DOI: 10.18462/iir.iccc2022.1131

Modelling of Crystallization During Freeze-Concentration of Hydrolysates

Muhammad Umar KHAN[a], Ignat TOLSTOREBROV [a], Kristina N. WIDELL[b], Armin Hafner[a],Tom Ståle NORDTVEDT[b]

[a] Norwegian University of Science and Technology, Department of Energy and Process Engineering
Trondheim, 7491, Norway, ignat.tolstorebrov@ntnu.no
[b] SINTEF Ocean
Trondheim, 7465, Norway kristina.widell@sintef.no

ABSTRACT

Dewatering of fish protein hydrolysates is energy intensive process. The freeze concentration is one of the solutions, which provide high quality of concentrate, energy efficiency and sustainability of the hydrolysate production. This study investigates two important aspects: crystallization of water in fish protein hydrolysates and separation of the ice from the concentrate. The processes were modelled using Modelica tools and MATLAB. The models were validated via experimental campaign and literature review. When the influence of the following factors were taken into account: refrigeration temperature, fluid flow, concentration of solids and ice fraction.

Keywords: fish protein hydrolysates, freeze-concentration, separation, crystallization

1. INTRODUCTION

Fish and marine products are one of the most used protein sources for human consumption. However, a big part of the catch is utilized for production of cheap by-products such as fish meal and oil. At the same time, a growing amount of fishery and, consequently, fishing waste demands efficient solutions for their utilization since they have good nutritional source, which is highly underestimated (Petrova et al., 2018).

Fish protein hydrolysates (FPH) are produced form hydrolysation technique which involves breakdown of proteins and fats present in internal tissues of fish into smaller parts (Damodaran et al., 2007). The reaction usually takes place in a controlled condition, enzymatic hydrolysis and chemical hydrolysis were found to be the widely used hydrolysation techniques. However the enzymatic hydrolysis is more sustainable process. (Slizyte R, 2010).

An improved functional properties was reported by He et al., (2013) and Kristinsson & Rasco., (2000) when comparing the FPH to the origin protein due to breakdown of larger proteins into finer ones. The other important properties like anti-oxidative, anti-hypertensive behaviour of FPH was found to be improved as reported in several studies (Chalamaiah et al., 2012; He et al., 2013; Sarmadi & Ismail, 2010).Jenkelunas & Li-Chan., (2018) investigated and reported that FPH can be used in cryoprotectants application for fish products which are in frozen state.

Liquid FPH is a water mixture of hydrolysed proteins, the original product, which contains up to 95% of moisture. FPH in a liquid form is highly unstable moreover the transportation costs are high due to strict requirements of cold chain. Thus, dried FPH is preferable due to long shelf-life, cheap storage, and transportation. Nevertheless, at the same time, the removal of such a big amount of water from liquid FPH is a difficult and costly task, which is one of the challenges of dried FPH production (Petrova et al., 2018). Conventionally, spray dryers were widely used to remove the moisture content and convert it into final powder state. However, the industrial spray dryers are the major energy consumers of around 4 500 and 11 500 kJ/kg of moisture removed (Mujumdar, 2007).

As an alternative technique, freeze concentration and evaporation methods can be adopted before drying, which reduces the overall energy consumption rate. Freeze concentration technique is a novel method for dewatering of food products. Concentration is to stabilize the quality of food, increase shelf-life and decrease energy costs for further processing. The multistage evaporation of 1 kg of water requires energy less than 2,700 kJ/kg and for freeze concentrators ~ 330 kJ/kg of water as reported in studies by Miyawaki et al., (2005). These dewatering methods can reduce the moisture content significantly down 50-70%. This makes drying methods like freeze drying applicable due to significant decreasing of raw product flow.

The aim of this paper is to design an energy efficient freeze concentration process for fish protein hydrolysates. Dynamic modelling of crystallizer and wash column was carried out in MATLAB while simulation of refrigeration system was carried out in Dymola. Simulations were carried out to study the dynamic profile of solution's bulk temperature, diameter of crystals, ice fraction, propagation of ice, bulk cooling, calculation of freezing capacity and heat recovery.

2. SYSTEM DESIGN

2.1. Hydrolysation process

The hydrolysation process starts with the mincing of rest raw material (RRM), after the mincing process, the minced RRM is pumped to a tank. In the tank the required amount of water and enzymes are added usually 50 % of water and 0.1% of enzymes are added. The tank is heated to 50℃ and this temperature is maintained for 1 hour, which is the ideal temperature for enzymes to breakdown minced RRM to smaller peptides and amino acids. After the hydrolysation process the tank is maintained at 90℃ to terminate all enzyme activities. At the end the filtration process is carried out to separate FPH from ash and slug. The crystallizer forms a slurry of ice and concentrated hydrolysates and with the help of hydraulic wash column ice and concentrated hydrolysates solution is separated.

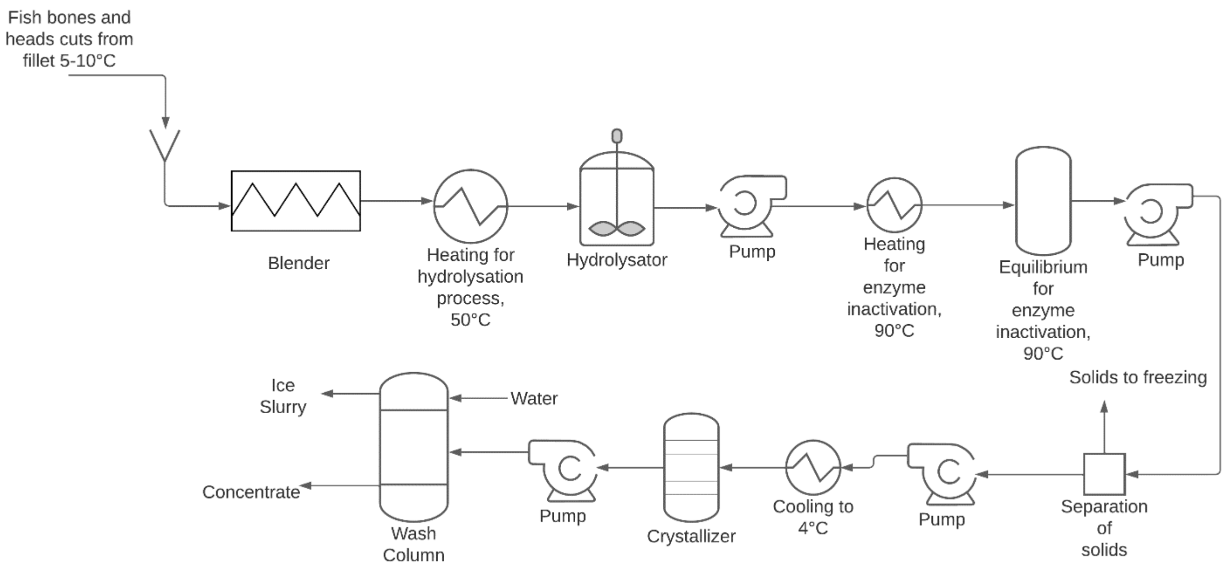

Figure 1 Systematic diagram of complete process

2.2. Simulation software

The following simulation of crystallizer and wash column were carried out in MATLAB R2018a, and refrigeration system simulation was carried out in Dymola. This software contains components and refrigerant libraries from TLK-Thermo GmbH which were used for dynamic simulations. Three libraries were used, TIL 3.90 for components such as compressors, heat exchanger and vales. TIL 3.90 was used for refrigerants and secondary fluid while TIL 3.9.2 to read and input refrigeration load files. Dave is a software from TLK which can be used to plot Dymola results. Ph and Ts diagrams can also be visualized with the help of TLK Dave. The software can read two inputs load formats MATLAB(.mat) and Excel(.csv). The software has a built-in control of different parameters and boundary conditions.

2.3. Model description

To simulate crystallizer, six coupled partial differential equations were solved, and the time discretization of those partial differential equation (PDE's) is given below:

$$\mu_0^{n+1} = \mu_0^{n} + dt * (B_0 * V) \qquad \text{Eq (1)}$$

$$\mu_1^{n+1} = \mu_1^{n} + dt * (\mu_0^{n} * v_{ice}) \qquad \text{Eq (2)}$$

$$\mu_2^{n+1} = \mu_2^{n} + dt * (2 * \mu_1^{n} * v_{ice}) \qquad \text{Eq (3)}$$

$$\mu_3^{n+1} = \mu_3^{n} + dt * (3 * \mu_2^{n} * v_{ice}) \qquad \text{Eq (4)}$$

$$T_b^{n+1} = T_b^{n} + dt * (-\frac{U * A * (T_b - T_\infty)}{V * (\rho_l * Cp_l + (\rho_{ice} * Cp_{ice} - \rho_l * Cp_l) * k_v * \mu_3^{n})} - \frac{\mu_3^{n+1} - \mu_3^{n}}{dt} * \frac{((\rho_{ice} * Cp_{ice} - \rho_l * Cp_l) * k_v * T_b - \rho_{ice} * h_{ice} * k_v))}{\rho_l * Cp_l + (\rho_{ice} * Cp_{ice} - \rho_l * Cp_l) * k_v * \mu_3^{n}}) \qquad \text{Eq (5)}$$

$$T_f^{n+1} = T_f^{n} + dt * (\frac{R * T^2}{\Delta_f * H} * \frac{-\frac{m_{s,0}}{M_s} * \frac{\rho_{ice} * k_v * V}{M_w}}{\left(\frac{m_{s,0}}{M_s} + \frac{m_{w,0}}{M_w} - \frac{\rho_{ice} * k_v * V * \mu_3^{n}}{M_w}\right) * \left(\frac{m_{w,0}}{M_w} - \frac{\rho_{ice} * k_v * V * \mu_3^{n}}{M_w}\right)} * \frac{\mu_3^{n+1} - \mu_3^{n}}{dt}) \qquad \text{Eq (6)}$$

$$v_{ice} = k_v * \left(T_f^{n} - T_b^{n}\right)^a \qquad \text{Eq (7)}$$

$$B_0 = k_n * \left(T_f^{n} - T_b^{n}\right)^b \qquad \text{Eq (8)}$$

The first four moments (Eq (1)-Eq (4)) which are used in this study, describes total number crystals, total length of crystals, total area, and total volume of crystallized material. Density multiplied by the third moment gives the total mass of crystalized material per volume of the suspension. The initial conditions are the moments of the size distribution of the seeds, the initial bulk temperature (4°C), and the initial freezing point (-0.61°C). It is assumed that the seeds are of size zero which means that the moments μ_0, μ_1, μ_2 and μ_3= 0. The total mass of hydrolysates in crystallizer were 1741 kg with 7% solids. Fish protein hydrolysates comprise of 93% of water,6.3% of protein, 0.35% of fat and 0.35% of ash, the estimation of solution was carried out to predict the properties of FPH and will be validated by experiments.

All these six equations were solved simultaneously in one time step. The simulation was run for 3600 seconds with a time step of 0.0001 seconds. The constant values used in calculation are given in nomenclature.

K_n, K_v, a and b are coefficients that are generally determined experimentally. For now, these parameters were taken from literature. Similarly, it goes of molar weight of protein but for this project molar weight of sucrose was used.

Two different approaches were used to calculate the filtration length of the wash column and the simulation to find the length was carried out in MATLAB. The time discretization of those partial differential equation (PDE's) is given below:

$$L_f^{\,n+1} = L_f^{\,n} + dt * \left(\frac{\emptyset_{feed} - \emptyset_s}{A_c * (1 - \varepsilon)}\right) \quad \text{Eq (9)}$$

$$L_f^{\,n+1} = L_f^{\,n} + dt * \left(\frac{\emptyset_{feed} - \emptyset_s}{A_c * (1 - \varepsilon)}\right) \quad \text{Eq (10)}$$

$$X^{n+1} = X^n + dl * C * e^{-a*L} \quad \text{Eq (11)}$$

$$L_w^{\,n+1} = L_w^{\,n} + dt * \left(\frac{\emptyset_{w,l} - C_l}{\varepsilon_w * A_c}\right) \quad \text{Eq (12)}$$

$$\emptyset_{ml,bottom} = A_c * \varepsilon * \left(\frac{L_w^{\,n+1} - L_w^{\,n}}{dt}\right) \quad \text{Eq (13)}$$

The refrigeration system was simulated using Dymola software with some simplifications. A simple sub critical CO_2 system was developed, with the addition of desuperheater and subcooler to increase the COP of the refrigeration system. Plate heat exchangers (heat exchanger type in Dymola) were used for condenser, desuperheater and subcooler while tube and tube heat exchanger (heat exchanger type in Dymola) were used for evaporator.

Five PI controllers were used to control the refrigeration system, the first PI controller was used to control the opening of throttling valve which senses the condenser pressure which was fixed 50 bar while the other PI controller controls the frequency of efficient compressor (compressor type in Dymola) to maintain the required suction pressure of 10 bar. Outlet temperature from the desuperheater is controlled by the mass flow of pump with PI controller, which takes outlet temperature of desuperheater as input. Inlet and outlet temperature of desuperheater is fixed to 0°C and 25°C respectively. The outlet temperature of condenser is controlled by adjusting the water flow in condenser with PI controller such as the refrigerant condenses completely. To remove the condenser heat, ice, and water slurry at 0°C is used. To increase the COP of system a subcooler was used and the outlet temperature of subcooler is controlled by adjusting the water flow to subcooler with PI controller such that the refrigerant is cooled down to 5°C.

To increase the COP of the system flooded evaporator was used and to ensure no liquid enters compressor a phase separator was included. Isentropic efficiency of compressor is fixed to 70%. Dymola doesn't contain any crystallizer library so to visualize this heat exchanger named as “evaporator” was used which cooled down hydrolysates. Due to limitation of Dymola water was used instead of hydrolysates and ice slurry.

3. RESULTS AND DISCUSSION

Based on refrigeration load subcooler, condenser and desuperheater capacities were 15.35 kW,101.65 kW and 68.5 kW respectively. After wash column the ice is washed by water which forms an ice water slurry at 0°C, the slurry was pumped through sub-cooler and condenser and the mass flow rate of this slurry was controlled by the capacity of subcooler and condenser. The requirement to melt the ice from the slurry was 111.2 kW which was covered by subcooler and condenser.

The COP was calculated by evaporation load and a constant evaporation load was maintained during the simulation by PI controller which resulted in constant COP of 2.16. There are couple of reasons why the COP of the refrigeration system is low. Single compression was used to achieve a 55-K temperature difference which increased the discharge gas temperature of CO_2 and increased the compressor work. Secondly the condenser temperature is close to critical temperature which reduces the evaporation capacity drastically.

Figure 2 shows the dynamic profile of bulk temperature. Initially the hydrolysates were at 4°C. The temperature goes down to -1.4°C without any crystallization of water which is known as subcooling process. Point a to b shows subcooling process. Point b is known as seeding point where crystallization starts, and latent heat of fusion is released which increases the temperature till initial freezing point (-0.61 °C). From b the freezing process starts and because of dissolved solutes in water the freezing point decreases and water crystallizes which is opposite to pure liquid freezes. The bulk temperature decreases till wall temperature of heat exchanger. The equilibrium was not achieved till 3600 seconds because of small surface area of heat exchanger.

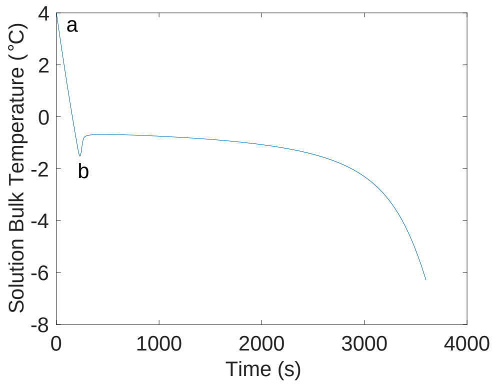

Figure 2 Bulk Temperature Vs Time

Figure 3 shows the depression of freezing point of liquid hydrolysates with respect to time. At time zero the freezing point of hydrolysates is -0.61℃ this is the initial freezing point found out experimentally using differential scanning calorimetry (DSC). With progression of time water freezes out which increases the concentration of solutes which further decreases the freezing point of hydrolysates. At the end of simulation, the concentration of solid increased till 36% which resulted in -6.3℃ freezing point depression.

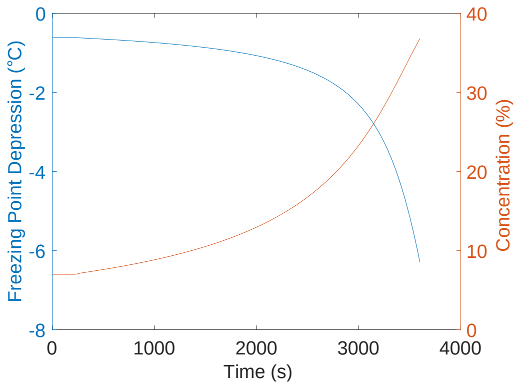

Figure 3 Concentration and Freezing point depression Vs Time

The propagation of ice in the solution is shown in ***Figure 4***. The seeding time was recorded as 230 seconds meaning that it takes above mentioned time to start the propagation of ice in water. The nucleation of ice starts at 230 seconds which gives the maximum speed of 0.9*10^{-6} m/s. Temperature difference between freezing depression point and bulk temperature is the driving force for the propagation of ice as expressed by Eq (7). Maximum subcooling is achieved during the nucleation which results in maximum propagation of ice after that the subcooling drops to zeros which decreases the propagation of ice. At the end of simulation, the propagation speed was found out 1.182*10^{-9} m/s which is approaching zero.

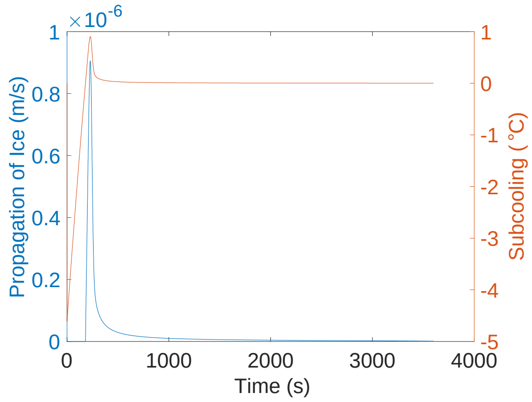

Figure 4 Propagation of Ice and Subcooling Vs Time

The simulation can be used to calculate the appropriate crystal size for subsequent washing in wash column. At nucleation the effective diameter of crystals was 0.067 mm while at the end of simulation the mean crystal diameter was found out 0.045mm. This happens because initially the number of crystals is less which results in bigger diameter as temperature drops the number of crystals increases which results in small and fine crystal diameter as shown in ***Figure 5***.

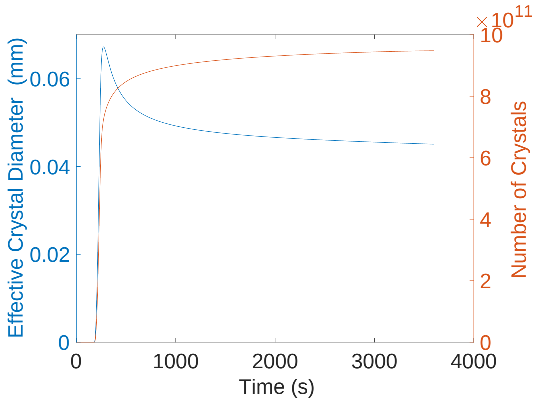

Figure 5 Effective Crystal diameter and Number of crystals Vs Time

The below graph (***Figure 6***) shows the increase of ice fraction in solution with respect to time. At the end of simulation, it was found out that 86.9 % of water turned into ice. Based on simulation results 36% of concentration was achieved. According to GEA if the viscosity of the concentrated solution increases from 30–50 mm^2s^{-1} for smooth operation it is recommended to have multiple stage step crystallizer(van Beek, 2018).

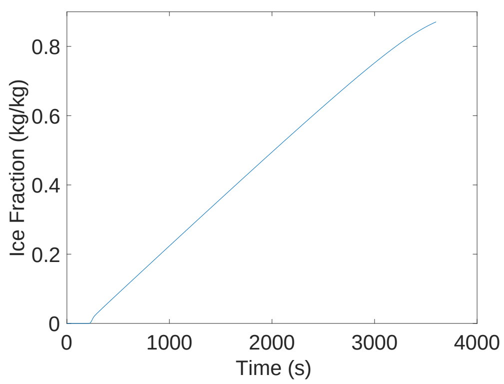

Figure 6 Ice Fraction Vs Time

The dynamic model was developed to calculate the length of filtration and wash section. Inputs such as ice fraction and feed mass flow rate were obtained from crystallizer simulation Two different approaches were used to calculate the filtration length. The first one uses exponential estimation to calculate filtration length and simulation ends with ice fraction reaches 100%. While the other simulation shows how the fluid flows and separate by passing through filters. The second one is more accurate as in includes the volume flow rate of slurry and the diameter of wash column. The first simulation results in 1.4 m of filtration length while the second simulation gives 1.3 m. These are the minimum lengths needed to separate concentrate solution from ice, the volume flow rate and wash liquid is controlled with the help of pump. Below graph (***Figure 7***) shows the simulation result.

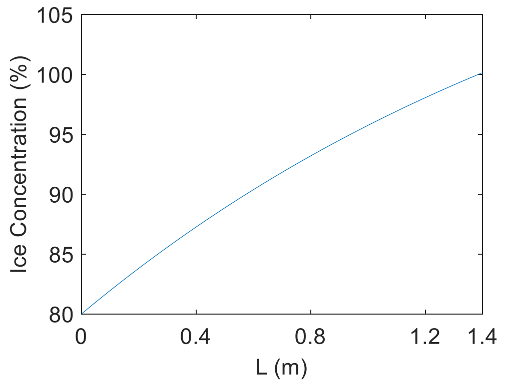

Figure 7 Ice Concentration Vs Filtration Length

After filtration ice separates from concentrated solution to wash the ice, minimum length was required by wash liquid to easily pick ice from wash column without entering filtration length was 1.1m. The total length of wash column is the sum of filtration and wash section length based on the simulation carried out the total length was calculated as 2.4 to 2.5 m. Mass flow rate of concentrated solution and ice slurry was calculated. The mass flowrate of concentrated solution can be used to calculate the energy consumption of further drying process while the mass flow rate of ice slurry was used to calculate the energy needed to melt ice. Mass flow rate of concentrated solution and ice slurry were 0.1457 kg/s and 0.3668 kg/s respectively. The mass flowrate of ice in ice slurry was 0.3328 kg/s and 111.2 kW is the required energy to melt ice. The mass flowrate of ice was calculated by subtracting the makeup water for the creation of slurry.

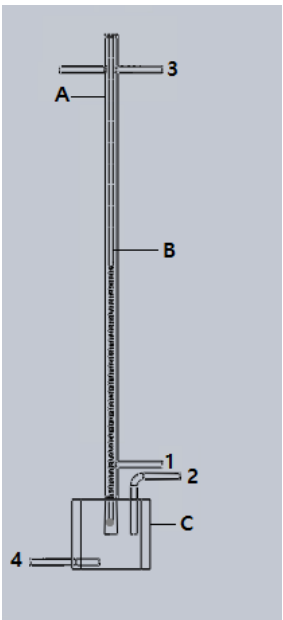

Figure 8 Front View of designed Wash column

Wash columns contains three parts named as tower(A), filter tube (B) and tank (C) as shown in ***Figure 8***. Slurry enters the wash column from (1) it fills the wash column till top, due to density differences the ice floats at top while concentrated solution settles down. Filter tube contains pores of 150µm with the help of vacuum pump attached at (2) all concentrated solution is sucked in and collected in tank. Another pump attached at (4) pumps all the concentrated solution for further drying while water enters from (3) and washes all wash column for next batch.

4. CONCLUSION

In this paper a freeze concentration process was analysed with CO_2 as a refrigerant. MATLAB and Dymola software were used to carry out dynamic simulations. Refrigeration system was designed with a maximum capacity of 127 kW, the heat recovery based on subcooler, condenser and desuperheater were 15.35 kW,101.65 kW and 68.5 kW respectively. The heat capacity of condenser and subcooler were enough to melt the ice from ice slurry and desuperheater was able to heat the recovered water up to 25℃ and the COP of the refrigeration system was 2.16.

Height and diameter for crystallizer was estimated as 2.5 m and 1m respectively. Euler time discretization was used to solve 6 coupled equations. At the end of simulation bulk temperature, depression of freezing point, mean diameter of crystals, ice fraction and propagation of ice came out as -6.2℃, -6.3℃, 0.045mm, 0.869 and $1.182*10^{-9}$ m/s respectively. Large U, heat exchanger area and lower wall temperature drastically reduced time for crystallization process. Maximum concentration of 36 percent was achieved, for smooth operation it is recommended to have multiple stage step crystallizer.

The two methods were developed to estimate the filtration length of wash column. Filtration length from exponential and dynamic simulations were 1.4m and 1.3m respectively. Dynamic wash column simulation was also used to calculate the wash section length, mass flow rate of concentrated solution and ice slurry. Wash section length, mass flow rate of concentrated solution and ice slurry were estimated as 1.1 m, 0.1457 kg/s and 0.3668 kg/s respectively.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the Research Council of Norway and industrial project partners for the financial support for carrying out the present research [NFR project No. 294662, CoolFish].

NOMENCLATURE

T_b	Bulk temperature (K or℃)	v_{ice}	Ice velocity (linear ice growth rate) (m/s)
T_{fp}	Freezing point of solution (K or℃)	B^o	Nucleation intensity (numbers/s*volume)
a	Exponent in ice growth equation (1)	b	Exponent in nucleation equation (1.25)
k_n	Nucleation constant ($1*10^{10}$)	k_v	Volume form factor ($1*10^{-6}$)
Cp	Specific heat capacity (kJ/kg.K)	U	Total heat transfer coefficient (W/m^{2}k)
M	Molar weight (kg/mole)	$Ø_{feed}$	Feed flow (0.0005 m^3/s)
L_f	Filtration Length (m)	Øs	Crystal flow (m^3/s)
A_c	Cross sectional area (m^2)	ε	Porosity in the filtration and stagnant section (0.2)
L_w	Wash section length (m)	$ε_w$	Porosity in the wash section
$Ø_{ml,bottom}$	Mother liquor flow (m^3/s)	α	Crystal fraction in feed (0.8)

REFERENCES

Chalamaiah, M., Dinesh kumar, B., Hemalatha, R., & Jyothirmayi, T. (2012). Fish protein hydrolysates: Proximate composition, amino acid composition, antioxidant activities and applications: A review. *Food Chemistry*, *135*(4), 3020-3038. https://doi.org/https://doi.org/10.1016/j.foodchem.2012.06.100

Damodaran, S., Parkin, K. L., & Fennema, O. R. (2007). *Fennema's food chemistry*. CRC press.
He, S., Franco, C., & Zhang, W. (2013). Functions, applications and production of protein hydrolysates from fish processing co-products (FPCP). *Food Research International*, *50*(1), 289-297. https://doi.org/https://doi.org/10.1016/j.foodres.2012.10.031
Jenkelunas, P. J., & Li-Chan, E. C. Y. (2018). Production and assessment of Pacific hake (Merluccius productus) hydrolysates as cryoprotectants for frozen fish mince. *Food Chemistry*, *239*, 535-543. https://doi.org/https://doi.org/10.1016/j.foodchem.2017.06.148
Kristinsson, H. G., & Rasco, B. A. (2000). Fish Protein Hydrolysates: Production, Biochemical, and Functional Properties. *Critical Reviews in Food Science and Nutrition*, *40*(1), 43-81. https://doi.org/10.1080/10408690091189266
Miyawaki, O., Liu, L., Shirai, Y., Sakashita, S., & Kagitani, K. (2005). Tubular ice system for scale-up of progressive freeze-concentration. *Journal of Food Engineering*, *69*(1), 107-113. https://doi.org/https://doi.org/10.1016/j.jfoodeng.2004.07.016
Mujumdar, A. S. (2007). Handbook of industrial drying. http://www.crcnetbase.com/isbn/9781574446685
Petrova, I., Tolstorebrov, I., & Eikevik, T. M. (2018). Production of fish protein hydrolysates step by step: technological aspects, equipment used, major energy costs and methods of their minimizing. *International Aquatic Research*, *10*(3), 223-241. https://doi.org/10.1007/s40071-018-0207-4
Sarmadi, B. H., & Ismail, A. (2010). Antioxidative peptides from food proteins: A review. *Peptides*, *31*(10), 1949-1956. https://doi.org/https://doi.org/10.1016/j.peptides.2010.06.020
Slizyte R, G. L., Storrø I. (2010). *Processing of secondary raw materials from herring to oil and protein hydrolysate*.
van Beek, T., Budde, M. and van Esch, J. . (2018). Membrane-Freeze Concentration Hybrid for Temperature-Sensitive Biomolecules. Investigation, Application, and Techno-Economic Benefits. *Chemical engineering and technology*, 2385-2392.