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Factors affecting the drying process of shrimp powder from black tiger shrimp (*Penaeus monodon)* head meat

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Abstract:

The most important waste material in shrimp processing industries is shrimp head, comprising about 30÷35% of whole shrimp weight. This waste is rich in nutrients are being wasted. This waste is mainly dried to powder and use for food and feed industries. This study was designed to evaluate the factors affecting the drying process of shrimp head meat. The water activity (a_w) value, color parameters, and the protein content were the main investigations of this research. In this study, minced shrimp head meat was heated at temperature ranging from 60 ºC to 70, 80 and 90 ºC for 5 to 50 minutes with 10 minutes interval. The water activity value and the color parameter at respective heating temperature were also investigated. The results showed that drying at 65 ºC has low a_w value and high soluble protein content is suitable for product. In addition, thermal inactivation of protease at temperature ranging from 60 to 90 ºC of shrimp head meat resulted in a fractional conversion model. When minced shrimp head meat was treated at 80ºC for 30 minutes before drying at 65ºC to reach 6 % moisture was the most suitable value to grind into powder. The rate of powder production through sieve (Size: 1mm x 1mm diameter) is over 90%, and showed special color of dried shrimp, low water activity (0.38) and high soluble protein content with approximately 13 % of dry material. Therefore, the study results demonstrated that drying and grinding shrimp head meat with above condition has potential application in feed and food industries, which could increase economic efficiency and reduce the waste in the environment.

Keywords: drying, moisture, shrimp head meat powder, thermal inactivation, water activity

1. Introduction

Vietnam has advantage for the development of the fisheries industry because of its natural conditions and became one of the world's top ten seafood exporters to the world market in more than ten years. Every year, about 65.000 tons of shrimp head is discharged from the factories (34% of raw materials) in Vietnam [1]. For discharging these by-products into river or soil involved higher cost while treating with modern technology and cause environmental pollution.

M.S Heu *et al.* [2] have studied the composition and nutritional quality of waste products such as shrimp head, shell and tail. The study results indicated that they contain protein (9.3 ÷ 11.6%), lipid (0.7%), minerals (Ca, P, Na, Mg) and small amount of heavy metals (Hg, Pb and Cd). It contains also a small amount of valuable carotenoids. Proteins represent the major component of shrimp heads [3]. Currently, the shrimp head is mainly use as a source of protein in processing animal feed [4] and shrimp shells to recover chitin, or chitosan by chemical procedures [5]. However, the production of chitosan requires removing meat from the shrimp head that leads to a huge impact on the environment. Therefore, the study using shrimp meat in food processing to improve the commercial value of black tiger shrimp while reducing the environmental impact shrimp waste is needed. The studies of shrimp meat are mainly in the extraction and purification of protease in shrimp head. [6,7]. Muoi *et al.* [8] studied the additional processing of shrimp head meat to produce sausage. Khan and Nowsad [9] also use shrimp head meat powder in processing biscuit.

Shrimp head meal production is a new approach to solve the problem. However, enzyme

protease in shrimp mostly concentrates in digestive system, which is located in the head [7]. This enzyme will quickly cause spoilage during the processing if not inactivated. Therefore, the main objective of the study was identifying thermal inactivation kinetics of protease in shrimp head meat and also to determine the other factors affecting drying process during the production of shrimp meat powder.

2. Materials and Methods

2.1. Sample collection and preparation

Shrimp head meat (already shelled) as a by-product of black tiger shrimp (*Penaeus monodon)* were purchased in Thoi Binh district, Ca Mau province, the south of Viet Nam (ensure samples were refrigerated below 4 ºC and 12 hours maximum from separation head to collect head meat). After collection, shrimp head meat was transported to the laboratory of Food Technology department, Can Tho University in iced condition not more than 4 hours. The by-product then was washed under running water, packed in plastic bags containing 1.0 kg in each bag and stored at -25 ºC until use.

2.2. Preparation protease extracts of black tiger shrimp head meat

Protease extraction method is based on the research results of Ha N.L [10].

Frozen shrimp head meat is mixed with water (cooled to 2 to 4°C) the ratio of 1:3. Next, the mixture was crushed by a blender (rotational speed of the motor at 2000 to 3000 rpm) for 3 minutes before extracting enzyme. During the grinding process, the temperature does not exceed 5 ºC. After grinding, the sample is poured into a glass, annealed at different temperature and time to extract enzymes with each 5 minutes stir. The extract obtained by the filter has size of 1 x 1mm to remove large sections of insoluble dry substance (shrimp residue), then cooled 15 minutes before centrifugation in 20 minutes with 3000 rpm speed to remove the residue, obtained extracts, known as crude protease extract.

2.3. Determination of protease activities

Protease activity in crude enzyme extracts was determined according to the modified Anson's method. 1.0 ml enzyme solution was mixed with 5.0 ml substrate (1% casein in 0,133 M Sorensen's phosphate buffer) and incubated at 37 ºC for 30 minutes. At the end of 30 minutes, 10.0 ml of 10% TCA (trichloroacetic acid) was added to stop the reaction. The precipitated casein was then filtered off and 1.0 ml of the filtrate was taken in a test tube. To this 2.0 ml of 0.5 N NaOH solutions and then 0.6 ml of the folin ciocalteu reagent (one ml diluted with 2.0 ml of distilled water) were added. Final readings were taken in a spectrophotometer at 660 nm. Blanks of the samples were prepared by adding the TCA before the addition of substrate.

Standard curve is created by using a graphing program changing absorbance of standards on the Y axis, versus the amount in micromoles for each of 5 tyrosine standards (from 0 to 1 micromole each 0.2 micromole) on the X axis.

Protease activity (UI/ml) = x.V/t.v

With x: micromole tyrosine equivalent from the standard curve; V: Total volume (in milliliters) of assay (11 ml); v: Volume of enzyme (in milliliters) of enzyme used (1 ml); t: Time of assay (in minutes) as per the unit definition (30 min);

1 UI (Anson) = 1 µmol Tyrosine/ml/mi or 1 µmol/mg/min.

2.4. Thermal inactivation enzyme protease in shrimp head meat

The effect of time and temperature on inactivate enzyme protease were studied by heating 50g shrimp head meat which contain in a plastic tube in water bath. The temperature was set at different level (60, 70, 80 and 90°C). Each temperature had 6 rates of time (5, 10, 20, 30, 40, 50 minutes). After thermal inactivated, sample was cooled rapidly under running water to finish the process, conducted protease extraction using method presented above and assayed the residue protease activity by modified Anson's method.

2.5. Determination of thermal inactivation enzyme protease to the color and quality of shrimp head powder

The sample with suitable inactivation time in each temperature above would be dried at 60°C until reached 6% final moisture before grinding into powder by a blender (2000rpm in 1 minute) and jigged through sieve (1mm x 1mm diameter). Water activity and color of the powder were measured by water activity meter and color meter.

2.7. Determination of final moisture to shrimp head powder

Choose one value of thermal inactivation enzyme protease from the result above; begin dry at 60°C until reach different final moisture (4, 6, 8, 10 and 12%). Continue the grinding and jigging process as mention.

2.8. Chemical analysis

All the analyses were performed in triplicate. Moisture content was determined by oven drying samples at 105 °C until constant weight [11]. The total nitrogen content of the raw material was determined using the Kjeldahl method [12]. Crude

protein was estimated by multiplying the total nitrogen content (%N) by 6.25.

2.9. Color and water activity

Each sample was measured three times and the average values were reported. The color (L*, a*) of the shrimp head powder was evaluated by a colorimeter (Shenzhen, model SJ-0520-C, China). The water activity of shrimp head powder was measured by a water activity meter (HANNA, model HI9564, Romania)

2.10. Kinetic data analysis

The inactivation kinetics of enzyme protease was analyzed by using a fractional conversion model as Eq (1):

$$A = A_\infty + (A_o - A_\infty)\, e^{-kt} \quad (1)$$

Where A is residual enzyme activity at time t; A_∞ is the residual enzyme activity after thermal treatment; A_o is the initial enzyme activity and k is the reaction rate constant (min−1).

The value of standard deviation and reliability of thermal inactivation kinetics of enzyme protease were measured by (SAS, 1990):

$$R^2 = 1 - (m-1)\frac{1 - \frac{SSQ_{regression}}{SSQ_{total}}}{(m-j)}$$

$$SD = \sqrt{\frac{SSQ_{residual}}{(m-j)}}$$

Where m is the observations; j is parameters; SSQ is sum of squares and SD is standard deviation.

2.11. Statistical analysis

All data presented are means ± standard deviations. Analysis of variance (One way ANOVA) was performed by Statgraphics centurion XVI version 16.1.11 (Manugistics Inc., USA). The method used to discriminate among means was Fisher's least significant difference (LSD) procedure. Mean were accepted as significantly different at 95% level ($p \leq 0.05$).

3. Results and Discussion

3.1. Basic moisture content, total nitrogen and pH of black tiger shrimp head meat

Processing of shrimp head meat to get shrimp head powder was influenced by many factors, including the initial moisture content, total nitrogen and pH, play an important role that directly affect the product quality. Basic moisture content, total nitrogen and pH of shrimp meat are showed in Table 1.

The results in Table 1 indicated that black tiger shrimp head meat contains higher moisture content (85.42 ± 0.69) %, near neutral pH (7.70 ± 0.07) value, while the pH value of shrimp meat fluctuate from 6.8 ÷ 6.9 [13]. In addition, shrimp head contains a small amount of fat [2] and higher protein content (approximate 12.62 % wet average material). According to Adams and Moss [14], the spoilage microorganisms' optimal conditions (neutral pH, environment, humidity > 80 %) for growth could be easily spoiled the shrimp head meat therefore, thermal treatment along with good storage method could be able to prevent the declining in quality of shrimp head meat.

Table 1. *Basic moisture content, total nitrogen and pH of black tiger shrimp head meat*

Components	Contents
Moisture (%)	85.42 ± 0.69
Total Nitrogen (% wet material)	12.62 ± 0.31
pH	7.70 ± 0.07

3.2. Effect of thermal treatment on inactivation enzyme protease result

The processing of shrimp could be interfered by enzyme protease, which is contained in shrimp head, and become a major spoilage cause during storage. Therefore, inhibition temperature to inactivate the enzyme required being determined. Therefore, protease activity at different temperature was carried out to evaluate the changing patterns using Anson method. The results of the kinetic parameters were shown in Table 2; the changes of kinetic of protease activity were summarized in Table 3

Based on the result in Table 2, the kinetic equation showed high reliability due to low SD value and very high, nearly 1 R^2 value. Therefore, shrimp head meat protease activity patterns in different temperature follow fractional conversion model (Table 3). The residue protease activity decreased with temperature from 60 ºC to 90 ºC while the inactivation rate constant k (1/min) increased. Beside, the ratio A/A_o (ratio of residue enzyme activity after thermal treatment compared with the initial activity) decreased from 5 to 50 minutes thermal treated (Table 3). This proves that inactivated speed increased with time and temperature; the higher the temperature, the more decreased the residue protease activity.

At 60 ºC and 70 ºC, residue protease enzyme activity after thermal treatment is still high compared with the others as the result from heat durability of this type of enzyme in about 52-67 ºC [10]. At the same level of time when increasing temperature from 60 to 90 ºC, the enzyme protease activity decreased. At a temperature of 80 ÷ 90 ºC, residue protease activity showed the lowest value. This result could explain that enzyme is basically protein; if processed at high temperatures would denature protein leads to the inactivation enzyme.

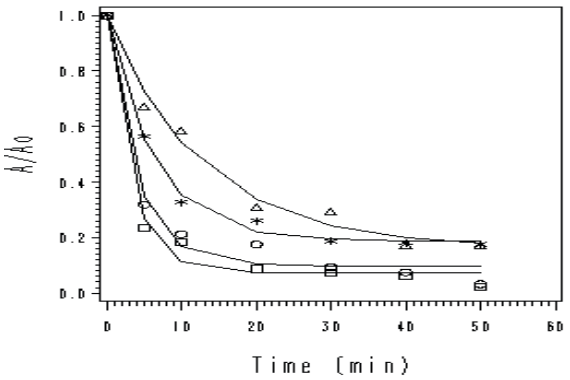

Fig 1. *Thermal inactivation kinetics of shrimp head meat protease: 60 °C (△); 70 °C (✳); 80 °C (○); 90 °C (□).*

Thermal inactivation protease in a long period of time, enzyme activity rapidly decreased in the beginning and then slightly decreased but not decreased to 0 values (Fig.1). This can be explained because protease in shrimp head includes 2 categories, endo-protease and exo-protease. The thermal treatment conditions could fully inactivated exo-protease enzyme however, was not able to inactivated endo-protease [6]. The result in this study confirm the hypothesis that only partial enzyme protease was inactivated.

Moreover, determination of the suitable time for inactivation at each temperature was done and recorded in Table 4. Due to the inactivation of high temperature of any enzyme, thermal treatment at 90 ºC showed lowest residue enzyme protease. Thermal treatment at 60 ºC for 40 minutes, the residue protease activity decreased from 1.03 IU/g to 0.19 IU/g, however, it took only 30 minutes to decrease into this value at 70ºC. On the other hand, the residue protease activity after treating at 80 ºC declined to 0.1 IU/g and 0.09 IU/g and treating at 90 ºC in 20 minutes, achieved the similar protease activity, respectively. Therefore, thermal treatment at 60 ºC, 70°C, 80 ºC and 90 ºC for 40 minutes, 30 minutes, 30 minutes and 20 minutes, respectively required inactivate the protease.

3.3. Effect of thermal inactivation enzyme protease on the drying kinetics and head shrimp powder

Table 5 showed the statistical difference in drying time between samples using heat treatment and no heat treatment. The drying time of heat treatment of sample 2 and 3 were the shortest (460 minutes) compared with other two remaining treatment samples, 486 and 526 minutes for heat treatment 1 and 4, respectively. It is explained that the inactivation before drying makes the tissue softer and the outer membrane broken helps water escape easily. But when the temperature rises up to 90°C, materials clumping lead the difficulty in draining, prolong the drying time. Beside, with the higher treating temperature, the lower water activity was because at higher temperature, protein denatured decrease free water in material.

Some relevant research and trial experiment proved that 60 ºC is suitable temperature for drying shrimp head. The drying time gradually decreased along with increasing inactivation temperature at temperature (60°C) and final moisture (6%) (Fig 2).

The survey showed that the color have significant improvement through its brightness and special red after pretreatment comparison with the sample without treating. At 80 and 90°C, the color improved better than the rest temperature (see in Table 6).

This can be explained by the pre-treatment at higher temperature, protein denatured limited chemical change as well as the inhibition of protease activity. Besides, the drying process make astaxanthin which is sensitive from heat and turn red, represented by a * value. Heat treatment process prevents Maillard reaction occurring during the drying process, will limited brown color and helps product become brighter [15].

The survey showed that the pretreatment *temperature starting materials for improved product quality better than the untreated sample can be expressed through* color and improved for shorter drying time.

3.4. Effect of product's moisture on the grinding into powder

Moisture contents of the shrimp head meat (% db) decreased with time. The moisture decreased rapidly in the early hours of the drying process and lower in the next hour. Therefore, the slope of the drying curve decreases with time. Because the samples are dried at the same temperature (60 ºC), so the drying curves with different final moisture had nearly similar shape. The product moisture was lower, the drying time was longer. The drying time was 340 minutes to achieve the 12% moisture products, while 10%, 8%, 6% and 4% moisture products, the drying time is also increased respectively in 350 minutes, 360 minutes, 400 minutes and 430 minutes.

Based on Table 7, statistical results showed that the water activity of the product had significant difference 5%. Specifically, the water activity of 12 % moisture product (0.580 ± 0.013) reduced to 0.456 in product 4% moisture. The grinding process is hard if product has higher moisture content.

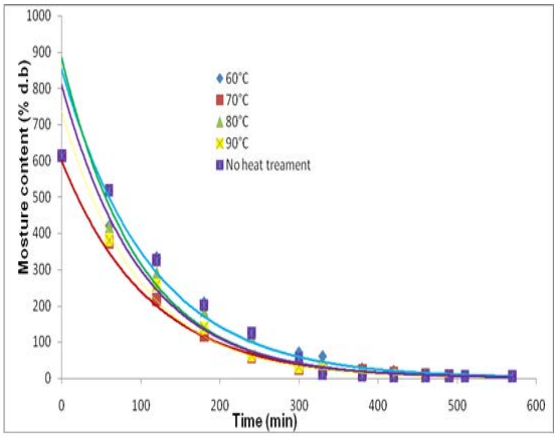

Fig 2. *Drying curve of different thermal treatment*

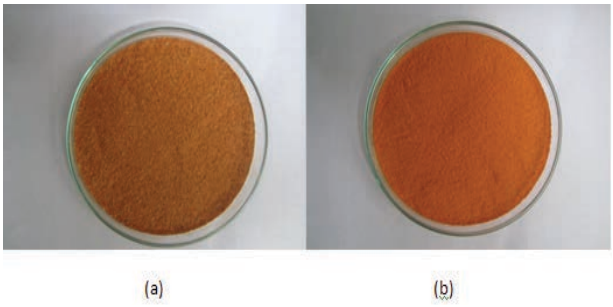

Fig 3. *Shrimp head meat powder with different thermal treatment before drying (a) not using heat treatment, (b) treating at 90°C in 20 minutes*

Table 2. *Estimated kinetics parameters for thermal inactivation of shrimp head meat protease at different temperature*

Temperature	SD	k (1/min)	R2	A_∞
60°C	0.0420	0.0792 ± 0.0107	0.994	0.1695 ± 0.0367
70°C	0.0224	0.1588 ± 0.0106	0.998	0.1913 ± 0.0128
80°C	0.0510	0.2544 ± 0.0405	0.987	0.1001 ± 0.0261
90°C	0.0417	0.3122 ± 0.0450	0.990	0.0743 ± 0.0208

Table 3. *Kinetics equations for thermal inactivation of shrimp head meat protease at different temperature*

Temperature	A_o (UI/g)	Kinetic equation
60°C	1.0267	$A/A_o = 0.1651 + 0.8349\exp(-0.0792t)$
70°C	1.0267	$A/A_o = 0.1863 + 0.8137\exp(-0.1588t)$
80°C	1.0267	$A/A_o = 0.0975 + 0.9025\exp(-0.2544t)$
90°C	1.0267	$A/A_o = 0.0724 + 0.9276\exp(-0.3122t)$

Table 4. *Effect of thermal treatment on inactivation of protease enzyme*

Time (min)	Residue protease activity in shrimp head meat at different temperature (UI/g)			
	60°C	70°C	80°C	90°C
0	1.03^{d}	1.03^{f}	1.03^{d}	1.03^{c}
5	0.69^{c}	0.58^{e}	0.33^{c}	0.24^{b}
10	0.60^{c}	0.34^{d}	0.22^{b}	0.19^{b}
20	0.32^{b}	0.27^{cd}	0.18^{b}	0.09^{a}
30	0.30^{b}	0.19^{ab}	0.10^{a}	0.08^{a}
40	0.19^{a}	0.19^{ab}	0.08^{a}	0.06^{a}
50	0.18^{a}	0.18^{a}	0.06^{a}	0.05^{a}

Different letters indicate significant differences ($P < 0.05$).

Table 5. *Effect of thermal treatment on drying time, water activity and rate of powder through sieve*

	Drying time (min)	a_w (%)	Rate of powder through sieve (%)
No heat treatment	523.33^{a}	0.550^{c}	82.067^{a}
Heat treatment 1 (60°C-40 min)	486.67^{b}	0.583^{c}	85.957^{ab}
Heat treatment 2 (70°C-30 min)	460.0^{c}	0.472^{b}	90.327^{bc}
Heat treatment 3 (80°C-30 min)	460.0^{c}	0.413^{a}	92.467^{c}
Heat treatment 4 (90°C-20 min)	526.67^{a}	0.436^{ab}	93.077^{a}

Different letters indicate significant differences ($P < 0.05$).

Table 6*. Effect of thermal treatment on color value of the powder*

	Color value	
	L*	a*
No heat treatment	80.77^{a}	20.63^{a}
60°C, 40 min	82.67^{ab}	27.89^{c}
70°C, 30 min	83.55^{b}	27.33^{bc}
80°C, 30 min	86.72^{c}	26.95^{bc}
90°C, 20 min	86.24^{c}	26.29^{b}

Different letters indicate significant differences ($P < 0.05$).

Table 7*. Effect of moisture's product on water activity and rate of powder through sieve*

Moisture (%)	Water activity (a_w)	Powder through sieve rate (%)
4	$0.456^{a} \pm 0.014$	$90.467^{a} \pm 0.929$
6	$0.469^{a} \pm 0.019$	$90.200^{a} \pm 1.054$
8	$0.513^{b} \pm 0.012$	$85.900^{b} \pm 1.308$
10	$0.542^{c} \pm 0.016$	$81.867^{c} \pm 1.914$
12	$0.580^{d} \pm 0.013$	$79.233^{d} \pm 0.723$

Different letters indicate significant differences ($P < 0.05$).

4. Conclusion

Protease activity was affected by temperature and time. Shrimp head powder with pre-cooking gives better color. Moisture content had a strong influence on drying time, color and water activity. The rate of powder production from shrimp head through sieve is over 90%, showed special color of dried shrimp, low water activity and high soluble protein content. Therefore, the study results demonstrated that drying and grinding shrimp head meat with above condition has potential application in feed and food industries, which could increase economic efficiency and reduce the waste in the environment.

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