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Effect of Different Bleaching Temperatures on the Quality of Refined Catfish (*Clarias gariepinus*) Oil

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Abstract

Catfish (*Clarias gariepinus*) oil contains a high amount of unsaturated fatty acids, however process of refining will damage the double bond of unsaturated fatty acids. This study was aimed at develop a better refining process of catfish oil. The material used in this research were crude catfish oil as a by product from flouring industry, and magnesol XL as its adsorbent. Oil was purified by two-step, neutralization and bleaching. The various bleaching temperatures (25^0 C; 70^0 C; 100^0 C) were applied. The study showed that refined oil at temperature of 25^0C resulted in a best value of FFA, PV, anisidin numbers, and the lowest number of total oxidation.

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Keywords: refining, bleaching temperature, catfish (*Clarias gariepinus*) oil, unsaturated fatty acid

INTRODUCTION

Catfish is one of fisheries commodity in Indonesia and the production has increased every year. Therefore, now a day catfish processing has grown with a variety of ways, for example flouring production for the manufacture of catfish biscuits [1]. Flouring process produces a byproduct that still contain high amount of unsaturated oils.

The increase in the catfish processing industry resulting in the increase of by product volume. The main nutrients contained in these oils are unsaturated fatty acids which is known to have positive benefits on health, such as preventing the incidence of coronary heart disease [2], lowering cholesterol [3], improving cognitive function [4], and serving as anti-inflammatory function [5].

Catfish oil from the flouring must be processed before consumption. One of the process is called purification. Purification is done with the aim at improving the quality of this oil. A purification process includes four stages;

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degumming, neutralization, bleaching, and deodorization [6]. Degumming is done to separate the gum with the oil fraction, this stage is usually performed on vegetable oil. Neutralization aims at reducing levels of FFA, bleaching aims to improve the color quality of the oil, deodorization aims to reduce of unwanted odor from fish oil [7]. However, the oil processed by high temperatures can damage the bond of unsaturated fatty acids (both MUFA and PUFA). Therefore, it is necessary to study the process of purification that can maintain the bond of unsaturated fatty acids contained in catfish oil. Conventional bleaching process, usually carried out at temperatures above 100^0C, it will damage the double bond of unsaturated chain [8]. The purpose of this study is to find the best method of bleaching temperature to maintain the bond of unsaturated fatty acids in catfish oil. The benefit of this research is to provide an alternative purification process of fish oil that are able to maintain the content of unsaturated fatty acids.

MATERIALS AND METHODS

The materials used in this study were a by product of flouring catfish. Materials for the neutralization process were NaOH, adsorbent used for the bleaching process was Magnesol XL as much as 5% [9]. The sample was homogenized and characterized (Free Fatty Acid, Peroxide Value, P-Anisidin, Total Oxidation Numbers, and Fatty Acid) before purification. Neutralization process is done by the addition of NaOH according to the amount of free fatty acid, then the oil in the bleaching treatment temperature difference (25^0C, 70^0C, 100^0C).

Free fatty acid (FFA)

Free Fatty Acids in this research was analyzed by a following procedures. First, oil was weighed into a flask followed by neutralized 95% ethyl alcohol and phenolphthalein indicator. The mixture was then titrated against sodium hydroxide solution until a permanent pink color persisted for at least 30 s. Percentage of FFA by weight was calculated on either an oleic, palmitic, orlauric acid basis, depending on the type of oil being analyzed [12]. Each sample was titrated in triplicate.

FFA percentage is calculated based on the following equation:

$$\%\text{FFA} = \frac{A \times N \times M}{10\,G}$$

A = the number of titration KOH (mL)

N = normality KOH

G = samples weight

M = Fatty acids dominant molecular weight

Peroxide Value

Peroxide value was analyzed by a few steps, first weight of oil sample (2 g) was dissolved in 30 mL chloroform: acetic acid (3:2, v/v) then 1 mL freshly prepared saturated KI (potassium iodide) solution was added and the mixture vortexed for exactly 1 min. Distilled water (30 mL) and stock solution (0.5 mL, starch 1%) were added and the liberated iodine was titrated with sodium thiosulfate (0.1 mol L-1). Determination of the peroxide value in the unit meq/kg was determined by the following equation [10]:

Peroxide value (mEq/kg) = (S-B) x N x 1000

S = volume of sodium thiosulfate sample

B = volume of sodium thiosulfate blanco

N = normality of sodium thiosulfate

G = samples weight

Anisidin value (AV)

Anisidin Value was analyzed with the following procedures; First, made a solution of test 1 by means of dissolving 0.5 g samples into 25 mL trimethylpentane. Later made a solution of test 2 with a way of adding 1 mL solution p-anisidine (2.5 g/l) into a solution of 1,5 mL test then shaken and avoid of the light. Later made a solution of a reference to a way of adding 1 mL solution p-anisidine (2.5 g/l) into 5 mL solution trimethylpentane, then shaken and avoid of the light. Then a solution of measured absorbance, the value of a solution of test 1 on 350 nm by using trimethylpentane as a solution of compensation. A solution of test 2 on 350 nm just 10 minutes after solution prepared, by the use of a solution of referencing as compensation [11]. The value of anisidine set with an equation the following:

$$\text{Anisidine value} = \frac{25(1.2A1 - A2)}{m}$$

A1 = absorbance test solution 1

A2 = absorbance test solution 2

m = the mass of the sample use for test solution 1

Total Oxidation Value/Totoks

Total oxidation value obtained by summing the value 2PV with PAV, where PV (Peroxide Value) is the number of peroxide and p-AV (P-anisidine Value) is the p-anisidin [13]. Total oxidation was calculated based on the following equation:

Total oxidation = 2PV + p-AV

PV = Peroxide Value

p-AV = Anisidin Value

RESULTS AND DISCUSSION

The results of this study indicated that the crude catfish oil contained Free Fatty Acid (FFA), Peroxide Value (PV), P-Anisidin Value, Total Oxidation Number as follows: 11.32%, 9.23 mEq/kg, 1.22 mEq/kg, and 19.62 mEq/kg, respectively. FFA values indicated the degree of primary oxidation, it measures the amount of fatty acids (a component of oil) that cleaved from their main molecules (triglycerides or phospholipids). Cleavage of a free fatty acid from its main molecules showed hydrolytic breakdown and was often used in whole biological systems as an indication of stress. The FFA value of crude catfish oil of this research exceeded FFA values of IFOS standard (1-7%) [14]. It means, the crude catfish oil was highly oxidized.

Free Fatty Acid Value (FFA)

There was an improvement of oxidation values after refining process. The value of free fatty acids after purifying at a temperature of 25^0C, 70^0C, and 100^0C were 0.14%, 0.26%, and 0.5%, respectively. Free fatty acids in the oil which was purified at a temperature of 25^0C decreased by 98.76%. Refined oil at a temperature of 70^0C has decreased 97.72%, while the 100^0C temperature decreased by 95.5%. Based on the statistical analysis, the different temperature of the treatments had a significant influence on the value of free fatty acid value ($P < 0.05$). Treatment temperature of 25^0C indicated that at this temperature bonding of unsaturated fatty acids was more stable and less oxidation. The bonds of unsaturated fatty acids were highly susceptible to heat, therefore a lower temperature treatment can maintain its bonds [15]. Diagram of free fatty acids value from purified catfish oil by temperature differences is presented in Figure 1.

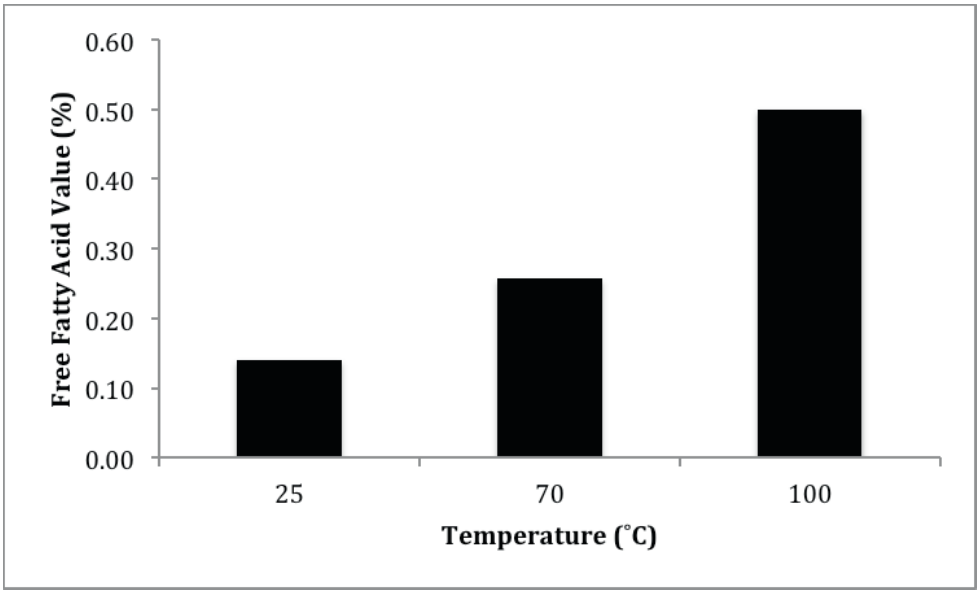

Figure 1. Diagram of free fatty acids value from purified catfish oil by temperature differences

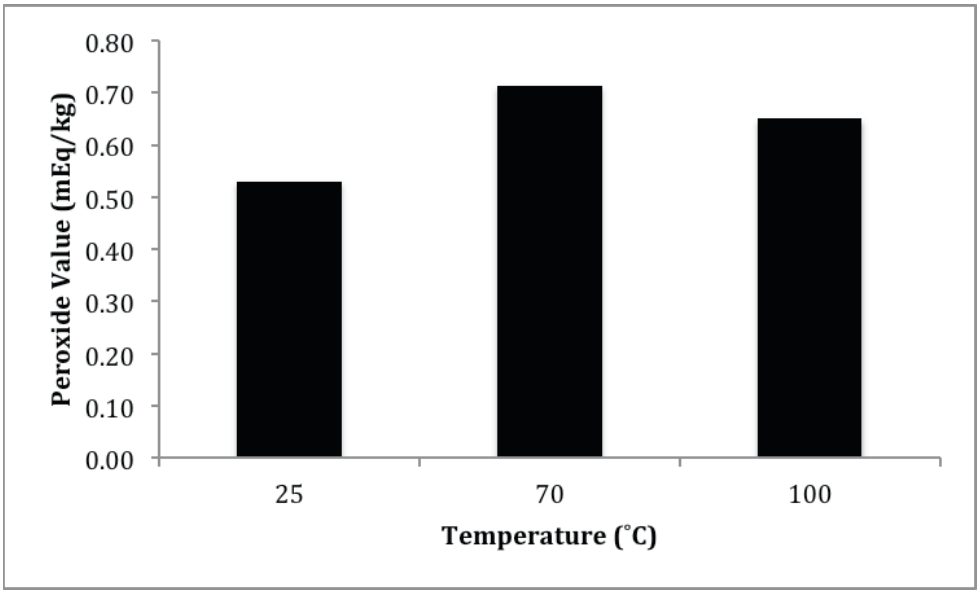

Figure 2. Diagram of peroxide value from purified catfish oil by temperature differences

Peroxide Value

The lowest oxidation number was achieved by the bleaching treatment at 25^0C, i.e. 0.53 mEq/kg, followed by a treatment at 100^0C and 70^0C, that were 0.71 mEq/kg and 0.65 mEq/kg, respectively. Peroxide in purified oil at a temperature of 25^0C decreased by 72.82%. Refined oil at a temperature of 70^0C has decreased 59.03%, while the 100^0C temperature decreased by 49.32%. Based on the statistical analysis, the various temperatures had no significant influence on the value of free fatty acid oil. Primary oxidation processes in the oil mainly form hydroperoxides, which were measured by the PV. In general, the lower the PV, the better the quality of the oil. However PV has decreased as secondary oxidation products (Figure 1). Most customers would require a PV of less than 10 in marine oils, but PV may

be needed to be as low as 2, depending on the market demand. Diagram of peroxide value of purified catfish oil by temperature differences are presented in Figure 2.

P-Anisidin Value

The secondary stage of oxidation occurs when the hydroperoxides decompose to form carbonyls and other compounds, in particular aldehydes. In this study, the lowest P- anisidin value was on the bleaching treatment at 25^0C, i.e. 0.17 mEq/kg, followed by a treatment at 70^0C and 100^0C, i.e. 0.5 mEq/kg and 0.7 mEq/kg, respectively. P-Anisidin value of the purified oil at temperature of 25^0C decreased by 85.92%. Refined oil at a temperature of 70^0C has decreased 58.82%, while the 100^0C temperature has decreased by 42.38%. Based on the statistical analysis, the different temperature treatments had no significant influence on the value of P-anisidin. The lower the AV, the better the quality of the oil. Diagram of P-anisidin value from purified catfish oil by temperature differences are presented in Figure 3.

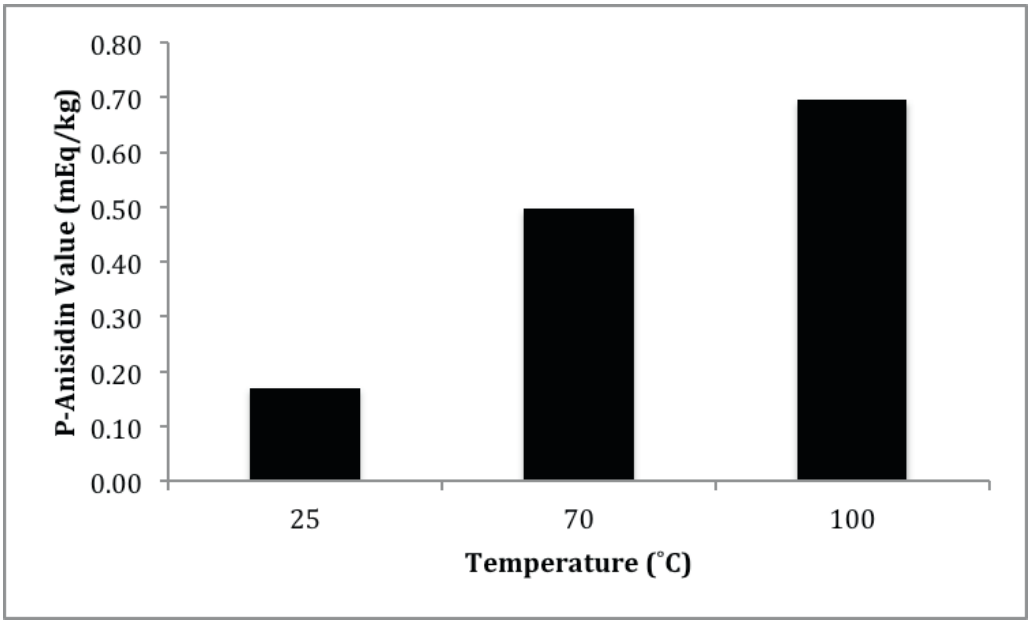

Figure 3. Diagram of P-anisidin value from purified catfish oil by temperature differences

Total Oxidation Value (Totox Value)

The Totox value was calculated by the formula AV + 2PV to indicate an oil's overall oxidation state. The lowest oxidation has been achieved by bleaching treatment at 25^0C, i.e. 5.18 mEq / kg, followed by a treatment at 70^0C and 100^0C i.e. 8.05 mEq/kg and 10.04 mEq/kg, respectively. Numbers on the total oxidation of purified oil at a temperature of 25^0C has decreased by 75.62%. Refined oil at a temperature of 70^0C has decreased 59.02%, while the 100^0C temperature has decreased by 48.89%. Based on the statistical analysis, the different temperature treatments had no significant influence on the value of free fatty acid oil. The lower value of Totox, the better the quality of oil. Diagram of the total oxidation value of purified catfish oil by temperature difference are presented in figure 4.

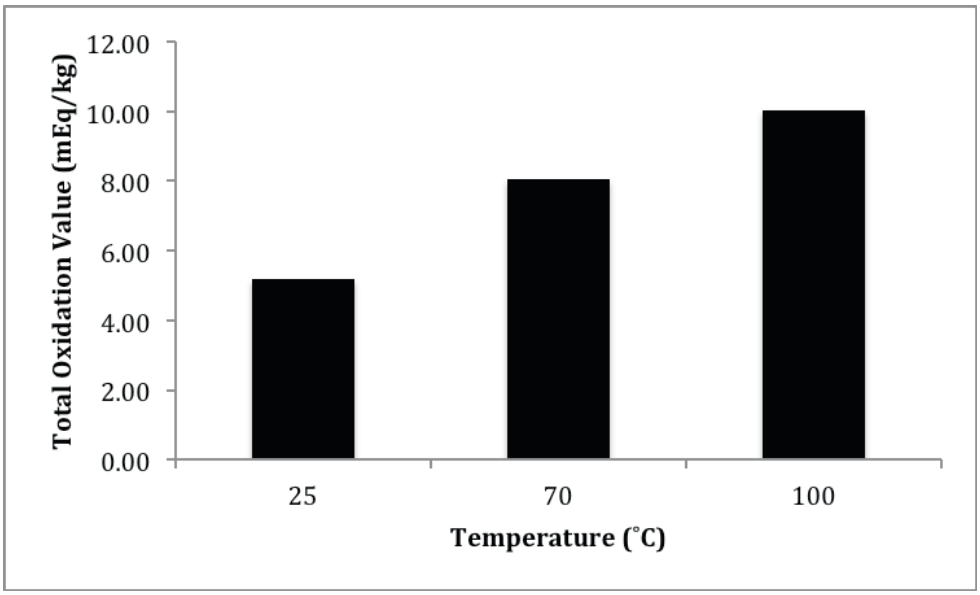

Figure 4. Diagram total oxidation value from purified catfish oil by temperature differences
Fatty Acids

Table 1. Fatty acids profile in catfish oil

No.	Fatty Acid	Precentage
1	Lauric Acid, C12:0	0.37
2	Myristic Acid, C14:0	1.04
4	Pentadecanoic Acid, C15:0	0.18
5	Palmitic Acid, C16:0	21.27
7	Heptadecanoic Acid, C17:0	0.20
8	Cis-10-Heptadecanoic Acid, C17:0	0.14
9	Stearic Acid, C18:0	5.32
14	Arachidic Acid, C20:0	0.10
18	Heneicosanoic Acid, C21:0	0.04
20	Behenic Acid, C22:0	0.10
25	Tricosanoic Acid, C23:0	0.03
26	Lignoceric Acid, C24:0	0.06
28	Nervonic Acid, C24:0	0.06
	SFA	**28.88**
6	Palmitoleic Acid, C16:1	3.65
3	Myristoleic Acid, C14:1	0.06
10	Elaidic Acid, C18:1n9t	n.d
11	Oleic Acid, C18:1n9c	30.92
16	Cis-11-Eicosenoic Acid, C20:1	0.53
22	Erucic Acid, C22:1n9	0.04
	MUFA	**35.19**
12	Linolelaidic Acid, C18:2n9t	n.d
13	Linoleic Acid, C18:2n6c	12.37
15	g-Linolenic Acid, C18:3n6	1.31
17	Linolenic Acid, C18:3n3	0.68
19	Cis-11,14-Eicosedienoic Acid, C20:2	0.30
21	Cis-8,11,14-Eicosetrienoic Acid, C20:3n6	0.71
23	Cis-11,14-Eicosedienoic Acid, C20:2	0.03
24	Arachidonic Acid, C20:4n6	0.56
27	Cis-5,8,11,14,17-Eicosapentaenoic Acid, C20:5n3	0.28
29	Cis-4,7,10,13,16,19-Docosahexaenoic Acid, C22:6n3	1.01
	PUFA	**17.23**

n.d : not detected

The dominant fatty acids in catfish oil were oleic acid, palmitic acid, and linoleic acid, i.e. 30.92%, 21.27%, and 12.37%, respectively. Total SFA, MUFA, and PUFA in catfish oil were 28.88%, 35.19%, and 17:23%. It is known that MUFA and PUFA can reduce LDL cholesterol concentration and total/HDL cholesterol ratio. Oleic acid has a function as an anti breast cancer [16].

However, the high amount of MUFA and PUFA in catfish oil will accelerate the oxidation process in the oil catfish. Therefore after purifying catfish oil, it was needed to add the antioxidants (natural or synthetic) to maintain the shelf life of the oil [17]. Fatty acids profile in catfish oil is presented in Table 1.

CONCLUSION

The lower the temperature used in the refining process would decrease the oxidation parameter of catfish oil. The treatment at 25˚C resulted in best value of FFA, PV, anisidin numbers, and the lowest number of total oxidation i.e. 0.14%; 2.5.mg Eq/kg; 0.17 mEq/kg; 5.18 mEq/kg, respectively

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