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Enrichment of omega-3 fatty acids, waste oil by-products canning tuna (thunnus sp.) with urea crystallization

Ni Wayan Suriani[1,*] and Alfrits Komansilan[2]

[1]Department of Natural Science Education, Manado State University, Tondano, Indonesia
[2]Department of Physics, Manado State University, Tondano, Indonesia

*suriani_wayan@yahoo.com

Abstract. Enrichment test of omega-3 fatty acids from tuna canning waste oil in Bitung North Sulawesi Indonesia have been conducted. The purpose of this study was to utilize tuna canning waste oil and enriched the concentration of omega-3 fatty acids with urea crystallization. The results showed that the characteristics of fish oil quality of tuna canning waste 0.9% moisture content, free fatty acids (FFA) 3.4%, copper (Cu) 0.1 ppm, iron (Fe) 2.5 ppm and phosphorus (P) 32,5 ppm still meets IFOMA quality standards Liquid fatty acid profile contains total SFA 33.7%, 27.6% PUFA, 1.4% omega-6 fatty acids, omega-3 fatty acids 25.9% , EPA 4.2% and DHA 21.4%, MUFA 18.8%, omega-9 fatty acids 13.9%, while concentrations of omega-3 fatty acids contained a total SFA of 7.7%, PUFA 70.9%, omega-6 fatty acids 0.8%, omega-3 fatty acids 70.1%, EPA 4.2% and DHA 21.4%, MUFA 2.7%, omega-9 fatty acids 1.5%. The urea crystallization process increases the levels of polyunsaturated fatty acids (PUFAs) such as omega-3 (EPA and DHA.), the enrichment rate is 2.7 times.

1. Introduction

Quality fish oil if it contains fatty acids that are beneficial to health. Omega-3 is an unsaturated fatty acid that is important and needed, especially for people with high cholesterol. The dominant types of omega-3 in fish oil are EPA and DHA. Fish cannot produce EPA and DHA alone, sea plants such as algae and algae can produce EPA and DHA. Fish can contain EPA and DHA through their food in the form of algae, and when we consume fish containing both of these fatty acids [1]. EPA and DHA have a good impact on people with heart disease if taken continuously, and about 45% of the risk of sudden death can be avoided compared to people who eat foods that do not contain EPA and DHA [1]. Foods containing EPA and DHA can also cure keloid disease [2], reduce blood cholesterol, anti-inflammatory and anti-platelet aggregation [1].

Tuna fish oil also contains PUFA, such as EPA and DHA [3]. EPA plays an important role in the growth and development of the life cycle is also useful in preventing and treating hypertension, arteriosclerosis, and arthritis [4]. In addition DHA is considered a promising nutrient because it has a good impact on the development of the brain and retina of the eye [5]. Because it is useful for health, EPA and DHA (omega-3) have the potential to be functional food.

EPA and DHA (omega-3) contained in fish oil will be beneficial for health, but will have a negative impact on health if the oil contains a lot of trans fatty acids and saturated fatty acids. This is because saturated fatty acids can cause obesity while trans fatty acids can trigger cancer risk factors

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[6]. (PUFA) as well as omega-3 (EPA and DHA), levels can be increased through the process of crystallizing urea [7] [8].

2. Research and Method

2.1. Time and place of research
The study was conducted from March 2017 to December 2017 and was conducted at the FMIPA UNIMA Chemical Laboratory, LAB. ENT. Brawijaya University Malang, Agricultural Technology Laboratory, Gadjah Mada University, Yogyakarta.

2.2. Research Tools and Materials
The ingredients used in making concentrations of omega-3 fatty acids are urea, hexane, HCl, NaOH, Na2EDTA, methanol, ethanol, HCl, urea (pro-analysis), Whatman No.1 filter paper, coarse hydrogen gas paper filters, nitrogen gas and helium gas.
The tools used in this study are rotav, refrigerator, homogenizer, digital scales, pH-meters, magnetic stabilizers, vortexers, glassware, and tools used for the analysis of fatty acids are GC- (Gas Chromatography. Stages of making omega-3 fatty acid ingredients from tuna oil [9].

2.2.1 Saponification Stage. Prepare NaOH solution by dissolving NaOH of 480 g and Na2EDTA in 5 g into 400 ml of water, then add 1600 ml of ethanol. Take 1000 g of tuna oil mixed with 2000 ml of NaOH (5 N) solution in water / ethanol. The mixture was refluxed for 30 minutes at 60 ^{0}C with a magnetic stirrer on the hot plate.

2.2.2. Stage of fatty acid extraction. Weigh 400 ml n-hexane, add the saponification sample and stir it for about 1 hour then transfer it into a separating funnel and leave it for about 1 hour so that 2 layers are formed, where the upper layer is discarded material that is discarded. the bottom layer is taken then concentrated HCl is added, stirred with a magnetic stirrer until it reaches pH 4, the sample is transferred to a separating funnel left for 1 hour until 2 layers are formed, then the top layer is taken and evaporated with a rotary evaporator vacuum at 30 ^{0}C until all solvents are used up the saponification produced is 2500 ml

2.2.3. Stage of urea crystallization. The extracted fatty acid sample was put into an urea solution and heated at a temperature of 60-65 ^{0}C in a methanol solution and stirred for 5’. The amount of dissolved urea is adjusted with a ratio of 3: 1 between fatty acids and urea, then the sample is heated to clear. To make an urea solution, 200 ml of methanol is needed for 25 g of fish oil. The oil and urea mixture is stirred for 5’, then allowed to stand for 24 hours until crystals form at 100 ^{0}C. The sample is filtered until the urea crystals separate from the solvent containing omega-3.

2.2.4. Omega-3 extraction stage. Take 3 liters of filtrate as a result of crystallizing urea, then add 500 ml of concentrated HCl solution and 1 liter of n-hexane solution, then stir it for about 1 hour with a magnetic stirrer and put it in a separating funnel and leave it to form 2 layers, top layer taken. (I) Take the bottom layer then add 1500 ml of water and re-extract it by adding 1000 ml of hexane which is stirred for about 30 minutes, then put in a separating funnel and left for 60 minutes until 2 layers are formed and the upper layer is taken. (II) The first and second extracts were stirred until mixed and then evaporated at ± 30 ^{0}C until the n-hexane solvent evaporated (± 2 hours), using a rotary vacuum evaporator.

3. Results And Discussion

3.1. The characteristics of the waste oil canning tuna
Description of the quality characteristics of the waste oil of tuna canning.

Table 1. Quality Characteristics of oil Waste canning of tuna.

PARAMETERS	LIQUID WASTE	STANDARD IFOMA
Water Content (%)	0,9	< 1
FFA (%)	3,4	1 - 7
Peroxide Numbers (mek/Kg)	13,8	3 - 20
Cu (ppm)	0,1	<0,3
Fe (ppm)	2,5	0,5 – 0,7
P (ppm)	32,5	5-100

Data from the analysis of the quality of tuna canning waste oil in Table 1 shows:

3.1.1. Water content. Tuna canning waste oil has a moisture content of 0.9%. The water content of the oil from this study still meets the water content standard <1. The quality of fish oil will be lower if the water content in fish oil is higher because the hydrolysis reaction process is also getting faster [10].

*3.1.2. Free fatty acid levels.*T he level of FFA in tuna canning waste oil was 3.4%. According to Toisuta *et al*. fat content of tuna on head 1.1%, skin 2%, liver 1.99% liver and gonad 3.8% [11]. Usually the initial indicator of fat / oil damage due to the hydrolysis process, if there are free fatty acids in fat / oil.

3.1.3. Peroxide number. Tuna canning waste oil has a peroxide level of 13.8 (mek / kg). The oxidation process in oil can be accelerated by the presence of Fe, because Fe can act as a catalyst in oxidation reactions. The results of peroxide number 13.8 (mek / kg) are still in accordance with the standard peroxide number between 3 and 20 meats / kg). According to Pak, if it is heated at high temperatures, it will produce peroxide due to a primary oxidation reaction [12].

3.1.4. Copper content (cu). Catalysts for the process of autoxidation in oil are usually metals, although generally in very small fatty foods contain metals [13]. The copper (Cu) metal content needs to be analyzed because its presence can easily catalyze the automatic oxidation reaction. The canning oil of tuna oil containing Cu is 0.1 (ppm). The results of Cu content of liquid waste oil of 0.1 (ppm) are still good according to IFOMA provisions.

3.1.5. Level of iron (Fe). The automatic oxidation reaction in oil occurs because Fe metal acts as a catalyst. Tuna canning waste oil has a Fe content of 2.5 (ppm). The yield of Fe content is above the IFOMA standard (value 0.5-0.7 ppm). In general Cu and Fe metals form complexes with proteins in fish [14].

3.1.6. Phosphorus Level (P). The results of the analysis of phosphorus content of 32,5 ppm tuna canning oil, this value has met oil quality standards according to IFOMA, namely 5-100 ppm,

3.2. Fatty Acid Composition of Tuna Canning Waste Oil and Omega-3 Concentrate

Table 2. Composition of fatty acids wastes oil of tuna canning and concentrate of omega-3 fatty acids resulting from crystallization of urea.

Fatty acid profile (% relative)	Liquid waste oil	Concentrated omega-3
Capric acid	0,1	1,3
Lauric acid	1,9	0, 01

Meristic acid	4,2	0,4
Palmitic acid	19,3	2,5
Stearic acid	6,3	0,3
Arachidic acid	0,5	0,6
Behenic acid	2,2	2,7
Total SFA	33,7	7,7
Palmitoleic acid (omega-7)	4,8	1,2
Oleic acid (omega-9)	13,9	1,5
Total MUFA	18,8	2,7
Linoleic acid (omega-6)	1,4	0,8
Linolenic acid (omega-3)	0,4	0,5
EPA (omega-3)	4,2	9,9
DHA (omega-3)	21,4	59,7
EPA + DHA	25,5	69,6
Total Omega-3	25,9	70,1
Total PUFA	27,6	70,9
Total USFA	46,4	73,6

Data from analysis Table 2 results are that SFA levels dropped from 33.7% to 7.7%, while MUFA dropped from 18.8% to 2.7%, omega-9 dropped from 13.9% to 1.5% and omega-6 drops from 1.4 to 0.8%. The method of crystallizing urea can reduce unsaturated fatty acids and saturated fatty acids with one double bond (MUFA).

Concentration of PUFA (EPA and DHA) can be obtained by crystallizing urea. Saturated fatty acids and monoenoic acid can be eliminated by this technique [15]. Crystallization of urea can separate fatty acids not saturated with saturated fatty acids, because of the two alkyl chains the linearity is different. Unsaturated fatty acid and saturated fatty acids are straight alkyl chains, because the double bonds have curves. [16].

According to Yeo and Harris that in complex urea inclusions, urea molecular molecules bind through hydrogen bonds to form parallel tunnels [17]. The urea channel has a stable structure, if the channel is filled with guest compounds form a tight structure. Urea channels have urea duct diameters varying between 5.5 - 5.8 A based on the radius of the van der Waals bond. Only suitable molecules can become guest compounds that form complex inclusions. PUFA increased from 27.6% to 70.9%, with an enrichment rate of 2.6 times, while the levels of omega-3 fatty acids increased from 25.9% to 70,9%, with an enrichment rate of 2.7 times, EPA levels increased from 4.2% to 9.9%, with an enrichment rate of 2.4 times, DHA levels rose from 21.4% to 59.7%, with an enrichment rate of 2.8 times, the amount of DHA + EPA rose from 25.5% to 69.6%, with an enrichment rate of 2.7 times.

According to Yuwono, the initial level of EPA + DHA contained in fish oil from tuna eyes was 31.3%, after crystallization of urea it increased to 83.9% so the enrichment rate was 2.6 times. According [18]. Estiasih et al. reported that oil from tuna fishing with EPA + DHA levels between 61.2 - 82.3%, enrichment level of EPA + DHA from fish oil by 2.9 - 3.9 times [9]. The levels of EPA + DHA contained in fish oil in omega-3 concentrates from fish canning byproducts were lower than previous studies, but still higher than Fatimah's research that the levels of EPA + DHA omega-3 concentrates with tuna (liquid waste) are 50.7 % with the ratio of urea and fatty acids 3 to 1, and for crystallization of urea for 24 hours the DHA + EPA level was 50.2% [19]. This difference may be due to different fish species and different tuna fishing areas.

The results of this study indicate a higher enrichment rate than the Yuwono study which was considered due to the level of fish oil from EPA + DHA byproducts of lower tuna siege [17]. The content of omega-3 in fish oil is influenced by the quality of fish food, and this is phytoplankton [20].

Factors that influence the composition of fatty acids are fish species, sexual maturity, gender, fishing area, water temperature, food and season.

The results of analysis of fatty acid profiles containing high omega-3 (EPA + DHA) from tuna canning oil in the city of Bitung, North Sulawesi can be made by crystallizing urea.

4. Conclusion

- The characteristics of quality of waste oil from tuna canning meet the requirements as determined by the International Fish Meal and Oil Manufactures Association (IFOMA)
- The crystallization process of urea can increase omega-3 fatty acid concentrates (EPA and DHA.), With an enrichment rate of 2.7 times.

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