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Building the Method to Determine the Rate of Freezing Water in *Penaeus monodon* of the Freezing Process

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Abstract: The method of determination the rate of freezing water in *Penaeus monodon* of freezing process was established on base the equation of energy balance in warming up process *Penaeus monodon* after freezing to determine specific heat of *Penaeus monodon*. The result obtained was built the mathematical model (19) to determine the rate of freezing water according to the freezing temperature of *Penaeus monodon*. The results indicated that when water was completely frozen (ω = 1 or 100%), the optimal freezing temperature of *Penaeus monodon* was-22.00°C.

Keywords: Food freezing, the freezing process of *Penaeus monodon*, the method determining rate of freezing water

INTRODUCTION

The freezing technology for using in processing and preservation of foods were very important problems that has ever attracted considerable attention, it ensured food security for the world, (Heldman, 1992; Cleland, 1982). The problem posed here is how to determine the optimal freezing temperature and the optimal freezing time of food to save energy for the freezing process. Currently, there are 2 ways to determine the optimum freezing temperature and freezing time of a product, (Dzung, 2007; Clary, 1968).

- Determining the time of the freezing process in order that the center temperature of foods reach freezing point. It means that water inside the product completely crystallized, (Cleland, 1977, 1979a)
- Determining the time of the freezing process in order that the product temperature reaches the optimal freezing temperature. When water is completely frozen (ω = 1 or 100%), (Cleland, 1979a, b; Bon, 2002)

There were many researches on mathematical modeling about the rate of freezing water of flat–shaped cattle meat (Plank, 1913), frozen velocity of water inside flat–shaped fish fillet (Lame, 1931), rate of freezing water in wet materials (Heldman, 1992). However, mathematical modeling of these authors was not suitable for determining rate of freezing water in *Penaeus monodon* in ĐBSCL of Vietnam because experimental results showed that error between the mathematical model and experimental data was higher than 38.45% (Cleland, 1979b; Gebhart, 1992; Holman, 1986; Heist, 1979). Because of water in food always contents dissolving compounds. Therefore, crystallization temperature, latent heat of freezing of water and other thermo physical parameters constantly change during the freezing process (Holman, 1986; Heist, 1979). These are the main causes of error between the mathematical models with experimental data. In case of large error, it will not allow the use of mathematical modeling to determine the technological mode, (Figura, 2007; Heldman, 1982). For this reason, the problem posed here was finding a new method to determine the rate of freezing water according to the freezing temperature of *Penaeus monodon* and to determine the optimal freezing temperature of *Penaeus monodon* in freezing process.

BUILDING THE METHOD TO DETERMINE THE RATE OF FREEZING WATER

The basic concepts: The freezing process of *Penaeus monodon* has 3 stages (Fig. 1), (Heldman, 1992; Cleland, 1982). In Fig. 1, if the process carried out from A to E (A → B → C → F → E), it would be called the cooling and the freezing process. Whereas, if the carried out from E to A (E → F → C → B → A), it would be called the melting and the warm up process (Heist, 1979; Heldman, 1983).

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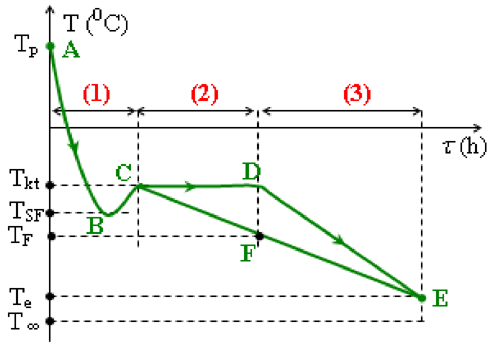

Fig. 1: The freezing process of Penaeus monodon
AB: cooling stage; BC: extreme cold stage; CD: crystalline water inside materials stage of theory ; CF: crystalline water inside material stage of actuality; DE, FE: super freezing stage.

- **Cooling stage:** reduce *Penaeus monodon* temperature from the initial temperature T_P = 25°C (room temperature) to the freezing temperature of water inside the *Penaeus monodon* T_{kt} = -1.21°C before freezing the *Penaeus monodon*, (Heist, 1979; Charm, 1962; Can, 1999)
- **Freezing stage:** crystallize water inside the *Penaeus monodon* in environment with temperatures of T_e = -45°C. This stage finished when the water inside the *Penaeus monodon* completely crystallized (ω = 1 or 100%). At this point, the optimal freezing temperature of *Penaeus monodon* is T_F (°C), (Can, 1999; Dzung, 2012).
- **Energy balance stage**: reducing the temperature of *Penaeus monodon* from T_F (°C) to the final temperature T_e (°C) with $T_e \leq T_F$, (Can, 1999; Dzung, 2012). It is obvious that *Penaeus monodon* is frozen to reach the freezing temperature of T_E (°C), in Fig. 1, after heat supply to carry out the melting and the warm up process to determine specific heat of *Penaeus monodon*. And via the determination of specific heat of the *Penaeus monodon* will build the new method to determine rate of water freezing inside *Penaeus monodon*

Building the method to determine rate of freezing water: This method was built on base the energy balance equation in warming up process *Penaeus monodon* after the freezing process to determine specific heat of *Penaeus monodon* by the experiment. The results obtained could be applied to determine the optimal freezing temperature of *Penaeus monodon* of the freezing process ($T = T_F$). When temperature of *Penaeus monodon* reached the optimal freezing temperature, the rate of freezing water in *Penaeus monodon* was 100% (ω =1), (Heist, 1979; Dzung, 2012). The rate of freezing water (ω) inside *Penaeus monodon* was defined as follow, (Heist, 1979):

Fig. 2: The System of DL-4, the temperature freezing environment (-50÷ -45)°C

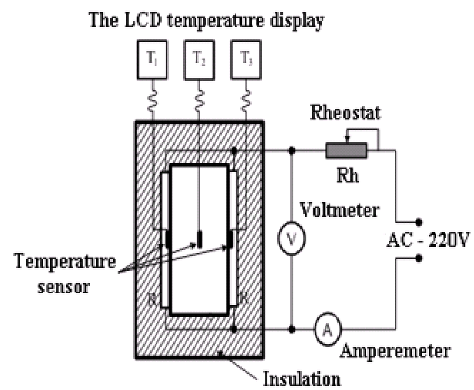

Fig. 3: Principle diagram of the equipment determine the specific heat of moist material

$$\omega = \frac{G_{db}}{G_n} \quad (1)$$

where, G_{db}, G_n – amount of crystallized water and total water inside *Penaeus monodon*, kg. The rate of freezing water ω ($0 \leq \omega \leq 1$) was determined via the determination of specific heat of the *Penaeus monodon* with equipment in Fig. 3. The *Penaeus monodon* was put into the copper box of equipment in Fig. 3. The freezing process was carried out until the temperature of *Penaeus monodon* in the copper box reached -40.5°C after putting this box in the system of freeze DL-4 (Fig. 2) and before determining the specific heat of the *Penaeus monodon*. The heat was supplied by the electric resistance ($Q = UI\tau$, J) to determine specific heat of the *Penaeus monodon*. It was divided into 3 parts as follows:

$$Q = Q_s + Q_{cu} + Q_{dn} \quad (2)$$

where, Q_s (J): the loss of heat pass the heat-insulated surrounding area of equipment in Fig. (3). Q_{cu} (J): the heat warm up the copper box in equipment in Fig. (3):

$$Q_{cu} = G_1 c_1 (T_c - T_d), \text{(J)} \quad (3)$$

Q_{dn} (J): The heat warm up *Penaeus monodon* to put into the copper box of equipment in Fig. (3):

$$Q_{dn} = Gc\,(T_c - T_d),\ (J) \quad (4)$$

From (2) can write as follows:

$$Q_s = Q - (Q_{cu} + Q_{dn})$$

$$\varphi = \frac{Q_s}{Q} = 1 - \frac{(G_1c_1 + Gc)}{UI\tau}(T_c - T_d) \quad (5)$$

where, φ is the loss of heat coefficient, it was determined by the denatured protein, the specific heat of the denatured protein was $c_0 = c = 2045.1$ J/(kg. K). the heat was supplied by electric resistance after putting $G_0 = G = 0.112$ kg denatured protein into the copper box of equipment in Fig. 3 with $T_d = 28.85°C$ until the time reached $\tau = 80$s to determine U = 60V; I = 0.25A; $T_c = 32.51°C$. From (5), the loss of heat coefficient determined $\varphi = 0.1101$.
From (4) can write as follow:

$$\begin{aligned} Q_{dn} &= (1 - \varphi)\,Q - Q_{cu} \\ &= (1 - \varphi)\,UI\tau - G_1c_1\,(T_c - T_d),\ (J) \end{aligned} \quad (6)$$

The heat warm up *Penaeus monodon* to determine specific heat. It was divided into 4 parts as follows:

$$Q_{dn} = Gc\,(T_c - T_d) = Q_1 + Q_2 + Q_3 + Q_4,\ (J) \quad (7)$$

where,

Q_1 (J): The heat warm up to thaw a part of the crystallize water inside the *Penaeus monodon*:

$$Q_1 = LW_a\,(1 - \omega)\,G,\ (J) \quad (8)$$

Q_2 (J): The heat warm up to vary temperature of the crystallize water inside the *Penaeus monodon* form T_d to T_c:

$$Q_2 = c_{nd}GW_a\omega\,(T_c - T_d),\ (J) \quad (9)$$

Q_3 (J): The heat warm up to varies temperature of water after thawing inside the *Penaeus monodon* form T_d to T_c:

$$Q_3 = c_nG\,W_a\,(1 - \omega)\,(T_c - T_d),\ (J) \quad (10)$$

Q_4 (J): The heat warm up to temperature of the matter inside the *Penaeus monodon* form T_d to T_c:

$$Q_4 = c_{ck}G\,(1 - W_a)\,(T_c - T_d),\ (J) \quad (11)$$

Substituting (8), (9), (10) and (11) into (7) found:

$$c = c_nW_a(1-\omega) + c_{nd}W_a\omega + c_{ck}(1-W_a) + \frac{LW_a(1-\omega)}{(T_c - T_d)} \quad (12)$$

- When $T > T_{kt}$, $\omega = 0$, $Q_1 = 0$, $Q_2 = 0$

and

$$c = c_nW_a + c_{ck}(1 - W_a) \quad (13)$$

- When $TF < T \le T_F < T \le T_{kt}$, $0 \le \omega \le 1$

and

$$c = c_nW_a(1-\omega) + c_{nd}W_a\omega + c_{ck}(1-W_a) + \frac{LW_a(1-\omega)}{(T_c - T_d)} \quad (14)$$

- When $T \le T_F$, $\omega = 1$, $Q_1 = 0$, $Q_3 = 0$

and

$$c = c_{nd}W_a + c_{ck}(1 - W_a) \quad (15)$$

From Eq. (14), the rate of freezing water can be written as follow:

$$\omega = \frac{c - \left((c_nW_a + c_{ck}(1 - W_a))(T_c - T_d) + LW_a\right)}{\left((c_{nd} - c_n)(T_c - T_d) + L\right)W_a} \quad (16)$$

where,

$$\begin{aligned} c &= \frac{(1-\varphi)\,UI\tau - c_1G_1(T_c - T_d)}{G(T_c - T_d)} \\ &= \frac{(1-\varphi)\,UI\tau}{G(T_c - T_d)} - \frac{c_1G_1}{G},\ (J/(Kg.K)) \end{aligned} \quad (17)$$

From Eq. (16) and (17), the rate of freezing water was written as follow [11, 18]:

$$\omega = \frac{(1-\varphi)\,UI\tau - LW_aG}{\left((c_{nd} - c_n)(T_c - T_d) - L\right)W_aG} - \frac{\left[G\left(c_nW_a + c_{ck}(1 - W_a)\right) + c_1G_1\right](T_c - T_d)}{\left((c_{nd} - c_n)(T_c - T_d) - L\right)W_aG} \quad (18)$$

where, T (°C)–average temperature of *Penaeus monodon*, $T = (T_d + T_c)/2$.

With: $\phi_1 = LW_aG$
$\phi_2 = (c_nW_a + c_{ck}(1-W_a))G + c_1G_1$
$\phi_3 = GW_a(c_{nd} - c_n)$

Therefore,

$$\omega = \frac{(1-\varphi)UI\tau - \phi_1 - \phi_2(T_c - T_d)}{\phi_3(T_c - T_d) - \phi_1} \quad (19)$$

- Where: c_1, G_1: specific heat and weight of flat-shaped copper in equipment (Fig. 3); G: weight of *Penaeus monodon* sample; $T_d = T_1 = T_2 = T_3$: initial temperature of *Penaeus monodon* sample. $T_c = T_1' = T_2' = T_3'$: temperature of *Penaeus monodon* sample after supplying energy. U: number of voltmeter, I: number of ampere meter, τ: energy supply time
- The equipment (Fig. 3) was surrounded by heat-insulated material to ensure that almost energy from electric resistance transmit to *Penaeus monodon* sample and a little the loss of heat to surrounding (φ = 0.1101 = 11.01%)

MATERIALS AND METHODS

Materials: *Penaeus monodon* is grown in the Flat country of Mekong River (ĐBSCL) of Vietnam (Can, 1999). *Penaeus monodon* of approximately (40÷50) body/kg is cut off head and removed cover (Can, 1999).

Apparatus: Equipments used to determine specific heat of *Penaeus monodon* are listed (Dzung, 2012):

- Determining weigh of *Penaeus monodon* by Satoriusbasic Type BA310S: range scale (0÷350) g, error: ±0.1 g = ± 0.0001 kg, (Dzung, 2012)
- Determining temperature of *Penaeus monodon* by Dual Digital Thermometer: range scale (-50÷70) °C, error ±0.05°C, (Dzung, 2012). DL-4 Freezing System (Fig. 2) could reduce the temperature of environment to (-50÷-45) °C. The temperature profile is measured by the automatic control system PLC, (Dzung, 2012)
- Equipment used to identify specific heat was shown in Fig. 3. The equipment includes a Voltmeter (range scale: (0÷110) V, error: ±1V), an ampere meter (range scale: (0÷2) A, error: ±10 mA) and an automatic timer (error: ±0.001s). The Voltmeter is used to measure the potential difference of Resistance (R). The Ampere meter is used to determine the current intensity which passes through 2 Resistances (R) (Fig. 3).

Methods: To determine the rate of freezing water, the experiment was carried out through 5 steps as follow, (Dzung, 2012):

Step 1: Firstly, mass of the *Penaeus monodon* sample was weighed G (kg), this *Penaeus monodon* sample was placed in the copper box of equipment in Fig. 3, this weighed the sample was frozen the by the system of freeze DL-4 (Fig. 2) until the average temperature of the samples reached–40.5°C, (Dzung, 2012).

Step 2: Place the copper box content *Penaeus monodon* sample into the equipment in Fig. 3. The initial temperature of *Penaeus monodon* ($T_d = T_1 = T_2 = T_3$, °C) was determined. The sample was then supplied with energy from the resistance. Parameters such as U (V), I (A) and energy supply time τ (s) were determined. Subsequently, the system stopped supplying energy. Temperature of fillet samples

Table 1: The experimental value of T_d, T_c, T, ϕ_1, ϕ_2, ϕ_3 of *penaeus monodon*

T_d (°C)	T_c (°C)	T (°C)	ϕ_1	ϕ_2	ϕ_3
-2	2	0	27899.10	448.69	-175.18
-2.5	-1.5	-2	27898.92	448.29	-176.19
-4.5	-3.5	-4	27898.75	447.89	-177.20
-6.5	-5.5	-6	27898.57	447.49	-178.22
-8.5	-7.5	-8	27898.39	447.09	-179.23
-10.5	-9.5	-10	27898.22	446.69	-180.24
-12.5	-11.5	-12	27898.04	446.29	-181.25
-14.5	-13.5	-14	27897.87	445.89	-182.26
-16.5	-15.5	-16	27897.69	445.49	-183.28
-18.5	-17.5	-18	27897.51	445.09	-184.29
-20.5	-19.5	-20	27897.34	444.69	-185.30
-22.5	-21.5	-22	27897.16	444.29	-186.31
-24.5	-23.5	-24	27896.98	443.89	-187.32
-26.5	-25.5	-26	27896.81	443.49	-188.34
-28.5	-27.5	-28	27896.63	443.09	-189.35
-30.5	-29.5	-30	27896.45	442.69	-190.36
-32.5	-31.5	-32	27896.28	442.29	-191.37
-34.5	-33.5	-34	27896.10	441.90	-192.38
-36.5	-35.5	-36	27895.93	441.50	-193.40
-38.5	-37.5	-38	27895.75	441.10	-194.41
-40.5	-39.5	-40	27895.57	440.70	-195.42

Table 2: The experimental value of T, U, I and τ of *penaeus monodon* and the rate of freezing water with freezing temp rature of *penaeus monodon*

T (°C)	U (V)	I (A)	τ (s)	ω_E
0	120	2.50	111.24	0.0000
-2	120	2.50	90.01	0.1539
-4	120	2.50	75.51	0.2917
-6	100	2.50	68.39	0.4677
-8	100	2.50	48.94	0.6218
-10	90	2.50	36.74	0.7475
-12	90	2.50	28.59	0.8056
-14	80	2.50	19.80	0.8839
-16	80	0.25	94.26	0.9496
-18	60	0.25	42.89	0.9889
-20	60	0.25	22.38	0.9986
-22	60	0.25	19.33	1.0000
-24	60	0.25	19.22	1.0000
-26	60	0.25	19.12	1.0000
-28	60	0.25	19.01	1.0000
-30	60	0.25	18.91	1.0000
-32	60	0.25	18.80	1.0000
-34	60	0.25	18.69	1.0000
-36	60	0.25	18.59	1.0000
-38	60	0.25	18.48	1.0000
-40	60	0.25	18.38	1.0000

increased from (T_1, T_2 and T3) to (T_1', T_2', T_3'). When energy balance occurred, T_c = T_1' = T_2' = T_3' (°C), (Dzung, 2012).

Step 3: Calculate the average temperature of the samples $T = (T_d + T_c)/2$ determine c_n, c_{nd}, c_{ck} with T, (Dzung, 2012).

Step 4: Calculate ϕ_1, ϕ_2, ϕ_3, (Dzung, 2012).

Step 5: Finally, substituting ϕ_1, ϕ_2, ϕ_3 into the equation (19) to determine relationship between rate of freezing water inside *Penaeus monodon* sample and average temperature T, (Dzung, 2012). The results obtained were represented in Table 1 and 2.

From the experimental data in Table 1 and 2 were determined the rate of freezing water according to the freezing temperature of *Penaeus monodon* and optimal freezing temperature of *Penaeus monodon*.

RESULTS AND DISCUSSION

Determining the rate of freezing water according to the freezing temperature of *Penaeus monodon* by the mathematical model (19): Experiments were carried out according to five steps in section 3.3. With:

G_1 = 0.125 kg; c_1 = 380J/ (kg. K); G = 0.112 kg
C_n = 4184.7 + 1.74T (J/ (kg. K)
C_{nd} = 2090 + 7.79T (J/ (kg. K))
C_{ck} = 1805.36 + 1.91T (J/ (kg. K))
L = $-0.000021T^2 + 1.054T + 333601.5$ (J/kg)
T = $(T_d + T_c)/2$; $\varphi = 0.1101$

The results have determined T_d, T_c, ϕ_1, ϕ_2, ϕ_3, U, I and τ and were presented in Table 1 and 2. From Table 1 and 2, substituting value of T_d, T_c, ϕ_1, ϕ_2, ϕ_3, U, I and τ into the equation (19) to determine the rate of freezing water with the temperature of *Penaeus monodon* and were presented in Table 2.

Determining the optimal freezing temperature of *Penaeus monodon*: It was obvious that mathematical model (19) was built by the energy balance equation. In there, parameters of mathematical model (19) were determined by the experiment. From results in Table 1 and 2 was determined the optimal freezing temperature of *Penaeus monodon* in order that water inside *Penaeus monodon* was completely crystallized. When temperature of *Penaeus monodon* was -22.00°C ($T = T_F$ = -22.00°C). By the mathematical model (19), the rate of freezing water inside *Penaeus monodon* was determined 100% (ω_E = 100% or 1). Therefore, mathematical model (19) can be not only used to set up parameters for the operation of the freezing system but also to determine technological mode in freezing process of *Penaeus monodon* which grown in the Flat country of Mekong river, Vietnam.

Currently, factories often reduce the freezing temperature of *Penaeus monodon* to (-18÷-16) °C for using in preservation. In such low temperature, microorganisms test showed that microorganisms could not grow, reproduce and most of the microorganisms are inactivated. However, the optimal freezing temperature of *Penaeus monodon* has not exactly determined yet. Different with the technological freezing for using preservation only need the rate of freezing water inside *Penaeus monodon* to reach over 86%. Whereas, the technological freezing of *Penaeus monodon* for using in the freeze drying need to have to reach 100%. Therefore, the optimal freezing temperature of *Penaeus monodon* must be determined in order that the water in *Penaeus monodon* was completely crystallized. The results showed that the optimal freezing temperature of *Penaeus monodon* was–22.00°C and corresponding to ω_E = 100% or 1 (Table 2). These results were not only suitable to large-scale process but also a technological solution for factories to improve the freezing process, saving energy costs when the freezing system is operated, (Cleland, 1979a; Charm, 1962). In addition, results obtained were able to apply for building the mathematical model to describe about relationship the rate of freezing water inside *Penaeus monodon* and the freezing temperature of *Penaeus monodon*, it can see this result in (Dzung, 2012).

Nomenclature:

- $\omega \in [0,1]$: rate of freezing water:
- ω_E: rate of freezing water determined by experimental method

- W_a = 0.7467 = 74.67%: initial moisture of *Penaeus monodon*
- C_n = 4184.7 + 1.74T (J/ (kg. K): Specific heat of water
- C_{nd} = 2090 + 7.79T (J/ (kg. K)): Specific heat of ice
- C_{ck} = 1805.36 + 1.91T (J/ (kg. K)): Specific heat of the dry matter inside *penaeus monodon*
- C (J/kg/K) Specific heat of *Penaeus monodon* when water is crystallized
- C_1 = 380 (J/kg/K): Specific heat of copper
- G (kg): weight of *Penaeus monodon* sample
- G_1 = 0.125 (kg): weight of copper box in equipment determines specific heat moist material
- T_{kt} = -1.21°C: freezing temperature of water inside *Penaeus monodon*.
- T_p = 25°C: room temperature

T_F (°C): temperature of *Penaeus monodon* when water completely

- Crystallized:
- $T_d = T_1 = T_2 = T_3$ (°C): initial temperature of *Penaeus monodon* sample
- $T_c = T_1^{'} = T_2^{'} = T_3^{'}$ (°C): temperature of *Penaeus monodon* sample after supplying energy
- $T = (T_d + T_c)/2$ (°C): average temperature of *Penaeus monodon*
- $r_{nc} = L = -0.000021T^2 + 1.054T + 333601.5$ (J/kg): Latent heat of freezing of water
- U (V): number of voltmeter
- I (A): number of ampere meter
- τ (s): heat supply time

φ = 0.1101: the loss of heat coefficient

CONCLUSION

- The new method was built to determine the rate of freezing water according to the freezing temperature of *Penaeus monodon* by the energy balance equation of determining specific heat of *Penaeus monodon*
- From the energy balance equation has established the mathematical model (19) which was completely compatible with experiment. The results obtained also determined the optimal freezing temperature of *Penaeus monodon* which grows in the Flat country of Mekong River, Vietnam. It was completely compatible with large-scale process
- Calculating the mathematical (19) determined technological mode for the freezing process of *Penaeus monodon* in ĐBSCL, Vietnam

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