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Research Article

Building the Method and the Mathematical Model to Determine the Rate of Freezing Water inside Royal Jelly in the Freezing Process

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Abstract: The aim of this study is building the new method and the mathematical model to determine the rate of freezing water inside Royal jelly of the freezing process for using in preservation as well as for using in the freeze drying. The results obtained were used to determine the optimal freezing temperature of Royal jelly for preservation of -5.73°C (corresponding to the rate of freezing water inside Royal jelly of 86.02% over 86%) and for the freeze drying of -18.33°C (corresponding to the rate of freezing water inside Royal jelly of 100%). This is basic parameters and very essential to set up the technological mode of the freezing process Royal jelly for preservation as well as for freeze drying.

Keywords: Royal jelly, the freezing process, the freezing process of royal jelly, the mathematical model of determining rate of freezing water, the optimal freezing temperature of royal jelly, the rate of freezing water inside royal jelly, the royal jelly preservation

INTRODUCTION

The Royal jelly has been verified to be rich in essential nutrients. The chemical composition of Royal jelly contain many different substance but the principal constituents of Royal jelly are water, protein, sugars, lipids and mineral salts. Although they occur with notable variations the composition of Royal jelly remains relatively constant when comparing different colonies, bee races and time. This thing can be seen analytic data in Table 1.

Table 1: Composition of royal jelly (Lercker *et al*., 1984, 1992)

Substance	Minimum value	Maximum value
Water	57%	70%
Proteins (N×6.25)	17% of dry weight	45% of dry weight
Carbohydrate (sugars)	18% of dry weight	52% of dry weight
Lipids	3.5% of dry weight	19% of dry weight
Minerals	2% of dry weight	3% of dry weight

Protein of Royal jelly contains all amino acids essential for humans, including 29 amino acids and derivatives. The most important is still aspartic acid, glutamic acid and the free amino acids as proline and lysine. Besides, it also contains a number of enzymes including glucose oxidase phosphatase and cholinesterase and an insulin-like substance (Antinelli *et al*., 2003).

The sugars consist mostly of fructose and glucose in relatively constant proportions similar to those in honey. Fructose is prevalent. In many cases fructose and glucose together account for 90% of the total sugars. The sucrose content varies considerably from one sample to another. Other sugars present in much lower quantities are maltose, trehalose, melibiose, ribose and erlose (Lercker *et al*., 1992).

The lipid of Royal jelly contain biologically active substances rare. The lipid fraction consists to 80-90% (by dry weight) of free fatty acids with unusual and uncommon structures. They are mostly short chain (8 to 10 carbon atoms) hydroxy fatty acids or dicarboxylic acids, in contrast to the fatty acids with 14 to 20 carbon atoms which are commonly found in animal and plant material. These fatty acids are responsible for most of the recorded biological properties of Royal jelly (Schmidt and Buchmann, 1992). The principal acid is 10-hydroxy -2-decenoic acid (10-hydroxydecenoic acid) and it can be called 10-HDA. In addition to the free fatty acids, the lipid fraction contains some neutral lipids, sterols (including cholesterol) and an unsaponifiable fraction of hydrocarbons similar to beeswax extracts (Lercker *et al*., 1984, 1992; Hattori *et al*., 2007) (Fig. 1).

Fig. 1: The royal jelly

The total ash content of Royal jelly is about 1% of fresh weight or 2 to 3% of dry weight. The major mineral salts are, in descending order: K, Ca, Na, Zn, Fe, Cu and Mn, with a strong prevalence of potassium (Benfenati *et al*., 1986).

According to research of Schmidt and Buchmann (1992) showed that Royal jelly is extremely rich in vitamins to include water-soluble vitamins as B_1 (Thiamine), B_2 (Riboflavin), B_3 (Pantothenic acid), B_6 (Pyridoxine), PP (Niacin), B_c (Folic acid), H (Biotin) and fat-soluble vitamins as A (Retinol or Retinal), D (Calciumpherol), E (Tocopherol), K (Philoquinol).

It is obvious that the Royal jelly is kinds of pharmaceutical product, food to have a great value for human health. It has ability resistant to aging, increase energy and restore health to the body. For children it helps improve brain development. Therefore, the problem posed here is how to preserve the Royal jelly in order that they can be prolonged time of using and export but their quality is still contanst.

Currently, there are two methods the freezing and the freeze drying to apply for preservation the Royal jelly to achieve high effect. Therefore the problem of determining the technological mode of the freezing process for using preservation as well as for using freeze drying is extremely important. It solve problem about quality and expenses energy of final product. And one of basic parameters for determining the technological mode of the freezing process is the rate of freezing water of Royal jelly (Dzung, 2012). However, the problem of determining the rate of freezing water according to the freezing temperature of Royal jelly, simultaneously building the mathematical model about relationship between the rate of freezing water and the freezing temperature of Royal jelly are extremely complicated question.

According to overview of Bon and Tho (2002), there were many research 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 (Shijov, 1931), rate of freezing water in wet materials (Raoult, 1958; Sbijov, 1967; Golovkin, 1972; Luikov, 1974; Heldman and Daryl, 1992). However, mathematical model of these authors was not suitable for determining rate of freezing water in Royal jelly because experimental results showed that error between the mathematical model and experimental data was higher than 24.36%. Because of water in Royal jelly always contents dissolving compounds. Therefore, crystallization temperature, latent heat of freezing of water and other thermo physical parameters constantly change during the freezing process (Cleland and Earle, 1979; Heist, 1979; Holman, 1986; Gebhart, 1992). 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, (Heldman, 1982; Bon and Tho, 2002; Figura and Arthur, 2007).

As a result, the aim of this study was building a new method to determine the rate of freezing water according to the freezing temperature of Royal jelly, to set up the mathematical model about the relationship between the rate of freezing water and the freezing temperature of Royal jelly. On that foundation allow to determine the optimal freezing temperature of Royal jelly in freezing process (Dzung, 2012; Dzung *et al.*, 2012b).

BUILDING THE METHOD TO DETERMINE THE RATE OF FREEZING WATER

The freezing process of royal jelly: From Fig. 2 can see that the freezing process of Royal jellies include stages (Dzung, 2007; Dzung *et al.*, 2012):

- **Cooling stage (AB):** Reduce temperature of Royal jelly from the initial temperature T_R (Room temperature of 25°C) to the freezing temperature of water inside Royal jelly $T_{cr} = T_{Fp} = -1.06$°C before freezing the Royal jelly, (Heldman and Daryl, 1992; Dzung *et al.*, 2012).
- **Extreme cold stage (BC):** This stage occur in very short time when the temperature of Royal jelly is reduced under the freezing point of water in Royal jelly of $T_{cr} = T_{Fp} = -1.06$°C but water in Royal jelly is still no crystallization.
- **Freezing stage (CD):** Water inside the Royal jelly was crystallized in environment to has temperatures of $T_e = -45$°C. This stage finished when the water inside the Royal jelly crystallized 86% for preservation or 100% for freeze drying. And temperature at value of this rate of freezing water is called the optimal freezing temperature of Royal jelly (T_{Fopt}, °C), (Heldman and Daryl, 1992; Dzung, 2012; Dzung *et al.*, 2012).
- **Energy balance stage (DE)**: If freezing process is continued, this stage will be super freezing stage. It will be reducing the temperature of Royal jelly from T_{Fopt} (°C) to the final temperature T_e (°C) with $T_e \le T_{Fopt}$, (Heldman and Daryl, 1992; Dzung, 2012; Dzung *et al.*, 2012).

The thawing process of freezing royal jelly: From Fig. 2 can see that the thawing process will be carried out from E to A (Dzung, 2012; Dzung *et al.*, 2012):

- **Stage ED:** This stage warm up freezing Royal jelly to vary the freezing temperature of Royal jelly from T_e to T_{Fopt} but not make to thaw ice inside freezing Royal jelly.
- **Stage DB:** This stage make to thaw ice inside freezing Royal jelly. At point B, ice inside Royal jelly is completely thawed, the temperature of Royal jelly reach the crystallization temperature.
- **Stage BA:** This stage warm up Royal jelly after ice completely thawing, the temperature of Royal jelly increase from T_{cr} to T_R.

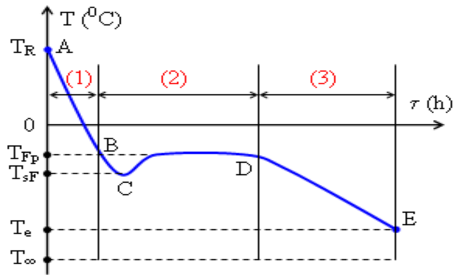

Fig. 2: The freezing process of royal jelly
AB: Cooling stage; BC: Extreme cold stage; CD: Crystalline water inside royal jelly stage; DE: Super freezing stage

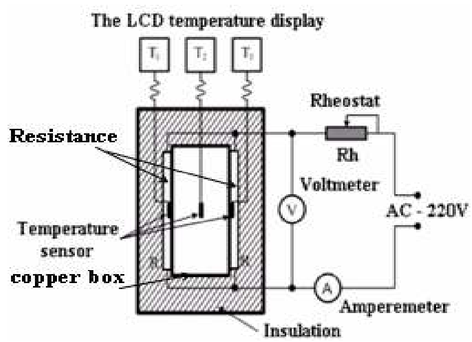

Fig. 3: Principle diagram of the equipment determine the rate of freezing water of moist material

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

It is obvious that Royal jelly is frozen to reach temperature of T_e (Fig. 2). At value of this temperature, it is supplied heat to carry out the warming up and thawing process. From the balance energy equation of the warming up and thawing process of freezing Royal jelly will build the method to determine the rate of water freezing inside Royal jelly and the mathematical model about the relationship between the rate of freezing water and freezing temperature of Royal jelly.

Building the method to determine rate of freezing water of royal jelly: This is a new method to determine the rate of freezing water according to freezing temperature of Royal jelly, it was built on base the energy balance equation in the warming up and thawing process of Royal jelly after being frozen by the experimental method. The results obtained could be applied to determine the optimal freezing temperature of Royal jelly of the freezing process ($T = T_{Fopt}$).

According to overview of Dzung (2007), if freezing Royal jelly use in preservation, the optimal freezing temperature will reach value of T_{Fopt}, corresponding to the rate of freezing water over 86%. Iffreezing Royal jelly use in freeze drying, the optimal freezing temperature will reach value of T_{Fopt}, corresponding to the rate of freezing water of 100%, (Dzung, 2012; Dzung *et al.*, 2012).

The rate of freezing water (ω, $0 \le \omega \le 1$) of Royal jelly was defined as follow, (Heist, 1979):

$$\omega = \frac{G_{db}}{G_n} \tag{1}$$

where, G_{db}, G_n (kg)-amount of crystallized water and total water of Royal jelly. The rate of freezing water ω was determined by equipment in Fig. 3.

Determine the loss of heat coefficient of equipment: Water was poured into the copper box of equipment in Fig. 3. All of them were put in the system of freeze DL-4 (Fig. 4). The freezing process is carried out until the temperature of water in the copper box reached -45°C, water was completely crystallized. Following, the copper box was taken out the system of freeze DL-4, the insulated lid of copper box and equipment in Fig. 3 must be closed. Next this stage, the warming up and thawing process were carried out to determine the loss of heat pass the heat-insulated surrounding area of equipment in Fig. 3 (Dzung *et al.*, 2012).

The heat was supplied for equipment in Fig. 3 (Electrical calorimeters) by the electric resistance: $Q = UI\tau$ (J). It was divided into three parts as follows (Jean *et al.*, 1996):

$$Q = Q_s + Q_{cu} + Q_{dn} \tag{2}$$

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 of equipment in Fig. 3 from T_d to T_c and to be determined as follows:

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

Q_{dn} (J) = The heat warm up ice inside the copper box of equipment in Fig. 3 from T_d to T_c and to be determined as follows:

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

From Eq. (2) can write as follows:

Table 2: The experimental data to determine the loss of heat coefficient of equipment

U (V)	I (A)	τ (s)	T_d (°C)	T_c (°C)	c (J/ (kg.K)	φ
110	0.25	54.39	43.53	45.39	4173.98	0.1312
110	0.25	52.24	14.63	16.42	4167.11	0.1309
110	0.25	54.09	-1.72	1.78	2062.48	0.1311
110	0.25	54.74	-16.29	-12.61	1974.49	0.1309
110	0.25	55.34	-41.06	-37.08	1824.88	0.1312

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

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

where,

φ : The loss of heat coefficient of equipment Fig. 3

$G_n = G = 0.156$ kg : Weight of water in copper box

$c = c_n$ or $c = c_{nd}$: Specific heat of water or ice

$T = (T_d+T_c)/2$: The average temperature of the samples

T_d (°C) : Temperature of the samples before warming up and heat balance

T_c (°C) : Temperature of the samples after warming up and heat balance

U (V) : Number of Voltmeter

I (A) : Number of Amperemeter

τ (s) : Time of the warming up process

Right here, the conditions of U = 110V and I = 0.25A were constant, carrying out experiment at different value of time obtained experimental data in Table 2.

Using Eq. (5) to determine the loss of heat coefficient of equipment in Fig. 3, it can see results after calculating in Table 2. The average loss of heat coefficient determined φ = 0.1311 (Dzung *et al*., 2012).

Building the mathematical model to determine rate of freezing water of royal jelly by experiment: The Royal jelly was also poured into the copper box of equipment in Fig. 3. All of them were put in the system of freeze DL-4. The freezing process was carried out until the temperature of Royal jelly in the copper box reached -30°C; water in Royal jelly was completely crystallized. Following, the copper box was taken out the system of DL-4, the insulated lid of copper box and equipment in Fig. 3 must be closed. Next this stage, the warming up and thawing process were carried out to determine the rate of freezing water according to freezing temperature of Royal jelly (Dzung, 2012; Dzung *et al*., 2012).

From Eq. (2) can write as follows:

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

The heat warm up freezing Royal jelly to vary temperature from T_d to T_c. This heat was divided into four 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 ice (crystallized water) inside the Royal jelly:

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

Q_2 (J) : The heat warm up to vary temperature of ice inside the Royal jelly 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 vary temperature of water after ice thawing inside the Royal jelly 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 dry weight inside the Royal jelly form T_d to T_c:

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

Note: $T = (T_d + T_c)/2$ -the average temperature of the Royal jelly samples.

If $T > T_{cr} = -1.06$°C:

$$\omega = 0,\ Q_1 = 0,\ Q_2 = 0,\ Q_3 \neq 0,\ Q_4 \neq 0$$

If $-1.06^0C = T_{cr} \leq T \leq T_{Fopt}$:

$$0 \leq \omega \leq 1,\ Q_1 \neq 0,\ Q_2 \neq 0,\ Q_3 \neq 0,\ Q_4 \neq 0$$

If $T < T_{Fopt}$:

$$\omega = 1,\ Q_1 = 0,\ Q_3 = 0,\ Q_2 \neq 0,\ Q_4 \neq 0$$

Substituting Eq. (6), (8), (9), (10) and (11) into Eq. (7). And it was written as follows:

$$(1 - \varphi)\, UI\tau - G_1c_1 (T_c - T_d) = LW_a (1 - \omega)\, G + c_{nd} GW_a\omega\,(T_c - T_d) + c_nG\, W_a (1 - \omega)(T_c - T_d) + c_{ck}G\,(1 - W_a)(T_c - T_d)$$

This equation can be written by Eq. (12):

$$\omega = \frac{(1-\varphi)UI\tau - LW_aG}{\left((c_{nd} - c_n)(T_c - T_d) - L\right)W_aG} - \frac{\left[G\left(c_nW_a + c_{ck}(1 - W_a)\right) + c_1G_1\right](T_c - T_d)}{\left((c_{nd} - c_n)(T_c - T_d) - L\right)W_aG} \quad (12)$$

where,

$\phi_1 = LW_aG$

$\phi_2 = (c_nW_a + c_{ck}(1 - W_a))\, G + c_1G_1$

$\phi_3 = GW_a (c_{nd} - c_n)$

Therefore, the rate of freezing water inside Royal jelly was determined by Eq. (13):

$$\omega = \frac{(1-\varphi)UI\tau - \phi_1 - \phi_2(T_c - T_d)}{\phi_3(T_c - T_d) - \phi_1} \qquad (13)$$

where,
c_1, G_1 : Specific heat and weight of copper box of equipment in Fig. 3
G : Weight of Royal jelly sample
$T_d = T_1 = T_2 = T_3$: Initial temperature of Royal jelly sample before supplying energy
$T_c = T_1' = T_2' = T_3'$: Temperature of Royal jelly sample after supplying energy
U : Number of voltmeter
I : Number of amperermeter
τ : Time of energy supply process

This much, the Eq. (13) is the mathematical model to determine the rate of freezing water according to freezing temperature of Royal jelly by the equipment and experiment.

Building the mathematical model about the relationship between the rate of freezing water and freezing temperature of royal jelly: According to overview of Bon and Tho (2002), the relationship the rate of freezing water and freezing temperature of moist material obey law the mathematical model of Sbijov (1967) as well as the mathematical model of Heldman and Daryl (1992) as follows:

$$\omega(T) = b_0 + b_1 \exp\left(b_2 + b_3 T + b_4 T^2\right) \qquad (14)$$

where, T (°C) is the average temperature of the freezing material samples; b_0, b_1, b_2, b_3, b_4 are parameters of the mathematical model (14); they are determined by the experimental data. This much, carrying out experiment and calculating according to Eq. (13) will obtain data of the rate of freezing water according to freezing temperature. Substituting this data into the Eq. (14) will determine parameters b_0, b_1, b_2, b_3, b_4.

MATERIALS AND METHODS

Materials: The Royal jelly is very thick solution and is grown in the Bao Loc area, Lam Dong province of Vietnam. The basic composition of Royal jelly is presented in Table 1 (Lercker *et al*., 1984, 1992).

Apparatus: Equipments used to determine rate of freezing water of Royal jelly are listed (Dzung *et al*., 2012):

- **Determining weigh of royal jelly by satoriusbasic type BA310S:** Range scale (0÷350) g, error: ±0.1g = ±0.0001 kg

Table 3: The experimental and calculating data to determine value of U, I,τ, T_d, T_c, of royal jelly

U (V)	I (A)	τ (s)	T_d (°C)	T_c (°C)	c_n (J/ (kg.K))
110	2.50	131.51	-0.20	0.20	4080.70
110	2.50	100.16	-1.98	-0.20	4085.40
110	2.50	58.66	-3.18	-1.98	4091.82
110	2.50	40.99	-4.08	-3.18	4096.35
110	2.50	27.29	-5.28	-4.08	4100.88
110	2.50	19.66	-6.18	-5.28	4105.40
110	2.50	10.46	-7.38	-6.18	4109.93
60	2.50	14.06	-8.28	-7.38	4114.46
60	0.25	83.10	-9.48	-8.28	4118.98
60	0.25	68.53	-10.38	-9.48	4123.51
60	0.25	47.52	-11.58	-10.38	4128.04
60	0.25	31.59	-12.48	-11.58	4132.56
60	0.25	33.63	-13.56	-12.48	4136.83
60	0.25	33.17	-14.68	-13.56	4141.57
60	0.25	29.37	-15.74	-14.68	4146.27
60	0.25	26.27	-16.72	-15.74	4150.67
60	0.25	28.34	-17.80	-16.72	4155.11
60	0.25	27.52	-18.86	-17.80	4159.72
60	0.25	25.91	-19.86	-18.86	4164.16
60	0.25	27.41	-20.92	-19.86	4168.60
60	0.25	28.90	-22.04	-20.92	4173.30
60	0.25	21.12	-22.86	-22.04	4177.48
60	0.25	34.95	-24.22	-22.86	4182.18
60	0.25	21.03	-25.04	-24.22	4186.88

Table 4: The experimental and calculating data to determine value of c_{nd}, c_{ck}, L, ϕ_1, ϕ_{2c}, of royal jelly

c_{nd} (J/ (kg.K))	c_{ck} (J/ (kg.K))	L = r_{nc} (J/kg)	ϕ_1	ϕ_2
2062.30	1705.85	333601.50	31203.75	539.16
2055.68	1704.35	333600.35	31203.64	539.50
2046.62	1702.30	333598.78	31203.50	539.97
2040.24	1700.87	333597.67	31203.39	540.30
2033.86	1699.44	333596.57	31203.29	540.63
2027.48	1698.02	333595.46	31203.18	540.96
2021.10	1696.61	333594.35	31203.08	541.30
2014.72	1695.21	333593.25	31202.98	541.63
2008.34	1693.81	333592.14	31202.87	541.96
2001.96	1692.42	333591.03	31202.77	542.30
1995.58	1691.03	333589.92	31202.67	542.63
1989.19	1689.66	333588.82	31202.56	542.97
1983.18	1688.37	333587.77	31202.47	543.28
1976.49	1686.94	333586.61	31202.36	543.63
1969.87	1685.54	333585.46	31202.25	543.98
1963.67	1684.23	333584.39	31202.15	544.31
1957.41	1682.91	333583.30	31202.05	544.64
1950.91	1681.55	333582.17	31201.94	544.98
1944.65	1680.25	333581.09	31201.84	545.31
1938.39	1678.96	333580.00	31201.74	545.65
1931.77	1677.60	333578.85	31201.63	546.00
1925.87	1676.39	333577.83	31201.54	546.31
1919.25	1675.05	333576.68	31201.43	546.66
1912.63	1673.71	333575.53	31201.32	547.02

- **Determining temperature of royal jelly dual digital thermometer:** range scale (-50÷70) °C, error±0.05°C
- DL-4 Freezing System (Fig. 4) could reduce the temperature of environment to (-50÷-45) °C. The temperature profile is measured by the automatic control system PLC
- Equipment used to identify the rate of freezing water of Royal jelly was shown in Fig. 3. The equipment includes a Voltmeter (range scale: (0÷110) V, error: ±1V), an amperemeter (range

Table 5: The experimental and calculating data to determine value of ϕ_3, T, ω_E, ω_{MH}, error of royal jelly

ϕ_3	T (°C)	ω_E (T)	ω_M (T)	Error (%)	$(\omega_M - \omega_E)^2$
-188.79	0.00	0.0000	0.0000	-	2.46596E-14
-189.85	-1.09	0.2609	0.2718	4.16	0.000117847
-191.30	-2.58	0.5674	0.5554	2.11	0.000142878
-192.32	-3.63	0.6978	0.6989	0.15	1.12297E-06
-193.34	-4.68	0.8058	0.8029	0.36	8.31163E-06
-194.36	-5.73	0.8602	0.8754	1.77	0.000230635
-195.38	-6.78	0.9337	0.9239	1.05	9.6488E-05
-196.40	-7.83	0.9515	0.9551	0.38	1.27715E-05
-197.42	-8.88	0.9787	0.9744	0.44	1.86328E-05
-198.44	-9.93	0.9814	0.9859	0.46	2.01456E-05
-199.46	-10.98	0.9934	0.9925	0.09	8.28968E-07
-200.48	-12.03	0.9967	0.9961	0.06	3.15655E-07
-201.44	-13.02	0.9978	0.9980	0.02	4.05735E-08
-202.51	-14.12	0.9984	0.9991	0.07	4.52419E-07
-203.57	-15.21	0.9993	0.9996	0.03	7.98232E-08
-204.56	-16.23	0.9997	0.9998	0.01	1.18221E-08
-205.56	-17.26	0.9999	0.9999	0.00	2.51455E-10
-206.60	-18.33	1.0000	1.0000	0.00	1.19831E-09
-207.60	-19.36	1.0000	1.0000	0.00	2.02576E-10
-208.60	-20.39	1.0000	1.0000	0.00	3.20484E-11
-209.66	-21.48	1.0000	1.0000	0.00	4.23653E-12
-210.61	-22.45	1.0000	1.0000	0.00	6.57414E-13
-211.67	-23.54	1.0000	1.0000	0.00	7.55243E-14
-212.72	-24.63	1.0000	1.0000	0.00	8.05528E-15

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 Amperemeter is used to determine the current intensity which passes through 2 resistances (R)

Methods: To determine the rate of freezing water by the experiment was carried out through 6 steps as follow, (Dzung, 2012; Dzung *et al.*, 2012):

Step 1: Mass of the Royal jelly sample was weighed G (kg) and put in the copper box of equipment in Fig. 3, it was frozen by the system of freeze DL-4 (Fig. 4) until the average temperature of the samples reached -30°C, water in Royal jelly was completely crystallized

Step 2: This copper box was taken out the system of freeze DL-4, the insulated lid of copper box and equipment in Fig. 3 must be closed. Untill energy balance of sample, the initial temperature of Royal jelly sample determined $T_d = T_1 = T_2 = T_3$, (°C). Next this stage, the sample was supplied with energy from the electric resistance. Simultaneously, parameters such as U (V), I (A) and energy supply time τ (s) were determined. Subsequently, the system stopped supplying energy. The temperature of Royal jelly samples increased from (T_1, T_2, T_3) to (T_1', T_2', T_3'). When energy balance occurred, $T_c = T_1' = T_2' = T_3'$ (°C)

Step 3: Calculating the average temperature of the samples $T = (T_d + T_c)/2$, determining c_n, c_{nd}, c_{ck} with T

Step 4: Calculating ϕ_1, ϕ_2, ϕ_3, (Dzung *et al.*, 2012)

Step 5: Substituting ϕ_1, ϕ_2, ϕ_3 into the Eq. (13) to determine the relationship between the rate of freezing water inside Royal jelly sample and average temperature T. The results obtained were represented in Table 3, 4 and 5

Step 6: Substituting the experimental data in Table 3, 4 and 5 into the Eq. (14) will be determined the mathematical model about the relationship between the rate of freezing water and freezing temperature of Royal jelly.

RESULTS AND DISCUSSION

Determining the rate of freezing water of royal jelly by the mathematical model (13) and experiment: The physical properties of the copper box, water, ice and the composition of dry matter inside Royal jelly are used to calculate the rate of freezing water according to freezing temperature of Royal jelly (Heldman, 1982; Heldman *et al.*, 1983), including:

- The physical properties of the copper box:

  $G_1 = 0.125$ kg; $c_1 = 380$ J/ (kg.K)

- The physical properties of the water (Heldman and Daryl, 1992):

When 0°C<T<150°C:

$$c_n = 4167.2 - 9086.4\times10^{-5}\times T + 5473.1\times10^{-6}\times T^2 \text{ (J/(kg.K))}$$

When -40°C≤T≤0°C, (In spite of water inside food under 0°C, it was still no crystallization):

$$c_n = 4080.7 - 5306.2\times10^{-3}\times T + 9951.6\times10^{-4}\times T^2 \text{ (J/(kg.K))}$$

- The physical properties of ice (the freezing water), (Heldman and Daryl, 1992):

  $c_{nd} = 2062.3 + 6076.9\times10^{-3}\times T$ (J/ (kg.K)); with T≤0°C

  $L = 333601.5 + 1.054\times T - 0.000021\times T^2$ (J/kg)

  Where the temperature T is taken to be the numerical value in °C.

- The physical properties of the composition of dry matter inside Royal jelly (Heldman and Daryl, 1992):

Protein:

$$c_{pro} = 2008.2 + 1208.9\times10^{-3}T + 1312.9\times10^{-6}\times T^2 \text{ (J/(kg.K))}$$

Carbohydrate:

$c_{glu} = 1548.8 + 1962.5\times10^{-3}\times T + 5939.9\times10^{-6}\times T^2$ (J/ (kg.K))

Lipit:

$c_{lip} = 1984.2 + 1473.3\times10^{-3}\times T + 4800.8\times10^{-6}\times T^2$ (J/ (kg.K))

Ash:

$c_{ash} = 1092.6 + 1889.6\times10^{-3}\times T + 3681.7\times10^{-6}\times T^2$ (J/ (kg.K))

The average specific heat of impurities inside the dry matter of Royal jelly: c_{im} = 1296.87 J/ (kg.K).
Dry matter:

$c_{ck} = X^{tp}_{pro}c_{pro} + X^{tp}_{glu}c_{glu} + X^{tp}_{Lip}c_{Lip} + X^{tp}_{ash}c_{ash} = \Sigma X_j c_j$ (J/ (kg.K))

where, X^{tp}_{pro} = 0.34951; X^{tp}_{glu} = 0.39093; X^{tp}_{Lip} = 0.09804; X^{tp}_{ash} = 0.02696; X^{tp}_{im} = 0.13456 were ratio of protein, sugars lipid, ash and impurities inside the composition of the dry matter of Royal jelly (the composition of impurities inside Royal jelly were cera flava, including: Myricyl palmitat, myricyl cerotatat, alcol myricylics, cerylic and some hydrocarbon); G = 0.158 kg; W_a = 0.5920; φ = 0.1311.

Experiments were carried out according to six steps as were presented method section. The results have determined T_d, T_c, ϕ_1, ϕ_2, ϕ_3, U, I and τ and ω_E were presented in Table 3, 4 and 5.

From Table 3, 4, 5, substituting value of T_d, T_c, ϕ_1, ϕ_2, ϕ_3, U, I and τ into the Eq. (13) to determine the rate of freezing water with the freezing temperature of Royal jelly and were presented in Table 5.

Determining the mathematical model about the relationship between the rate of freezing water and freezing temperature of royal jelly: The relationship between the rate of freezing water and freezing temperature of Royal jelly obey law of the Eq. (14), (Sbijov, 1967; Heldman and Daryl, 1992). The problem posed here is needed to determine parameters of mathematical model b_0, b_1, b_2, b_3 and b_4. The method determines these parameters as follows:

The residual Root Mean Square Error (RMSR) of the rate of freezing water in Royal jelly from the experimental data and the mathematical model was presented by Eq. (15), (Dzung, 2012):

$$\text{RMSR} = f(b_0, b_1, b_2, b_3, b_4) = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(\omega_E(T_i) - \omega_M(T_i)\right)^2} \quad (15)$$

where,

$\omega_E(T_i)$ = The rate of freezing water inside Royal jelly at temperature of T_i from experiment in Table 5
$\omega_M(T_i)$ = $b_0 + b_1\exp(b_2 + b_3T_i + b_4T_i^2)$: the rate of freezing water inside Royal jelly at temperature of T_i from the mathematical model (14)
i = 1÷N: the number of experiments
T_i = The average temperature of Royal jelly in Table 5

This much, the problem finding parameters b_0, b_1, b_2, b_3 and b_4 of mathematical model (14) was expressed as follow: Finding the root $b^{opt} = (b_0^{opt}, b_1^{opt}, b_2^{opt}, b_3^{opt}, b_4^{opt})$ in order to objective function of RMSR = f (b_0, b_1, b_2, b_3, b_4) reached the minimum value:

$$\text{RMS R}_{min} = \text{Min}\{f(b_0, b_1, b_2, b_3, b_4)\} = f(b_0^{opt}, b_1^{opt}, b_2^{opt}, b_3^{opt}, b_4^{opt})$$

$$= \text{Min}\left\{\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(\omega_E(T_i) - \omega_M(T_i)\right)^2}\right\} \quad (16)$$

From the data in Table 5, the minimum value of RMSR could be determined by using the meshing method (Dzung, 2012) programmed in MATLAB 7.0 software. After solving and calculating, the root of Eq. (16) found the results as follows:

RMS R_{min} = 0.0052

where,

b_0^{opt} = 1.0000; b_1^{opt} = - 0.55009; b_2^{opt} = 0.59767; b_3^{opt} = 0.27390; b_4^{opt} = - 0.01563

Consequently, mathematical model describing the relationship between the rate of freezing water with freezing temperature of Royal jelly was established by mathematical model (13) and experimental method as follow:

$$\omega_M(T) = 1 - 0.55009\times e^{0.59767 + 0.27390\times T - 0.01563\times T^2}$$

$$= 1 - 0.55009\times \text{Exp}\,(0.59767 + 0.27390\times T - 0.01563\times T^2) \quad (17)$$

Test compatibility of the mathematical model (17): Error of the mathematical model (17) with experimental data was examined by using the Eq. (18) as follows (Gebhart, 1992; Dzung, 2012):

$$\text{Er} = \frac{\left|\omega_E(T_i) - \omega_M(T_i)\right|}{\left|\omega_E(T_i)\right|} \quad (18)$$

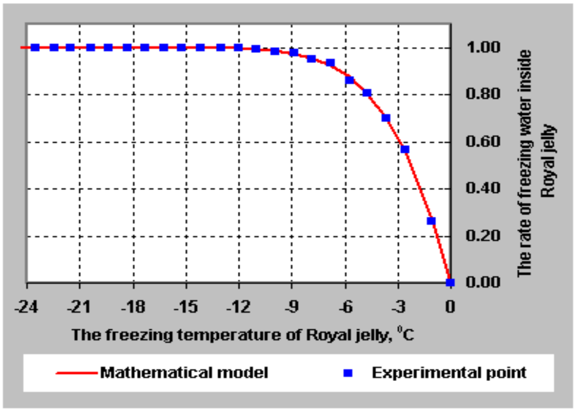

Fig. 5: Relationship between the rate of freezing water and freezing temperature of royal jelly

$$Er_{max} = \frac{\max\{|\omega_E(T_i) - \omega_M(T_i)|\}}{|\omega_E(T_i)|} = \frac{|0.2609 - 0.2718|}{0.2609}.100\% = 4.16\%$$

It was able to see that the mathematical model (17) was completely compatible with experimental results.

Because of the maximum error of mathematical model (17) with experimental data Er_{max} = 4.16%, it is smaller than 5% (Heldman and Daryl, 1992; Dzung *et al.*, 2012).

Therefore, the mathematical model (17) can completely use of calculating mass and energy balance in the freezing process (Holman, 1986).

In Fig. 5 described the rate of freezing water to vary according to temperature of Royal jelly in freezing process. When the freezing temperature of Royal jelly reduced, the rate of freezing water of freezing Royal jelly increased. At the time, the rate of freezing water of freezing Royal jelly was ω = 1, if the freezing process continue to reduce the temperature of freezing Royal jelly, the rate of freezing water of freezing Royal jelly will be still constant and ω = 1.

Determining the optimal freezing temperature of royal jelly: At the time, water inside Royal jelly begin to be crystallized over 0.86 (86%), the temperature of freezing Royal jelly will be the optimal freezing temperature of Royal jelly for using preservation. At the time, water inside Royal jelly begin to be completely crystallized (ω = 1, or 100%), the temperature of freezing Royal jelly will be the optimal freezing temperature of Royal jelly for using freeze drying. As a consequence of Table 5 and the mathematical model (17) building from experimental data determined the optimal freezing temperature of Royal jelly as follows:

- If the freezing process use of preservation, the optimal freezing temperature of Royal jelly will be T_{Fopt} = -5.73°C, corresponding to ω = 0.8602 or 86.02%, over 86%.
- If the freezing process use of freeze drying, the optimal freezing temperature of Royal jelly will be T_{Fopt} = -18.33°C, corresponding to ω = 1.0000 or 100% and water inside Royal jelly will be completely crystallized.

It was obvious that the problem to determine rate of freezing water inside freezing material has been difficult and complicated question. Currently, this problem has still not had experimental method to determine. For this reason, this study shown that building the experimental method and mathematical model (13) to determine the rate of freezing water was a practical technological solution for food processing factories and was the basic foundation of science for research into freezing field.

The mathematical model (17) was established by experimental data in Table 3, 4 and 5. It described rather suitable for relationship between the rate of freezing water and the freezing temperature of Royal jelly. Because testing compatibility of the mathematical model (17) shown that the maximum error of mathematical model (17) with experimental data was 4.16%, under 5% (Heldman and Daryl, 1992).

The mathematical model (13) and (17) were not only used to set up parameters for the operation of the freezing system and the freeze drying system but also to determine technological mode in freezing process and freeze drying of Royal jelly which grown in Vietnam.

Currently, freezing food processing factories often reduce the freezing temperature of freezing food 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 freezing food has not exactly determined yet. Results of This study 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 (Dzung, 2007, 2012).

NOMENCLATURE

ω ∈ [0, 1]	: The rate of freezing water
ω_E	: The rate of freezing water determined by experimental method
ω_M	: The rate of freezing water determined by mathematical model
W_a	: Initial moisture of Royal jelly
c_n, c_{nd} (J/ (kg.K)	: Specific heat of water
c_{nd} (J/ (kg.K)	: Specific heat of ice
c_{ck} (J/ (kg.K))	: Specific heat of the dry matter inside Royal jelly

c_1 (J/ (kg.K)) : Specific heat of copper
G (kg) : Weight of Royal jelly sample
G_1 (kg) : Weight of copper box in equipment determine rate of freezing water in Fig. 3
$T_{cr} = T_{Fp}$ (°C) : The freezing temperature of water inside Royal jelly
T_{sF} (°C) : The super freezing temperature
T_R (°C) : The room temperature
T_{Fopt} (°C) : The optimal freezing temperature of Royal jelly (when water was crystillized over 86 or 100%)
$T_d = T_1 = T_2 = T_3$ (°C): Initial temperature of Royal jelly sample
$T_c = T_1^{'} = T_2^{'} = T_3^{'}$ (°C) : The temperature of Royal jelly sample after supplying energy
$T = (T_d + T_c)/2$ (°C) : The average temperature of Royal jelly samples
r_{nc} = L (J/kg) : Latent heat of freezing water or lantent heat of thawing ice
U (V) : Number of Voltmeter
I (A) : Number of Amperemeter
X^{tp}_{pro}, X^{tp}_{glu}, X^{tp}_{Lip}, X^{tp}_{ash} and X^{tp}_{im} : Ratio of protein, carbohydrate, lipid, ash and impurities inside the composition of the dry matter of Royal jelly
τ (s) : Heat supply time
φ = 0.1311 (13.11%) : The loss of heat coefficient
RMSR : The residual Root Mean Square Error

CONCLUSION

The new method and the mathematical model (13) was built to determine the rate of freezing water according to the freezing temperature of Royal jelly by the energy balance equation of the warming up and thawing process of freezing Royal jelly. This method was the basic foundation of science for research into freezing field.

From the experimental data in Table 3, 4 and 5 has established the mathematical model (17) which was completely compatible with experiment. The results obtained also determined the optimal freezing temperature of Royal jelly. For the freezing process of Royal jelly was used in preservation, the optimal freezing temperature of Royal jelly would reached maximum value of -5.73°C. For the freezing process of Royal jelly was used in freeze drying, the optimal freezing temperature of Royal jelly would reached maximum value of -18.33°C. On that foundation will build and solve the optimization multi-objective problem to describe the freezing process, simultaneous determine the technological mode of the freezing process.

This much, the mathematical model (17) can be completely used to calculate and determine the technological mode for the freezing process of Royal jelly in Vietnam.

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