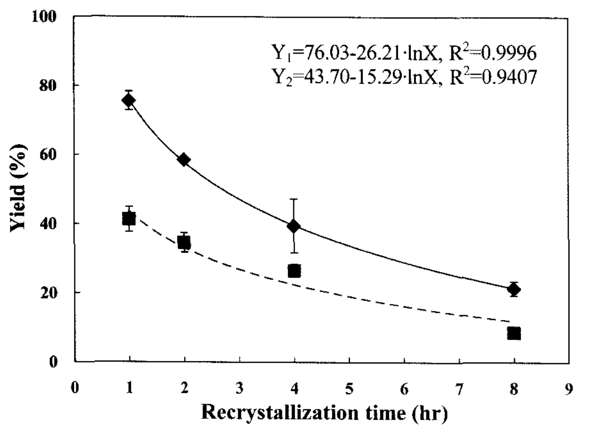


Fig. 5. Evolution of yield in freeze concentrated milk due to recrystallization time.

◆ ; first stage (measured), ■ ; second stage (measured)

—— ; first stage (calculated), - - - ; second stage (calculated)

Y_1: Yield (%) in the first stage process, Y_2: Yield (%) in the second stage process, X: Time (hr).

results of this study suggest that ice crystal size influences the yield of products and solute concentration during the freeze concentration process. The yield in each stage significantly decreased with recrystallization time, representing an inverse correlation with total solids and recrystallization time. Yield in the second stage was based on initial sample input at the first stage. Decreased yield was due to excessive ice-slurries in the concentration vessel. According to Miyawaki *et al.* (26), a large single ice crystal, as opposed to many small ice crystals, is advantageous for separating ice crystal and solution in the freeze concentration process. Therefore, there should be careful consideration as to not only ice crystal size but also the number of ice crystals generated during freeze concentration. In case of oil in water emulsion like milk, solute in the concentrate is captured by ice crystals and slurries, thus making it hard to increase the yield in the final products.

We determined that it is not desirable to progress the concentration process over 17% solute concentrate at the first stage process from the results of yield. Based on our results, we suggest that the proper degree of concentration of total solids should be 27% in the freeze concentration process which simultaneously satisfies the standard of condensed milk with relatively high yield. In the United States, federal standards for the concentrated milk require greater than 25% total milk solids in the final products (27), and our experimental results meet this qualification. Further studies are required to increase both solute concentration and yield in the relation to ice crystal size and number in the freeze concentration process.

Changes in Brix Brix results for the freeze concentration process are presented in Fig. 6. They significantly increased according to recrystallization time ($p<0.05$) and are similar to the profiles of total solids. In the first stage, brix results were 15.3 and 26.3% at 1 and 8 hr of recrystallization, respectively. Final concentrate after 8 hr of recrystallization in the second stage process was 31.7%, a value similar to that for total solids of 32.7%. In this study, Brix data were utilized as a rapid prediction of total solids in the middle of each experiment. The correlation between Brix and total solids is described in Fig. 7 and is numerically modeled with a linear regression. This numerical model was useful to predict the actual solute concentration based on a high R^2 value of determination. Caution was taken to avoid sampling ice crystals within concentrated liquid using a thin syringe (Ø 0.1 mm). Zhang and Hartel (6) used similar methods to measure the solute concentration (w/w) using the Brix index with a refractometer. In this study, there was little difference in total solids between measured and calculated values using the numerical model. Therefore, Brix measurement is as very reliable and convenient method to determine the solute concentra-

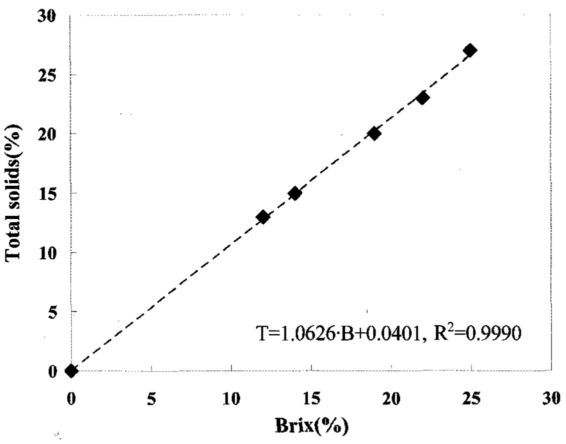


Fig. 7. The correlation profile between Brix and total solids.
◆ ; measured, - - - ; calculated.
B : Brix (%), T: Total solids (%).

tion in the middle of the freeze concentration process.

Changes in FP Figure 8 shows changes in FP due to total solids in freeze concentrated milk. The FP significantly decreased in relation to solute concentration ($p<0.05$), and these results were numerically modeled with a high R^2 of determination described in Fig. 8. The FP of raw milk was -0.56°C and it decreased to -1.93°C with a solute concentration of 33%. Similar results were obtained by Chen *et al.* (28) who reported the FP in whole milk and in concentrated milk. This FP depression in concentrated milk should be considered in the multi-stage freeze concentration process to maintain the sample temperature near the freezing point to induce the large ice crystals and proper freezing for flow behavior. Ice formation during aqueous solution flow is much more complex than ice formation from water flow due to the effect of mass transfer during phase change (29). Therefore, there should be careful consideration of FP in the freeze concentration process, and numerical modeling of FP in our research can also be utilized in the freeze concentration process.

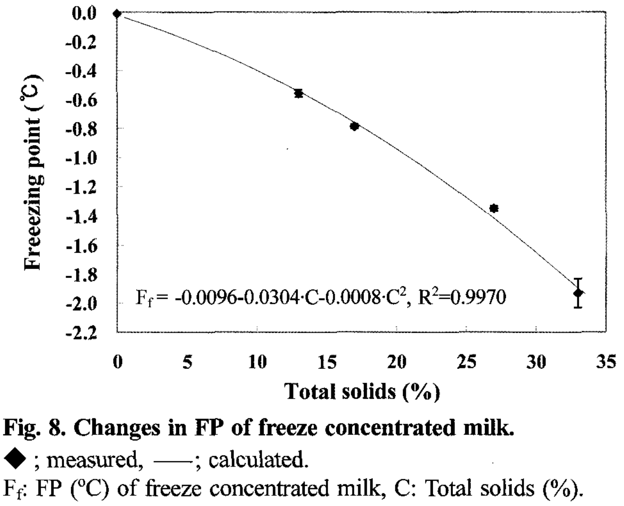


Fig. 8. Changes in FP of freeze concentrated milk.
◆ ; measured, ——; calculated.
F_f: FP (°C) of freeze concentrated milk, C: Total solids (%).

Acknowledgments

This study was supported by a grant (2004-2005) from Agricultural R&D Promotion Center.

References

1. van Mil, PJJM, Bouman S. Freeze concentration of dairy products. Neth. Milk Dairy J. 44: 21-31 (1990)
2. Vélez-Ruiz JF, Barbosa-Cánovas GV. Rheological properties of concentrated milk as a function of concentration, temperature and storage time. J. Food Eng. 35: 177-190 (1998)
3. Imm JY, Kim JG, Kim JU, Park SO, Oh SJ, Kim YJ, Chun HN, Jung HK, You SK, Whang KY, Kim SH. Microbial and nutritional quality of extended shelf life (ESL) milk. Food Sci. Biotechnol. 14: 752-757 (2005)
4. Muller JG. Freeze concentration of food liquids: theory, practice and economics. Food Technol. 21: 49-61 (1967)
5. Thijssen HAC. Freeze concentration. pp. 115-149. In: Advances in Preconcenration and Dehydration of Foods. Spicer A, Wiley J, Sons (ed). Academic Press, New York, NY, USA (1974)
6. Zhang Z, Hartel RW. A multilayer freezer for freeze concentration of liquid milk. J. Food Eng. 29: 23-28 (1996)
7. Kim CO, Yoo BS. Rheological properties of mustard suspensions: Effect of concentration and temperature. Food Sci. Biotechnol. 13: 525-527 (2004)
8. Wideham P, Cochet N. *Pseudomonas syringe* as an ice nucleator-application to freeze-concentration. Process Biochem. 39: 405-410 (2003)
9. Min SG, Wolf W, Morton I, Spiess WEL. Changes in crystal-size distribution during recrystallisation of ice in a hydrocolloid matrix. Food Sci. Technol. 8: 234-242 (1994)
10. Spiess WEL. Changes in quality of deep-frozen food in the frozen food change. Sci. Tech. de Froid. 1: 105-114 (1988)
11. Fennema OR. Frozen foods: challenges for the future. Food Aust. 45: 374-380 (1993)
12. Hartel RW, Espinel LA. Freeze concentration of milk. J. Food Eng. 20: 101-120 (1993)
13. Mellor JD. Fundamentals of Freeze-Drying. Academic Press. New York, NY, USA. pp. 67-68 (1978)
14. Smith CE, Schwartzberg HG. Ice crystal size changes during ripening in freeze concentration. Biotechnol. Progr. 1: 11 (1985)
15. Shirai Y, Sugimoto T, Hashimoto M, Nakanishi K, Matsuno R. Mechanism of ice growth in a batch crystallization with an external cooler for freeze concentration. Agric. Biol. Chem. 51: 2359-2366 (1987)
16. Ratkje SK, Flesland O. Modelling the Freeze Concentration Process by Irreversible Thermodynamics. J. Food Eng. 25: 553-567 (1995)
17. Thijssen HAC. Current developments in the freeze concentration of liquid foods. pp. 481-501. In: Freeze Drying and Advanced Food Technology. Goldblith SA, Rey L, Rothmayr WW (ed). Academic Press, New York, NY, USA (1975)
18. Rodríguez M, Luque S, Alvarez JR, Coca J. A comparative study of reverse osmosis and freeze concentration for removal of valeric acid from wastewaters. Desalination 127: 1-11 (2000)
19. Huige NJJ. Nucleation and growth of ice crystals from water and sugar solution in continuous stirred tank crystallizers. PhD thesis, Eindhoven University of Technology, Eindhoven, Netherlands (1972)
20. Stocking JH, King CJ. Secondary nucleation of ice in sugar solutions and fruit juices. Aiche J. 20: 131-140 (1976)
21. Kobayashi A, Shirai Y. A method for making large agglomerated ice crystals for freeze concentration. J. Food Eng. 27: 1-15 (1996)
22. Hartel RW, Chang MS. Contact nucleation of ice fluid dairy products. J. Food Eng. 18: 281-296 (1993)
23. Huige NJJ, Thijssen HAC. Production of large crystals by continuous ripening in a stirred tank. J. Cryst. Growth 13/14: 483-487 (1972)
24. Smith CE, Schwartzberg HG. Ice crystal size changes during ripening in freeze concentration. Biotechnol. Progr. 1: 110-120 (1985)
25. Woinet B, Andrieu J, Laurent M, Min SG. Experimental and theoretical study of model food freezing. Part II. Characterization

and modeling of the ice crystal size. J. Food Eng. 35: 395-407 (1998)
26. Miyawaki O, Liu L, Shirai Y, Sakashita S. and Kagitani, K. Tubular ice system for scale-up of progressive freeze-concentration. J. Food Eng. 69: 107-113 (2005)
27. Caric MJ. Concentrated and Dried Dairy Products. VCH Publishers, Inc. New York, NY, USA. p. 32 (1994)
28. Chen P, Chen XD, Free KW. Measurement and data input of the freezing point depression of milks. J. Food Eng. 30: 239-253 (1996)
29. Chen, P, Chen XD, Free KW. Solute inclusion in ice formed from sucrose solutions on a sub-cooled surface-an experimental study. J. Food Eng. 38: 1-13 (1998)