Journal of Bio & Geo Material and Energy (BiGME)
Volume 3 No. 1, March 2023
P-ISSN: 2808-1560 E-ISSN: 2808-1404

The Effect of Acetic Acid Concentration on the Physicochemical Properties of Shrimp Shell Powder (*Fenneropenaeus Merguiensis de Man*)

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Article info:

Submitted : January 2023
Accepted: March 2023
Published: March 2023

Abstract :
Sea waters in Indonesia are rich with various types of invertebrates, one of which is shrimp. Jerbung shrimp is one type of shrimp that is abundant in the market in the city of Jambi, shrimp can be processed into several processed products such as frozen shrimp, dried shrimp, canned shrimp, and others. In Indonesia, shrimp undergo a cold storage process where the head, tail, and skin are disposed of as waste. shrimp shell contains 42.23% protein; crude fiber 19.87%; fat 2.89%; calcium 13.23%; phosphorus 2.08%; and 9.56% chitin content; so that the shrimp shell has the potential to be processed into shrimp shell flour which can be further utilized as a biomaterial for the manufacture of bioplastics and biocoagulants. The purpose of this study was to determine the effect of acetic acid concentration on the physical and chemical properties of shrimp shell powder and to determine the concentration of acetic acid that produced the best physical and chemical properties. This study was conducted using a completely randomized design (CRD), including 5 concentrations of acetic acid (1%, 2.5%, 5%, 7.5%, and 10%) with 4 replications to obtain 20 experimental units. Test parameters include water content, protein content. Fat content, ash content, viscosity and color. The best treatment was shrimp shell powder soaked using 5% acetic acid solution concentration with 6.09% water content, 49.15% protein content, 0.75% fat content, 9.82% ash content, viscosity 69.50 Pa.s and color (L*72.75 a*0.75 b*22.50). The concentration of acetic acid had no significant effect on water content and color of the shrimp powder but it had a significant effect on protein, fat, and ash content as well as viscosity.

Keywords: Acetic Acid, Shrimp, Shrimp Shell Powder,

1. Introduction

Indonesia's waters are rich in various types of invertebrates, one of which is shrimp. Jerbung shrimp is a type of shrimp that is abundant in markets in the Jambi city area. Shrimp can be processed into several processed products such as frozen shrimp, dried shrimp, canned shrimp, etc. (Goligo, 2009). Before processing, the shrimp are cleaned, the head, tail and skin are discarded as waste. According to Kurnia (2004) waste is the remainder of a production process. This waste is considered something that has no use value or economic value, so to get rid of it, it must be thrown away or burned. Improper and incorrect waste handling can cause environmental pollution (Prabandari, 2005).

According to Mirzah (2019) shrimp shells contain 42.23% protein; crude fiber 19.87%; fat 2.89%; calcium 13.23%; phosphorus 2.08%; and chitin content 9.56%; so that shrimp shells have the potential to be processed into shrimp shell flour which can be further utilized as a biomaterial for making bioplastics and biocoagulants. According to Mirwandhono and Siregar (2004) shrimp waste flour is waste from the shrimp processing industry which consists of shrimp heads and shells. The proportion of shrimp heads and shells is estimated to be between 30-40% of the weight of fresh shrimp.

The use of shrimp shell waste has been reported by Hendrawati et al. (2015) where the chitin content in shrimp shells is converted into chitosan as a binder for heavy metals in water. Apart from that, chitosan resulting from processing shrimp shells can be used for bioplastic production. The processing of shrimp shells into chitosan goes through a demineralization and proteinization process, where there will be residual chemical waste mixed with protein and mineral content which can cause environmental pollution. Protein from shrimp shells is a raw material for making bioplastics and calcium carbonate minerals can be used to increase the mechanical strength of plastics, so that the shrimp waste processing process can be made efficient by processing it into biomaterials that can be used directly in various applications, including bioplastics. However, the characteristics of shrimp shells, which are hard and insoluble in water, require a process stage that can convert them into biomaterials that can be used as raw materials for bioplastics. In addition, the chitin in shrimp shells must be converted into a thermoplastic form so that it can be used as a raw material for bioplastics.

Flour from shrimp shells that does not go through a processing process first or is simply cleaned and then dried in the sun and immediately carried out by the size reduction process will produce a rough texture, so it needs further processing so that the resulting texture is smoother. According to Purwaningsih (2000), the chitin content in shrimp shells is 30% of the dry matter and the protein contained in shrimp shells is closely bound to chitin and calcium carbonate (in the form of a proteinchitin-calcium carbonate complex).

Chemical processing using acids including acetic acid is known to produce biomaterials with a protein content that is still quite high according to Andre et al (2015), namely 58.37% so that the protein produced can be used optimally. Apart from that, acetic acid can damage the protein-chitin-calcium carbonate complex. Further, chitin may undergo a partial deacetylation process which can change its characteristics to become more thermoplastic. The use of acetic acid (CH_3COOH) basically refers to the polymer structure of chitin. In the second C position in chitin is the acetamido group ($NHCOCH_3$), thus there is the possibility of dissolution of acetamido with acetate (Andre et al., 2015).

Based on these background, the authors processed shrimp shell waste into shrimp shell powder and determined the effect of the concentration of acetic acid solution on the characteristics of powder from shrimp shells.

2. Research Methods

Materials and Tools

The materials used in this research were shrimp shells, CH_3COOH, $CHCl_3$, Cu, Aquades, PP indicator, NaOH, borax acid, Methylene red blue, HCl, n-hexane. The tools used in this research were a desiccator, porcelain dishes, oven, ashing furnace, fume cupboard, measuring flask, measuring cup, erlenmeyer, filter paper, filter flask, soxhlet, RVA, color reader, petri dish.

Research Design

This research was carried out using a completely randomized design (CRD) with acetic acid concentration treatment consisting of 5 levels, namely:

P1: 1% acetic acid concentration
P2: 2.5% acetic acid concentration
P3: 5% acetic acid concentration
P4: 7.5 % acetic acid concentration
P5: 10% acetic acid concentration.

Each treatment was repeated 4 times so that 20 experimental units were obtained.

Preparation of shrimp shell Powder (Pratiwi, 2017)

The shrimp shell used was a type of jerbung shrimp in good condition with the characteristics of not having a bad smell, having a hard texture and still fresh, then the shrimp shell is washed using running water with the aim of getting clean shrimp shell (no dirt). The shrimp shells that have been cleaned were then soaked using acetic acid solution of 1%, 2.5%, 5%, 7.5% and 10%. According to Hernawan et al (2007), the most effective soaking time in acetic acid is 1 hour. The soaked shrimp shells are dried in the oven at 110-120°C for approximately one hour. After the drying process is complete, the size reduction process was carried out using a blender until smooth and then sifted with a 100 mesh sieve.

Water Content (AOAC, 2005)

The clean porcelain cup was dried in the oven at 105°C for 1 hour, then cooled using a desiccator (approximately 15 minutes) and weighed (A gram). Weigh a sample weighing approximately 4 g, then place it in a porcelain cup (B gram) and dry it in the oven at 105°C for 6 hours. Then it was cooled in a desiccator for 30 minutes, then weighed several times until the weight remained constant (C grams). Calculation of water content can be done using the following equation

$$\%\,Water\ Content = \frac{B-C}{B-A} \times 100\%$$

Ash Content (AOAC, 2005)

The porcelain cup was cleaned and dried in an oven at 105 for ± 30 minutes, then the porcelain cup was then placed in a desiccator (30 minutes) and weighed (A gram). A sample of 4 g was weighed and then put into a porcelain cup (B gram), and heated in the oven at 105°C for 1 hour. The porcelain cup containing the sample was burned in an ashing furnace at a temperature of 550°C until complete ashing was achieved. The furnace temperature was lowered to 200°C and the cup containing the sample was placed in a desiccator for 30 minutes. Cool the sample and weigh it until it remains constant (C grams). Calculation of ash content can be done using the formula:

$$\%\,Ash\ Content = \frac{C-A}{B-A} \times 100\%$$

Protein Content (AOAC, 2005)

The sample was weighed as much as 2 grams and put into a Kjedahl flask. Add 25 ml of sulfuric acid (H_2SO_4) and 1 gram of catalyst (Cu complex). This mixture is digested in a fume cupboard until it is green or clear, then cooled for 30 minutes. Pour 1 ml of chloroform solvent into a Soxhlet sized flask. The solution was diluted with 100 ml of distilled water in a measuring flask, then 25 ml of the solution was taken and put into a Kjedahl flask. Add 7 drops of pp indicator and 50% NaOH until alkaline so that a pink solution is formed. Then the Erlenmeyer is filled with 2% borax acid (H_2BO_3) as much as 25 ml and a mixed indicator (methylene red blue) is added so that the blue solution is collected and bound with borax (H_2BO_3) until a green 4 solution is formed. Distillation takes approximately 15 minutes. The distillation result is titrated with a standard acid solution (HCl 0.1 N) of known concentration until it turns blue. The same way is done for blanks without samples. Calculation of protein content can be done using the following equation.

$$\%Protein = \frac{(V1 - V2) \times N \times 14 \times fp \times fx}{w} \times 100\%$$

Fat Content (AOAC, 2005)

A total of 2 g (W1) of sample was weighed on filter paper and placed in a Soxhlet tube. The filter/fat flask was dried in the oven for 1 hour at 105°C and weighed (W2), connected to a Soxhlet tube. The Soxhlet tube was inserted into the Soxhlet tube extractor chamber and doused with 250 ml of n-hexane, then the tube was installed in the Soxhlet distillation apparatus and then distilled for 6 hours. The fat flask is dried in an oven at 105°C, after which the flask is cooled in a desiccator until the weight is constant (W3). Calculation of fat content can be done using the following equation.

$$\%Fat = \frac{W3 - W2}{W1} \times 100\%$$

Viscosity (An, 2005)

One tool for measuring viscosity is the Visco Analyzer. The Visco Analyzer is a rotational viscometer that combines variable heating, cooling and shear capabilities. The properties of several types of flour were observed and compared using a Visco Analyzer to evaluate the properties of starch gelatinization during the cooking process. The flour is weighed at 3 grams then 25 grams of water is added and heated in an aluminum tube equipped with a wooden plastic impeller.

When the test begins, the sample can in the Visco Analyzer rotates at a speed of 960 rpm for 10 seconds to homogenize the sample then slows down to 160 rpm. Each sample was heated and gelatinized for 12.5 minutes from 50°C. The temperature on the Visco Analyzer is set at 50°C for 1 minute, then the temperature is increased by 12°C/minute to 95°C, and maintained for 2.5 minutes, reduced again to 50°C, and maintained for 1 minute.

Color (Andarwulan Et al., 2011)

Analysis was carried out using a Konica Minolta CR-14 color reader. In principle, color readers work based on measuring the color differences produced by the sample surface. Measurements are carried out by placing flour samples in a uniform sized sample container (petri dish). Next, the L, a and b values were measured on the sample. Color descriptions based on L, a and b values are presented in table 7. Measurements were also made on the °hue values. When measuring the L* and °hue values, the values are obtained using the following equation.

$$L^{*} = \frac{L'}{70} \times 100\%$$

3. Results and Discussion

Water Content

Determining water content is a way to measure the amount of water contained in a material. The water content can be used as a parameter for the quality of a food ingredient which includes acceptability, freshness and durability of the food ingredient. Apart from that, water can affect the appearance, texture and taste of a food product (Winarno, 2008).

The results of analysis of variance on water content parameters show that the concentration of acetic acid has no significant effect on the water content of shrimp shell flour. It is known that the acetic acid concentration treatment has no significant effect on the water content of the shrimp shell flour produced. The moisture content value of shrimp shell flour ranges from 5.14% to 6.90%. 5 The lowest water content was obtained in the 7.5% acetic acid concentration treatment at 5.14% and the highest water content was obtained in the 2.5% acetic acid concentration treatment at 6.90%. Treatments with acetic acid concentrations of 1%, 5% and 10% were not significantly different, but the 2.5% treatment was significantly different from all treatments and the 7.5% treatment was also significantly different from all other treatments.

Testing the water content of shrimp shell flour is intended to determine the water content contained in shrimp shell flour. The water content of shrimp shell flour will affect its shelf life, because it is closely related to the metabolic activities that occur while the shrimp shell flour is stored. The difference in concentration values is more influenced by the level of dryness of the sample during preparation, one of which is during the sample drying process. Water molecules that are bound to other molecules such as O and N atoms require large amounts of energy to remove them. This required energy can come from the heating process. Heating will break the van der Walls and covalent bonds of hydrogen atoms, thereby reducing the ability of bound water in shrimp shells to bind with other compounds (Winarno, 2008). The maximum water content quality standard for flour is 14.5%. The highest water content in shrimp shell flour is 6.90% so it still meets the standards.

Protein Content

Proteins are long chains of amino acids held together by many bonds called peptide bonds. Protein is needed to repair or maintain tissue, growth and form certain active biological compounds, protein can also function as an energy source (Subandiyono and Hastuti, 2016). According to Mirzah (2019), shrimp shells contain quite high levels of protein, so shrimp shells have the potential to be used as a food ingredient, namely flour from shrimp shells.

It is known that the treatment of acetic acid concentration on shrimp shell flour has a significantly different effect on the protein content of the shrimp shell flour produced. The protein content value of shrimp shell flour ranges from 23.23% to 49.15%. The lowest protein content was obtained in the 1% acetic acid concentration treatment at 23.23% and the highest protein content was obtained in the 5% acetic acid concentration treatment at 49.15%. Using an acetic acid solution concentration of up to 5% can increase the protein value. According to Juliasti, et al (2014), increasing acid concentration causes more amino acid bonds to be broken so that more protein dissolves during the extraction process. The high amount of soluble protein causes the protein content in flour products to also tend to increase, increasing the concentration of the solution will increase the dissolved collagen, whereas in the treatment of 7.5% and 10% acetic acid the protein content decreases, but is still higher than with acetic acid 1 % and 2.5%.

Concentrations of acetic acid that are too high can also cause the protein structure to be damaged so that the resulting protein content decreases. According to Chamidah and Elita (2002), immersion in acetic acid solution causes structural proteins to experience swelling so that the coil structure opens. The high concentration of acetic acid solution causes hydrogen bonds to break and excessive opening of the collagen coil structure so that some of the amino acids are extracted and released from the collagen and carried into waste water, resulting in lower levels of protein obtained.

Fat Content

Fat is found in almost all types of food and each has different amounts of content. Therefore, analyzing the fat content of a food item is very important so that the calorie requirements of a food item can be calculated properly (Pargiyanti, 2019).

It is known that the treatment of acetic acid concentration on shrimp shell flour has a significantly different effect on the fat content of the shrimp shell flour produced. The fat content value of shrimp shell flour ranges from 0.43% to 1.18%. The lowest fat content was obtained in the 7.5% acetic acid concentration treatment at 0.43% and the highest fat content was obtained in the 1% acetic acid concentration treatment at 1.18%.

The fat content of shrimp shells according to Hartanto (2015) is 1.27%, the highest fat content of 6 shrimp shell flour by immersion in acetic acid solution with various concentrations is 1.18%. This indicates that soaking using acetic acid can hydrolyze the fat content. found in shrimp shells is characterized by a decrease in the fat content of shrimp shell flour. According to Sahril and Lekahena (2015), lower fat content in flour can prevent flour from experiencing a decline in quality due to the rancidity process. High fat content will make flour easily go rancid. One of the causes of rancidity in flour is fat oxidation.

Ash Content

Ash content is a mixture of inorganic or mineral components found in a food ingredient. Organic materials in the combustion process will burn but the inorganic components will not, which is why it is called ash content. Determining the ash content can be used to determine whether processing is good or not, knowing the type of ingredients used and as a parameter for the nutritional value of a food ingredient (Istifa, 2010).

It is known that the treatment of acetic acid concentration on shrimp shell flour has a significantly different effect on the ash content of the shrimp shell flour produced. The ash content value of shrimp shell flour ranges from 2.27% to 40.97%. The lowest fat content was obtained in the 10% acetic acid concentration treatment at 2.27% and the highest ash content was obtained in the 1% acetic acid concentration treatment at 40.97%.

The ash content of shrimp shell flour decreased as the concentration of the acetic acid solution used for soaking increased. This shows that the acid solution can hydrolyze the mineral content in shrimp shells, so that the ash content in shrimp shell flour decreases. According to Rahayu and Fihriya (2015), the higher the acid concentration, the more calcium will dissolve during the soaking process, so the ash content will be lower. In this process, acetic acid will react with calcium phosphate in shrimp shells to produce calcium citrate and phosphoric acid. This will produce calcium salts that dissolve and the shrimp shell becomes soft.

Viscosity

Viscosity is the ability to resist a fluid from flowing. The viscosity coefficient is the viscosity value of the fluid. The greater the viscosity coefficient value, the thicker the fluid. (Cahyani, 2019).

It is known that the treatment of acetic acid concentration on shrimp shell flour has a significantly different effect on the viscosity of the shrimp shell flour produced. The viscosity value of shrimp shell flour ranges from 10.15 m.Pa.s to 300.00 m.Pa.s. The lowest fat content was obtained in the 1% acetic acid concentration treatment of 10.15 m.Pa.s and the highest fat content was obtained in the 10% acetic acid concentration treatment of 300.00 m.Pa.s.

The viscosity of shrimp shell flour increases along with the increasing concentration of the acetic acid solution used for soaking. This viscosity value is not in line with the opinion of Cahyani (2019), which states that the higher the acid concentration, the more open the structure of the amino acid chain, which causes the amino acid chain to cut more. so that shorter chains are produced and the collagen molecular weight will be reduced, resulting in lower viscosity values. The high viscosity is related to the molecular weight of the flour and the length of the amino acid chain. According to Hao (2009), the high viscosity value is caused by the optimal conversion of collagen into flour so that the amino/oligopeptide chains formed are quite long and the viscosity is high.

Color

Color is the main parameter that determines the level of consumer acceptance of a product (Wilbur, 2013). A color test was carried out on flour from shrimp shells to determine the effect on the l* (brightness), a* (reddishness), and b* (yellowish) values of shrimp shell flour.

Based on the analysis of variance, the immersion treatment of various concentrations of acetic acid solution on shrimp shells had no significant effect on the brightness l*, redness a* and yellowness b* of shrimp shell flour. The average value of testing the color of shrimp shell flour with various acetic acid concentration treatments has an l* value ranging from 72.25-74.25. bright product value. The average value of testing the color of shrimp shell flour with various acetic acid concentration treatments has an a* value ranging from 0.5 to 1.0. The average value of shrimp shell flour color testing with various acetic acid concentration treatments had a b* value ranging from 19.50-22.50. The soaking treatment using various concentrations of acetic acid did not have a significant effect on the color produced from shrimp shell flour but was affected by the drying process which was carried out using heat energy. According to Trilaksani et al (2012), during heating during drying, a non-enzymatic browning process or Maillard reaction occurs between the amino groups in amino acids and the results of fat oxidation which are still quite high, which causes brown pigment or melanoidin.

Table 1. Data from analysis of shrimp shell flour

No	Analysis	Nilai				
		1	2,5	5	7,5	10
1	Water Content	6,60%	6,90%	6,09%	5,14%	6,73%
2	Protein Content	23,23%[a]	30,44%[a]	49,15%[b]	48,74%[b]	47,23%[b]
3	Fat Content	1,18%[b]	0,46%[a]	0,75%[a]	0.43%[b]	1,17%[b]
4	Ash Content	40,97%[c]	28,90%[d]	9,82%[c]	4,45%[b]	2,27%[a]
5	Viscosity	10,15[a] (m.pa.s)	21,95[a] (m.pa.s)	69,50[a] (m.pa.s)	64,50[a] (m.pa.s)	300,00[b] (m.pa.s)
6	Color l*	74,25	73,50	72,75	72,25	72,25
	a*	0,5	0,75	0,75	1,0	1,0
	b*	20,25	20,00	22,50	20,25	19,50

Conclusion

Soaking shrimp shells using various concentrations of acetic acid solution had a significant effect on protein content, fat content, ash content and viscosity of shrimp shell flour. The best treatment is shrimp shell flour which is soaked using a 5% acetic acid solution concentration with a water content of 6.09%, protein content of 49.15%, fat content of 0.75%, ash content of 9.82%, viscosity of 69.50 m.Pa.s and color (l*72.75 a*0.75 b*22.50)

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