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Freezing Time Prediction for Cuttlefish

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ABSTRACT The thermophysical properties of cuttlefish: moisture content, density, equilibrium freezing temperature, thermal conductivity, and specific heat were determined. The relationship between surface heat transfer coefficient and air velocity was also determined. A numerical model for freezing time prediction was developed. The freezing times calculated were compared with the experimental values and those calculated from the simplified analytical models, which were Plank model, IIR model, Cleland and Earle model, and the modified Pham model. The results showed that the developed numerical model gave the best prediction with 1.5% average error.

KEYWORDS: freezing time, thermal property, physical property, numerical model, analytical model, cuttlefish.

INTRODUCTION

Thailand has been one of the top exporters of seafoods in the world. Frozen cuttlefish is the second most exported product, after frozen shrimp. In order to improve the quality of frozen cuttlefish and reduce the cost of production, the freezing time should be at its optimum.

The freezing process consists of a reduction of temperature, generally to –18°C (0°F) or below, and crystallization of part of the water and some of the solutes.[1] Freezing time is defined by the International Institute of Refrigeration (IIR) as the nominal freezing time and the effective freezing time.[2] Freezing time as used here means time required to decrease the temperature of product at the thermal center from its initial temperature to the desired temperature which according to the international regulation is –18°C.[3] The freezing time of a product can be determined by experiment or from predictive models. The models are mostly based on analytical or numerical techniques. The Plank model[4] has the simplest equation, which assumes a uniform initial product temperature and constant density and thermal conductivity. The IIR model[2] is modified from the Plank model, which replaces the latent heat with the total heat removed from the sample during freezing. Cleland and Earle[5-6] modified the Plank model by using the equivalent heat transfer dimensionality (EHTD) for various geometric shapes of samples. Pham[7] developed a model to predict the freezing time by dividing the freezing process into 3 steps: precooling, phase change, and tempering. The time during the precooling and tempering steps was derived from Newton's equation, while the time during phase change was from the Plank model. Hossain et al.[8] modified the Pham model by including the EHTD in the model which gave a better prediction for products having more than 55% moisture content. To predict the freezing time the thermo-physical properties of products, such as moisture content, density, freezing point, thermal conductivity, and specific heat, must be known. The objective of this study was to develop a model for freezing time prediction based on the explicit finite difference technique and compare the accuracy of the prediction with various models.

MATERIAL AND METHODS

1. Sample preparation

Fresh cuttlefish (*Sepia pharaonis*) approx. 1.0-1.6 cm.-thick was purchased from the fish market (Saphan Pla) in Bangkok. The skin, viscera, and head of the cuttlefish were removed and washed under tap water, and only the mantle part was used.

2. Thermophysical properties measurement

Moisture content, apparent density, freezing point, thermal conductivity, and specific heat of frozen and unfrozen cuttlefish at temperatures of –30°C to 30°C were measured according to the methods described by Koonaree et al.[9] All measurements were done in nine replicates.

3. Surface heat transfer coefficient measurement

Aluminum plate (10x10x1.1 cm) was used as metal transducer. A hole under the surface of the plate was made in order to insert a thermocouple type T (0.076-cm diameter) which was connected to a temperature recorder (CHINO, DR015). All sides of the plate except the surface was insulated by 8-cm thick polystyrene foam having a thermal conductivitiy of 0.035 W/m.K. The initial temperature of the whole plate was controlled before placing in the air-blast freezer at $-27\pm3^{o}C$. The temperature of the cool air and the surface of the plate were recorded every 30 seconds until the surface temperature reached $-20^{o}C$. The surface heat transfer coefficient was calculated from the equation (1)[10]

$$h = (\rho_{al} V_{al} C_{pal}\, slope)/A_{al} \qquad (1)$$

where h = surface heat transfer coefficient, W/m.K
ρ_{al} = density of aluminum plate, kg/m^3
V_{al} = volume of aluminum plate, m^3
C_{pal} = specific heat of aluminum plate, J/kg.K
A_{al} = surface area of aluminum plate, m^2
$Slope = \frac{d[\ln(T_{al}-T_a)/(T_{ial}-T_a)]}{dt}$
T_{ial} = initial temperature of aluminum plate, ^{o}C
T_{al} = surface temperature of aluminum plate at any time t, ^{o}C
T_a = cool air temperature, ^{o}C
t = time, second

The schematic diagram of the sample during freezing is shown in Figure 1. The sample temperature was assumed to be uniformly constant at its initial temperature. The heat transfer during freezing was considered to be one-dimensional with the third kind of boundary condition.

4. Mathematical modeling for freezing time prediction

The numerical model for freezing time prediction was developed based on the explicit finite difference method. The calculated freezing time was compared with those calculated from Plank,[4] IIR,[2] Cleland and Earle,[6] and Pham[7] models. The computer program for the developed model was written in FORTRAN according to the flow chart shown in Figures 2 and 3, and run on FORTRAN Power Station version 1.0 for WINDOWS.

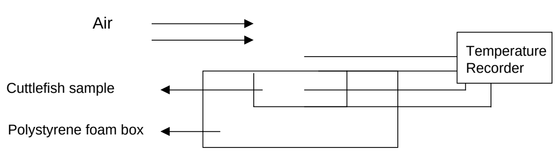

Fig 1. Schematic diagram of cuttlefish sample during air-blast freezing.

5. Verification of the model

Cuttlefish was cut to 10x10 cm slab. The dimension of the slab was measured using vernier. The thickness of the sample was varied from 0.5-4 cm. If the required thickness of the sample was more than 2 cm, several slabs were placed in layers. Thermocouples (type T, 0.076-cm diameter) were placed at both surfaces and at the thermal center or bottom layer of the sample. The sample was then put into a 10x10 cm, 8-cm thick, polystyrene foam box (thermal conductivity = 0.035 W/m.K),[10] and the heat transfer from the sample was considered to be one-dimensional. The uniform initial temperature of the sample was controlled at various temperatures from 0-30^{o}C. The sample was frozen in the air-blast freezer at -24 to $-31^{o}C$ until its thermal center temperature reached $-18^{o}C$. The air flew parallel to the surface of the sample at the velocity of 1-10 m/s. The freezing times of the sample were compared with those calculated from different models. The

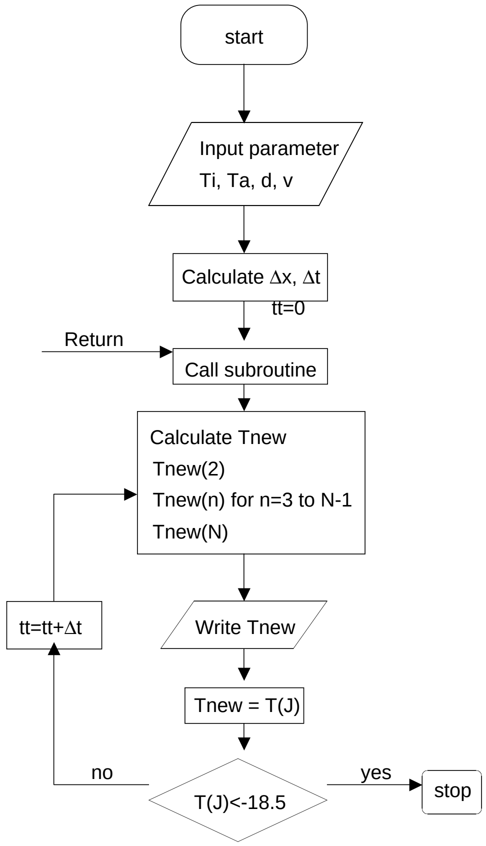

Fig 2. Flow chart for freezing time calculation program for the developed numerical model.

percentage of error was calculated from equation (2)

$$\% \text{ error} = \frac{\text{(The calculated value} - \text{The measured value)}}{\text{The measured value}} \times 100 \quad (2)$$

Results and Discussion

Thermophysical properties

The average moisture content of fresh cuttlefish was found to be 81.72 ± 2.01 % and the equilibrium freezing temperature was –0.8 to –1.5°C. This equilibrium freezing point agreed with that reported by Rahman and Driscoll[11] for seafood.

The densities of fresh cuttlefish at temperature above freezing point (0-30°C) showed no dependence on temperature and, thus, the average density was 1050.7 kg/m^3. Rahman and Driscoll[12] reported the density of fresh cuttlefish with 81.31% moisture content to be 1059 kg/m^3 at 20°C. At temperatures below the freezing point (-5 to –30°C), the densities of the frozen sample decreased with temperature (Table 1). This may be due to the increase in ice formation.[13] The relationship between the density of frozen cuttlefish and temperature was

$$\rho\ (\text{kg/m}^3) = 995.4 + 2.4406\,T + 0.04144\,T^2 \quad (R^2 = 0.882)$$

Thermal conductivity

At temperatures above freezing point (0-30°C), the thermal conductivity (k) of cuttlefish did not depend on temperature and was found to be 0.528-0.548 W/m.K (Table 2). This value was agreeable with those of chicken meat [14] and surimi. [15] The average thermal conductivity of fresh cuttlefish was found to be 0.536 W/m.K.

At temperature below the freezing point (-5 to –30°C), it was found that the values of k were higher than those found at temperature above freezing, as shown in Table 3. This was because the k of ice was about 4 times higher than that of water. These values were similar to those reported by Sweat *et al.* [14] for chicken meat, Wang and Kolbe[15] for surimi, and Barrera and Zaritzky[16] for beef liver. The relationship between k and temperature was

$$k\ (\text{W/m.K}) = 1.0206 - 0.0147\,T + 0.0002\,T^2 \quad (R^2 = 0.919)$$

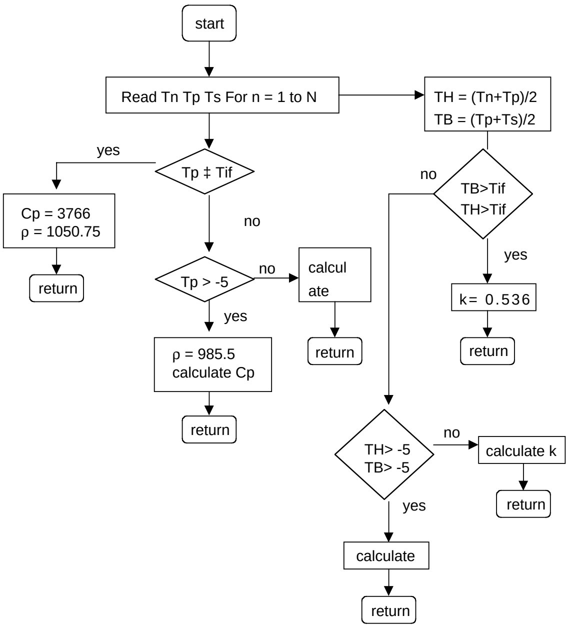

Fig 3. Subroutine TPP.

Specific heat

The average heat capacity of the calorimeter was found to be 12.01 ± 1.08 cal/°C and 19.54 ± 1.81 cal/°C for above and below freezing temperature. The calorimeter used was calibrated using glycerin at 32°C, and the measured specific heat was found to differ only 4.9% from the reported value of 0.576

Table 1. Apparent density of frozen cuttlefish at –5 to –30°C.

Temperature (°C)	Density (kg/m^3)
-5 ± 1	985.5 ± 3.5 ^{a}
-10 ± 1	972.7 ± 1.0 ^{b}
-20 ± 1	964.7 ± 4.5 ^{c}
-30 ± 1	959.0 ± 3.4 ^{d}

Means with different letters are significantly different at $p < 0.05$.

Table 2. Thermal conductivity of cuttlefish at temperatures above freezing (0 to 30°C).

Temperature (°C)	Thermal conductivity (W/m.K)
1 ± 1	0.528 ± 0.009 ^{b}
10 ± 1	0.527 ± 0.009 ^{b}
20 ± 1	0.548 ± 0.011 ^{a}
30 ± 1	0.543 ± 0.010 ^{a}

Means with different letters are significantly different at $p < 0.05$.

Table 3. Thermal conductivity of cuttlefish at temperatures below freezing (–5 to –30°C).

Temperature (°C)	Thermal conductivity (W/m.K)
-5 ± 1	1.124 ± 0.054 ^{c}
-10 ± 1	1.158 ± 0.064 ^{c}
-20 ± 1	1.424 ± 0.036 ^{b}
-30 ± 1	1.644 ± 0.057 ^{a}

Means with different letters are significantly different at $p < 0.05$.

cal/g°C.[17]

The average specific heat (C_p) of the cuttlefish at 0-30°C (Table 4) was similar to those reported by Rahman[18] for cuttlefish at 17±2°C (0.858 ± 0.021 cal/g°C). It was also found that the average specific heat of unfrozen cuttlefish increased slightly with increasing temperature ($p \leq 0.05$). This result agreed with those reported for apples[19] and surimi.[20] From the regression analysis, the relationship between C_p and temperature was found to be

$$C_p = 0.8842 + 0.0010\,T \qquad (R^2 = 0.991)$$

For temperatures below the freezing point, the calorimeter calibrated with chicken breast at –20° and –30°C were 0.596 and 0.465 cal/g°C, respectively. These values were only 2.1% and 6.8% different from those reported by Sanz et al[21] at the same temperatures. The average specific heat of frozen cuttlefish at –10 to –30°C (Table 5) decreased with decreasing temperature ($p \leq 0.05$), which was likely due to an increase in ice fraction in the sample. The specific heat of ice was about 2 times less than that of water.[2, 13] This result agreed with those found in cod,[22] lamb,[23] apple,[19] and surimi.[20] The relationship between C_p (cal/g °C) and temperature (-10 to –30°C) was found to be

$$C_p = 3.3477 + 0.21765\,T + 0.00415\,T^2 \quad (R^2 = 0.989)$$

Surface heat transfer coefficient

The average surface heat transfer coefficient (h) was found to increase with the air velocity (Table 6). This may be due to the increase in heat transfer rate from the surface. And the empirical correlation between the surface heat transfer coefficient and the air velocity in terms of Nusselt number and Reynolds number was

$$Nu = 0.1378\,Re^{0.5674} \quad (R^2 = 0.986)$$

where $Nu = hd_{al}/k_a$

$Re = d_{al}\,\rho_a\,v/\mu_a$

k_a = thermal conductivity of air = 0.02185 W/m.K

ρ_a = density of air = 1.4484 kg/m^3

v = air velocity, m/s

d_{al} = thickness of aluminum plate = 1.1x10^{-2} m

μ_a = viscosity of air = 1.472x10^{-5} kg/m.s

From the above equation the values of h at various air velocity can be calculated from

$$h = 14.421\,v^{0.5674}$$

Mathematical modeling for freezing time prediction

The density, freezing point, thermal conductivity, specific heat, and surface heat transfer coefficient data obtained were used in the numerical model, except those at the freezing temperature range. At the freezing temperature range (approx. –1° to –5°C) some values, such as k, were taken from an extrapolation procedure, C_p was from the equation reported by Schwartzberg,[24] and ρ was assumed to be constant of 985.5 kg/m^3. Table 7 shows the values used for the freezing time prediction.

The initial freezing temperature (T_{if}) was assumed to be –1°C, which was the value reported by IIR,[2] Pham,[25] Cleland and Valentas[26] for lean meat and high moisture foods. This temperature was also within the range of freezing points observed in this study which was –0.8° to –1.5°C. For the simplified analytical models, the values of moisture content, T_{if}, ratio of unfreezable water to solid (b), density of unfrozen cuttlefish (ρ_u), h, and thermal conductivity of unfrozen cuttlefish (k_u) were the same as those used in the numerical method. The other values

Table 4. Specific heat of cuttlefish at temperatures above freezing (0 to 30°C).

Temperature (°C)	Specific heat (cal/g °C)
1 ± 1	0.884 ± 0.054 [c]
10 ± 1	0.897 ± 0.008 [b]
20 ± 1	0.905 ± 0.008 [ab]
30 ± 1	0.914 ± 0.003 [a]

Means with different letters are significantly different at p < 0.05.

Table 5. Specific heat of cuttlefish at temperatures below freezing (–10 to –30°C).

Temperature (°C)	Specific heat (cal/g °C)
-10 ± 1	1.602 ± 0.075 [a]
-20 ± 1	0.645 ± 0.004 [b]
-30 ± 1	0.576 ± 0.017 [c]

Means with different letters are significantly different at p < 0.05.

Table 6. The average surface heat transfer coefficient of the plate at –20°C.

Air velocity (m/s)	h_{av} (W/m^2.K)
1.2	14.93 ± 0.12 [f]
3.0	25.27 ± 0.37 [e]
3.5	28.65 ± 1.00 [d]
5.2	33.79 ± 0.51 [c]
7.2	49.50 ± 0.50 [b]
9.8	54.21 ± 1.50 [a]

Means with different letters are significantly different at p ≤ 0.05.

used are shown in Table 8.

From thirty-five experimental runs the freezing time predicted from different models were compared with the experimental data and the percent errors are given in Table 9. It was found that the numerical model developed gave the best prediction with only 1.5% error, while the simplified analytical model by Plank[4] gave the highest percent error. The developed model from this study used the equations or values of C_p, k, and ρ with temperatures which resulted in a better prediction. However, the accuracy of the prediction depended on the time step (Δt) and space step (Δx) chosen. The Plank model had many assumptions such as the initial temperature of food product was at its initial freezing point, the water became ice at its freezing temperature, the ρ and k of the product remained constant during freezing, and the enthalpy used in the model did not include sensible heat during precooling and tempering. The IIR model gave a better prediction than that from Plank due to the inclusion of sensible heat during tempering, however, the sensible heat during pre-cooling was still not included. The simplified analytical models by Cleland and Earle[6] and the modified Pham model by Hossian et al[8] gave percent errors less than those by Plank and IIR. The Cleland and Earle model uses dimensionless parameters (geometric parameter, Plank number, Stefan number, and equivalent heat transfer dimensionality (EHTD)). While the modified Pham model, which gave predictions as good as those by the Cleland and Earle model, included sensible heat during both precooling and tempering and geometric factor, as well as the use of mean freezing temperature instead of freezing temperature, and EHTD. The possible error of the prediction from these models may be from the non-uniformity of the thickness of the sample, which was unavoidable.

Table 7. Data used for the freezing time equation derived from the numerical method.

Water fraction in cuttlefish	X_{WO} = 0.8172
Solid fraction in cuttlefish	X_S = 0.1828
Initial freezing temperature	T_{if} = -1.0
Ratio of unfreezable water to solid	b = 0.25
Density (kg/m^3)	Temperature range (°C)
ρ_u = 1050.75	$T \geq T_{if}$
ρ_f = 985.5	$-5 \leq T < T_{if}$
$r_f = 995.4 + 2.4406T + 0.04144T^2$	$T \leq -5$
Thermal conductivity (W/m.K)	Temperature range (°C)
k_u = 0.536	$T \geq T_{if}$
$k_f = -0.147T + 0.389$	$-5 \leq T < T_{if}$
$k_f = 1.0206 - 0.0147T + 0.0002T^2$	$T \leq -5$
Specific heat (J/kg °C)	Temperature range (°C)
$C_{pu} = 3699 + 4.6025T$	$T \geq T_{if}$
$C_{pf} = C_{pu} - (X_W - X_b)[(L_W T_{if}/T) + \Delta C_p]$	$T < T_{if}$
When $X_b = bX_S$	
Surface heat transfer coefficient (W/m^2.K)	
$h = 14.421\ v^{0.5674}$	
Space step (m) and time step (s)	
ΔX = 0.0005 m Δt = 0.25 s	d < 0.01 m
ΔX = 0.001 m Δt = 1.0 s	$d \geq 0.01$ m

Table 8. Thermophysical properties of cuttlefish used in the freezing time equation derived from simplified analytical methods.

Density of unfrozen cuttlefish (kg/m^3)	ρ_u = 1050.75
Density of frozen cuttlefish (kg/m^3)	ρ_f = 959
Thermal conductivity of unfrozen cuttlefish (W/m.K)	k_u = 0.536
Thermal conductivity of frozen cuttlefish (W/m.K)	k_f = 1.644
Specific heat of unfrozen cuttlefish (J/kg °C)	C_{pu} = 3766
Specific heat of frozen cuttlefish (J/kg °C)	C_{pf} = 2410
Latent heat (J/kg)	L = 272,945

Conclusion

The moisture content and equilibrium freezing temperature of fresh cuttlefish were found to be 81.72 ± 0.21 % and –0.8° to –1.5°C. The average ρ, k, and C_p of fresh cuttlefish were 1050.7 kg/m^3, 0.528-0.548 W/m.K, and 0.884-0.906 cal/g°C, respectively. The values of k increased parabollically with temperature between –5° to 30°C. The values of C_p increased linearly with temperature range above freezing and decreased parabollically with temperature below –10°C. The relationship between h and air velocity was $h = 14.421\ v^{0.5674}$. The freezing

Table 9. Percent errors in the freezing times of cuttlefish estimated from various models[a].

% Error	Numerical	Plank	IIR	C-E	Mod.Pham
Average	1.5	-34.6	-24.8	-3.3	-4.1
Std.deviation	4.5	5.7	6.5	4.2	4.5
Max. value	9	-24	-13	4	5
Min. value	-9.5	-47	-39	-12	-16

[a] Numerical = the developed numerical model
Plank = Plank model[4]
IIR = IIR model[2]
C-E = Cleland and Earle model[6]
Mod.Pham = modified Pham model[8]

time predicted by the developed numerical model gave the closest estimation of freezing time than those estimated by the simplified analytical models.

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