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Mathematical modeling and experimental validation of the mass transfer during unidirectional progressive cryoconcentration of skim milk

Alexandre Chabarov [a], Mohammed Aider [b,c,*]

[a] Cryogenic and Sub-Zero Process Development Consulting Group, Odessa 65000, Ukraine
[b] Department of Food Engineering, Université Laval, Québec, Qc G1V 0A6, Canada
[c] Institute of Nutrition and Functional Foods (INAF), Université Laval, Quebec, Qc G1V 0A6, Canada

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ABSTRACT

A mathematical model has been developed and experimentally validated to explain the process of unidirectional progressive cryoconcentration of skim milk. The capture coefficient determining the process efficiency was freezing rate dependent and the solute flow at the ice/liquid boundary layer was dependent of the competition between the heat and mass transfer phenomena. The dependence of the solute capture coefficient on the freezing velocity and the velocity of the ice/liquid interface zone was the key to understand the quantitative mass transfer to the bulk of the solution or the solute entrapment into the ice matrix. The experimental data for skim milk unidirectional progressive cryoconcentration showed that in a wide range of the ice/liquid interface velocity, and except for its smallest values, physical entrapment of the solute into the ice matrix during ice crystal growth is the predominant phenomenon. For practical purposes, it has been shown that the use of unidirectional progressive cryoconcentration for skim milk concentration is not efficient. Skim milk was cryoconcentrated from 8.50 ± 0.25% up to approximately 18% but the process efficiency significantly decreased as the ice thickness was increased. The highest process efficiency with an average value of 80% has been obtained up to 2 cm ice thickness. This efficiency drastically decreased after that to around of 3–4%. This decrease of the process efficiency was confirmed by the high solute entrapment into the ice matrix, a phenomenon that yielded in similar solute concentration in the liquid fraction and in the ice matrix.

Industrial relevance: Cryoconcentration (freeze concentration) is the best technological approach to concentrate liquid food with maintaining high quality of the concentrate. Cryoconcentration preserves the taste, aroma, color and high nutritive value of the product. Nowadays, this technique is still under used in the food industry. This is due to the serious lack of information on the mechanism and economic aspects of this technology. Several efforts have been made to improve the cryoconcentration process efficiency. The results obtained in this paper which are based on mathematical modeling followed by experimental validation showed that progressive cryoconcentration is not effective to concentrate liquid foods. The main reason is the high solute entrapment in the ice fraction. Thus, more detailed studies on other types of cryoconcentration techniques are required.

1. Introduction

The modern dairy industry is continuously seeking for new ways for effective and rational utilization of material and energetic resources. Considering the fact that whole milk is constituted by approximately 88% water, many processes involved in dairy technology can be improved if the milk is used in its concentrated form (Abd El-Gawad & Ahmed, 2011; Govindasamy-Lucey et al., 2007). For example, in the cheese making industry, the cheese yield could be significantly improved if the milk is used in a more concentrated form. Moreover, the cheese making from skim milk could be facilitated if skim milk is used in a concentrated form. In other fields of the dairy technology in which concentration is involved as a unit operation, the energy efficiency of the processes could be also improved. For example, the production of sterilized concentrated milk involves heat evaporation of the milk prior to its canning and sterilizing. The heat evaporation process requires large amount of energy supply and the product quality is affected by the process even if the latter is conducted under vacuum. The energy consumption during heat evaporation is related to the high heat of vaporization of water which is equal to 42.48 kJ/mole at 60 °C and 40.65 kJ/mole at 100 °C (IUPAC, 1977). Membrane processes are suitable for skim milk concentration because they keep the integrity of the milk constituents, mainly proteins, and do not affect the volatile compounds responsible for the specific taste of the milk. However, membrane processes require replacement of the membranes because of the fouling (Chan & Chen, 2004; James, Jing, & Dong Chen, 2003). The energy involved in membrane processes is also relatively high

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[*] Corresponding author at: Department of Food Engineering, Université Laval, Québec, Qc, G1V 0A6, Canada. Tel.: +1 418 656 2131x4051.
E-mail address: mohammed.aider@fsaa.ulaval.ca (A. Chabarov).

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because of the required pressure. Cleaning procedures are also a serious concern in the membrane processes involved in the dairy industry (Turan, Ates, & Inanc, 2002).

Cryoconcentration (freeze concentration) is recognized as the best concentration technique that can be used to avoid quality loss of liquid foods such as dairy products and plant extracts; including juices and pharmaceutics. Cryoconcentration is a dewatering process based on a freeze-induced crystallization phenomenon. Ideally, as water crystals appear during the nucleation phase and as the crystals grow, the solutes are expelled out to the solid–liquid interface. Thus, the concentration of the aqueous phase increases as pure water crystals are formed. The efficiency of concentrating solutions by freezing depends on the crystal purity, which in its turn depends of the kinetics of ice (nuclei) formation. This ice-solution exclusion phenomenon is common to all the cryoconcentration techniques. The differences between the known techniques are mainly based on how the ice is separated from the concentrated aqueous phase (Hernández, Raventós, Auleda, & Ibarz, 2010; Nakagawa, Nagahama, Maebashi, & Maeda, 2010). In our previous study (Aider & Ounis, 2012) we experimentally demonstrated that it is possible to cryoconcentrate skim milk up to 43.72 ± 0.69% (w/w) total dry matter by using four cryoconcentration cycles. Block cryoconcentration was used and it has been shown that this technique is the most promising among all the existing cryoconcentration techniques. The main limitation of the used cryoconcentration procedure is the relatively high amount of the entrapped solutes in the ice phase at the third and fourth cryoconcentration cycles. To improve the process efficiency, it is necessary to understand the mechanisms of the cryoconcentration technique from thermodynamic point of view, namely the coupled heat-mass transfer phenomenon that occurs when the concentrated phase is separated from the ice carcass. The ice carcass is the crystallized water which remains in a solid state while the concentrated fraction is drained through it. For more comprehensive details of the potential of the block cryoconcentration, it is necessary to compare this technique with the most used one, namely the progressive unidirectional oriented cryoconcentration.

Thus, the aim of this study is to highlight the main factors involved during unidirectional oriented progressive cryoconcentration of skim milk and how they control or define the limitation for obtaining highly concentrated skim milk with minimal solutes entrapped in the ice fraction.

2. Mass transfer mathematical model development

2.1. Problem formulation

Realization of a progressive cryoconcentration of an aqueous suspension involves heat transfer through a wall of a heat exchanger. In such process, the coordinates of the interface solid/liquid phase can be determined by solving the Stefan problem. Indeed, in mathematics and its applications for modeling of physical processes, particularly to phase transitions such as liquid to solid (water to ice), a Stefan problem can be used because it is a particular case of boundary value problem for a partial differential equation adapted to phenomena in which a phase boundary can move with time. The Stefan problem is used to describe the temperature distribution in a homogeneous medium undergoing a phase change such as ice thawing to water. This is accomplished by solving the heat equation imposing the initial temperature distribution on the whole medium, and a particular boundary condition, the Stefan condition, on the evolving boundary between the solid and liquid phases.

Mass transfer in the cryoconcentrator may be presented as an equation considering the crystallized (Mg) phase of the initial solution (Burdo, Kovalenko, & Kharenko, 2008).

$$\mathrm{M_i} = \beta_\mathrm{i} \cdot \left(\mathrm{C_p^\varphi} - \mathrm{C_p}\right) \mathrm{F}_i . \tau . \tag{1}$$

Where:

β_i: coefficient of the mass transfer to the crystallization front (m/s).

$\mathrm{C_p^\varphi}$ and $\mathrm{C_p}$: concentrations in the center of the solution and at the liquid/ice interface.

$\mathrm{F_i}$: surface crystalline phase (ice).

τ: cryoconcentration time (duration).

For practical purposes, it is assumed that (a) the thickness of the resulting solid phase (ice) is proportional to the square root of the freezing time, the validity of which is not in doubt for the boundary conditions of the first type, and (b) as a first approximation, for moderate values of the freezing process duration, it can be considered that the change of the thickness of the solid phase is almost the same. The resulting simplification for the identification of the time dependence of the thickness of the solid phase makes it possible to move to none conjugated mass transfer phenomenon of the problem (Philippov, 1986). This is based on the diffusion analogy when the process is undergoing in the closing conditions of the moving phase boundary of the solution resulting from the first Fick's law, which is expressed through the flow of solutes molar flux relative to the fixed coordinates (Rjazheskih, Stogney, Danilov, Lavrik, & Fokin, 2009).

$$N_p = \mu_p \cdot \left(N_p + N_g\right) - \mathrm{C}_\mu \cdot D \cdot \nabla \mu_p . \tag{2}$$

Where:

$N_p = \mathrm{C}_{\mu p} \cdot u$ and $N_g = C_{\mu g} \cdot \upsilon$ are the molar fluxes of the solutes and the dispersing medium, respectively.

$\mathrm{C}_{\mu p}$ and $C_{\mu g}$ are the molar concentrations of the solutes and solvent, respectively with $\mathrm{C}_\mu = \mathrm{C}_{\mu p} + C_{\mu g}$.

In the present study, considering that the model will be validated on skim milk, thus the dispersing medium will be the water in which the solutes are solubilized or dispersed.

The terms u and υ are the velocities of the movement of the interface zone and soluble solutes, respectively.