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Progressive Freeze-Concentration: a New Method for High-Quality Concentration of Liquid Food

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Abstract

Progressive freeze-concentration is a new concentration process in which only a single ice crystal is formed in the system so that the separation of the ice crystal from the concentrated mother solution is very easy. This makes the system much simpler to reduce the cost of freeze concentration substantially as compared with the conventional method of suspension crystallization. Principles, the method for scale-up, and expected applications of progressive freeze-concentration is discussed in this review.

Key words: freeze-concentration, ice crystal, partition constant, concentration polarization model, tube ice system

Introduction

Water is, in most cases, an overwhelmingly major component of food. Therefore, adjustment and control of water is ultimately important in food processing and preservation. Concentration is a dehydration process of food prior to transportation and preservation to reduce the process cost. This is very important for liquid food like fruits juice, milk, coffee extract etc. In the present paper, progressive freeze-concentration is discussed as a new method for high-quality concentration of liquid food.

Concentration of liquid food

In concentrating liquid food, three methods are available: evaporation, membrane concentration, and freeze concentration. Among these, the energy cost is the most expensive for evaporation (540 cal/g-water), intermediate for freeze concentration (80 cal/g-water), and the lowest for membrane concentration because of no need for phase transition in membrane separation. In evaporation process, however, multi-effect evaporation is available to recover thermal energy and some energy is required in membrane process when aroma recovery is necessary so that the difference in energy requirement among the three methods of concentration can be reduced substantially in practice (Ramteke *et al.*, 1993).

In quality, freeze concentration has been known to be the best among the three methods of concentration giving an excellent quality retaining flavors and thermally fragile compounds in concentration process (Deshpande *et al.*, 1982). In spite of this, practical application of freeze concentration is very limited so far because of the very expensive initial investment. In practice, membrane process is most frequently used although it is intermediate in quality and cost between evaporation and freeze concentration.

Conventional method for freeze concentration

In the conventional method of suspension crystallization for freeze concentration (Fig. 1(A)), separation of ice crystals from the concentrated mother solution is crucial in the process. Therefore, ice crystals are grown to large through the Ostwald ripening mechanism (Huige & Thijssen, 1972). The size of ice crystals, however, is still limited in this method so that the freeze concentra-

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tion based on this method needs very complicated system composed of surface-scraper heat-exchanger for generation of seed ice, recrystallization vessel for ice crystal growth, and washing tower for separation of ice crystals. This complicated system makes freeze concentration process the most expensive among the methods for concentration. Therefore, the application of freeze concentration is still limited in food industry.

Progressive freeze-concentration

Progressive freeze-concentration, as shown in Fig. 1 (B), is based on a completely different concept in the crystallization process as compared with the suspension crystallization method (Liu *et al.*, 1997). In this method, a large single ice crystal, instead of many small ice crystals, is grown from a cooling surface in a crystallization vessel so that the separation between the ice crystal and the mother solution is very easy. This makes the system very simple so that the process cost is expected to decrease substantially.

Historically, progressive freeze-concentration was proposed as a small-scale concentration technique for an analytical purpose applicable both to aqueous and organic solutions (Matthews & Coggeshall, 1959; Shapiro, 1961). Impurities in organic solvent were effectively concentrated by this method (Matthews & Coggeshall, 1959). However, no systematic investigation has been carried out so far on the mechanism of concentration and separation efficiency in the progressive freeze-concentration.

Figure 2 shows a test apparatus for progressive freeze-concentration used by our group (Liu *et al.*, 1997). This is composed of a cylindrical sample vessel of stainless steel, a cooling bath, and a driving system to plunge the sample vessel into the cooling bath at a constant speed to

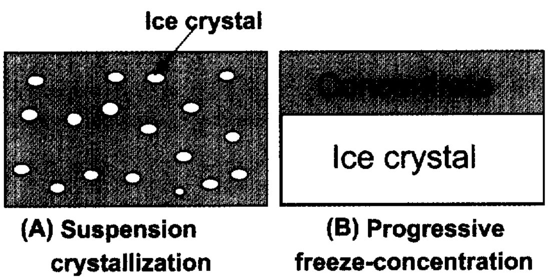

Fig. 1. Two methods for freeze-concentration.

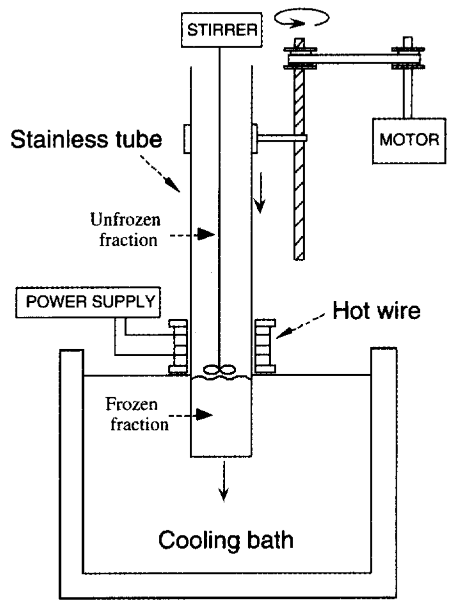

Fig. 2. Test apparatus for progressive freeze-concentration.

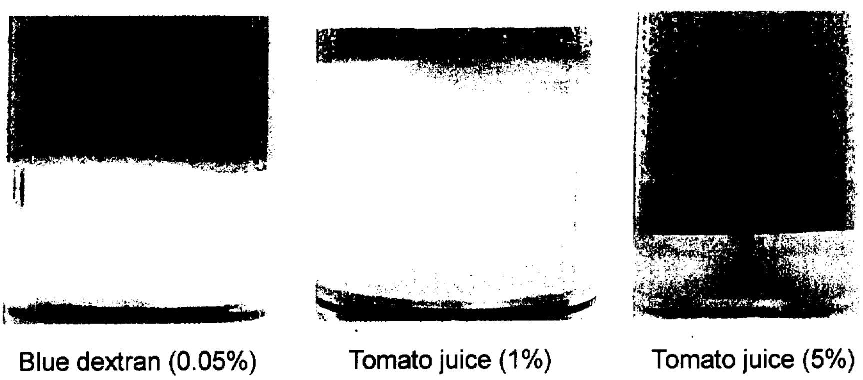

Fig. 3. Typical example of progressive freeze-concentration.

control the advance rate of ice front. The sample vessel was equipped with a propeller to stir the solution at the ice-liquid interface.

Figure 3 shows typical examples of progressive freeze-concentration of Blue Dextran solution and tomato juice. Under an appropriately chosen operating condition, an ice crystal with a high purity was obtained for the effective concentration of solute. Figure 4 shows typical changes in concentrations of solute (glucose) in ice and liquid phases with a growth of ice in the progressive freeze-concentration. The solute concentration in the liquid phase increased with a growth of ice while the solute concentration in the ice phase was kept low showing the effectiveness of the progressive freeze-concentration.

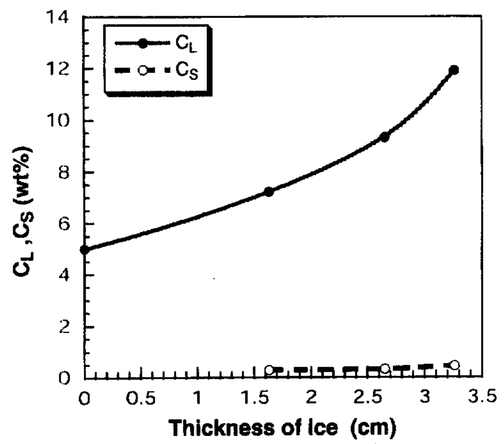

Fig. 4. Change in glucose concentrations in liquid (C_L) and ice phase (C_S) in progressive freeze-concentration of 5% glucose.

Partition of solute between ice and concentrated liquid phase

In the progressive freeze-concentration, effective partition constant of a solute, K, between the ice and the liquid phase is defined as follows:

$$K = C_S/C_L \tag{1}$$

where C_S and C_L are solute concentrations in ice and solution phase, respectively. The value of K changes between 0 (ideal freeze concentration) and 1 (no concentration). K determines the effectiveness of the progressive freeze-concentration and can be experimentally determined by the following equation (Liu *et al.*, 1997):

$$(1-K)\log(V_L/V_0) = \log(C_0/C_L) \tag{2}$$

where V_0 and V_L, respectively, are liquid phase volumes at the beginning and at an arbitrary time and C_0 and C_L, respectively, are solute concentrations at the beginning and at an arbitrary time.

Figures 5 and 6 show the plot of experimental data according to Eq. (2) to obtain K for the progressive freeze-concentration of 5% glucose. Linear lines show the effectiveness of Eq. (2) and K was obtained from the

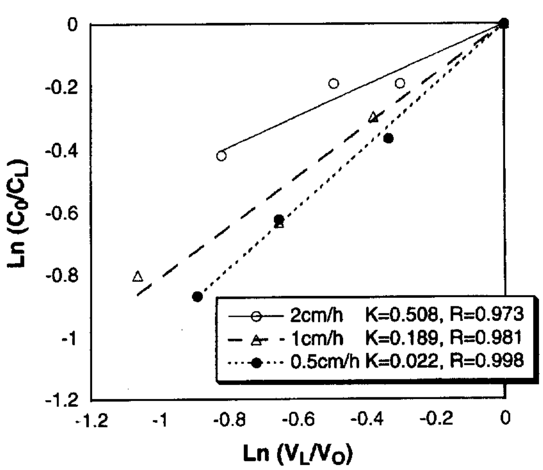

Fig. 5. Effect of advancing rate of ice front on effective partition constant (K) in progressive freeze-concentration at a stirring rate of 1400 rpm.

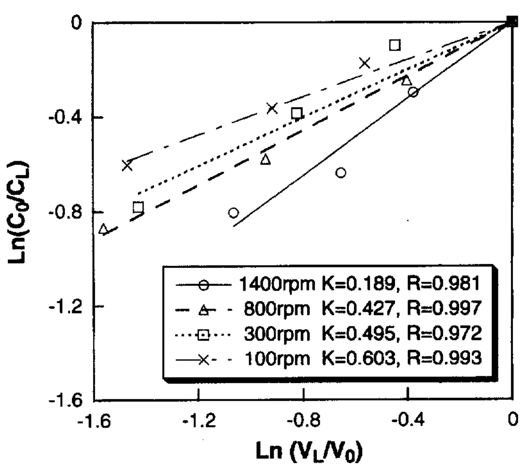

Fig. 6. Effect of stirring rate on effective partition constant (K) in progressive freeze-concentration at an advancing rate of ice front of 1 cm/h.

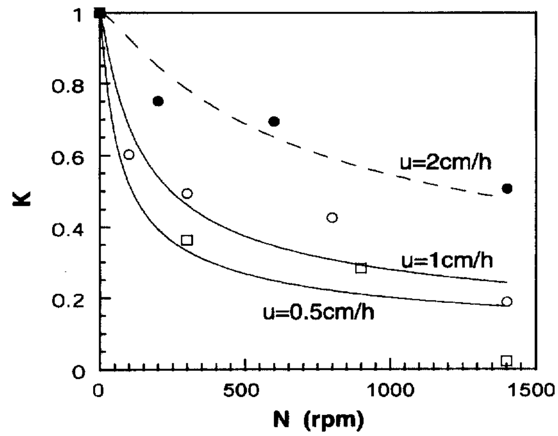

Fig. 7. Effect of stirring rate (N) and advance rate of ice front (u) on effective partition constant (K) in progressive freeze-concentration. Lines represent best-fit results by the concentration polarization model.

slope of the line.

K was strongly dependent on the advance rate of the ice front (Fig. 5) and the mass transfer at the ice-liquid interface determined by stirring rate (Fig. 6) (Liu *et al.*, 1997). K decreased, giving the higher ice purity, with a decrease in the advance rate of the ice front and/or an increase in the stirring rate. Effect of operating conditions on K was theoretically analyzed by using a concentration polarlization model as follows (Burton *et al.*, 1953; Miyawaki *et al.*, 1998):

$$K = K_0/[K_0 + (1 - K_0)\exp(-u/k)] \quad (3)$$

where K_0 is intrinsic partition constant at the ice-liquid interface, u is advance rate of ice front, and k is mass transfer coefficient at the interface. The mass transfer coefficient is expected to be related to the stirring rate, N, by the following equation.

$$k = aN^b \quad (4)$$

where a and b are parameters experimentally determined. The concentration polarization model expressed by Eq. (3) directly describes the effects of the advance rate of ice front and the mass transfer at the ice-liquid interface on the concentration efficiency in the progressive freeze-concentration. Experimental results at various operating conditions were successfully explained by this model as shown in Fig. 7 (Miyawaki *et al.*, 1998).

Table 1. Quality of reconstituted tomato juice after progressive freeze-concentration

	Control	Reconstituted (1)*	Reconstituted (2)**
Brix (%)	2.8	2.8	2.8
Concentration ratio	–	2.7	4.1
Conductivity (mS/m)	365.8	304.8	242.8
Acidity (%)	0.25	0.23	0.23
Vitamin C (mg%)	5.4	5.3	5.4
Color index			
L	24.1	22.2	22.1
a	5.28	5.76	5.94
b	13.1	11.7	11.7
a/b	0.4	0.49	0.51

*Freeze concentrated at u=0.5 cm/h and 1400 rpm.
**Freeze concentrated at u=0.5 cm.h and 600 rpm.

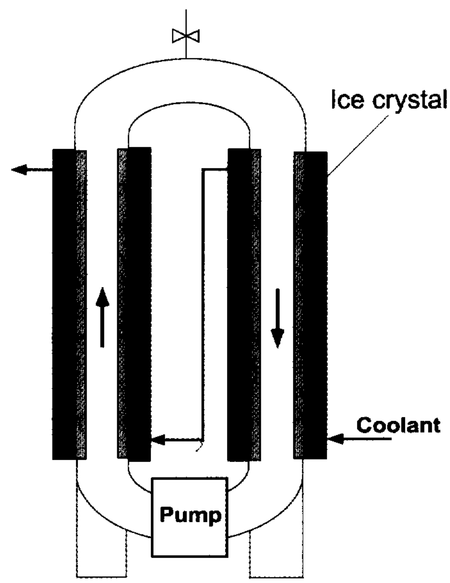

Fig. 8. Scale-up of progressive freeze-concentration by a tube ice system.

Progressive freeze-concentration was applied to concentration of tomato juice (Liu *et al.*, 1999). Tomato juice of 4.3 wt% was concentrated up to 18.8 wt%. After the concentration by the progressive freeze-concentration and reconstitution based on Brix, the quality of the juice was analyzed as shown in Table 1. No substantial differences, except for salt content, were observed in acidity, vitamin C content, or color index compared with a sample before freeze concentration showing the practical applicability of the progressive freeze-concentration to the concentration of tomato juice with a high quality.

Scale-up of progressive freeze-concentration

As compared with the suspension crystallization method, the progressive freeze-concentration with the test apparatus in Fig. 2 has much smaller surface area of ice crystal to grow so that the productivity of the apparatus was much lower. To increase the productivity of progressive freeze-concentration, a tube ice system was proposed for a scale-up as shown in Fig. 8 (Shirai *et al.*, 1999). In this method, ice crystal grows inside the cooling tube in the circulating flow so that the surface area of the growing ice increased much. In this manner, the productivity of the progressive freeze-concentration was increased to a level of practical application. By this method, tomato juice and coffee extract were effectively concentrated to high concentrations with good productivity.

Concluding remarks

Progressive freeze-concentration will change the concept of freeze concentration very much by reducing the process cost substantially. This will lead the drastic increase in the application field of freeze concentration as a method for high-quality concentration in food industry. Progressive freeze-concentration is also effective as a method for water recovery in waste water treatment. In addition, it is effective as a low-temperature energy storage and recovery system exploiting the inexpensive surplus electric power in night time. Thus progressive freeze-concentration can be a key technology in the expected environment-friendly society for the new century.

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