International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.6, pp 101-108, 2017

Effect of Degumming on the Characteristics of Fish Oil from By-Product of Sardine and Tuna Canning and Meal Processing

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Abstract : Fish oil from by-products of tuna and sardine canning and meal processing is rich in ω-3 fatty acids. Refining is required to process this by-product into edible fish oil. One step in crude fish oil refining is degumming to remove phosphatidic compounds. Water degumming with phosphoric acid is one simple degumming method. This study was aimed to evaluate the changes of fish oil characteristics from by-products of tuna and sardine canning and meal processing after degumming. The results showed that degumming decreased phosphorus content in all fish oils. Degree of phosphorus removal depended on fish oil type. Degumming did not change free fatty acid content of fish oil, although a slight decrease was found in fish oil from tuna canning processing. Degumming decreased peroxide value of all type of fish oil, meanwhile anisidine value tended to increase with the high increase was found in sardine oil. Oxidation level of fish oil generally increased after degumming. In conclusion, water degumming is suitable to use for removal phosphatidic compounds of fish oil from by-products of canning and meal processing. The changes of fish oil characteristics after degumming is affected by type of fish oils.
Keywords : by-product, degumming, fish oil, sardine, tuna.

1. Introduction

Sardine (*Sardinella* sp) and tuna (*Thunnus* sp) canning and meal industries produce a by-product of fish oil that rich in main ω-3 fatty acids, EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid). EPA and DHA have different role on health[1]. EPA has the ability to inhibit tumor growth[2]andcancer[3], increases immune system[4], prevents cardiovascular diseases[5], inhibits platelete aggregation[6] that contribute to artheroschlerosis, decreases blood triglyceride and LDL cholesterol[6], andpreventsinflammation[7]. DHA is a fatty acid that has a main function as brain constituent[8,9,10]andretina[11,12]. This fatty acid has a role in the structure of brain, nervous system[13], signalling[14], increasing memory[15,16], increasing learning ability[17]and its lack implies to decreasing cognitive and neurodegenerative diseases[13]such asdementia[18], also improving bone density[19].

The market for fish oil is divided into three categories, for pharmaceuticals, ingredient for food industries, and food fortificants. Currently, standard for fish oil processing has been available mainly related to the safety from heavy metal and contaminants. Main standards for crude fish oil and refined fish oil are *United States Pharmacopeia* (USP); monographof *Council for Responsible Nutrition* (CRN); *International Fish Oil Standard* (IFOS), and *European Pharmacopeia* (EP)[20].Beside*International of Fish Meal Manufacturers*

(IFOMA) and*International Fish Oil Standards* (IFOS), there is also standards for crude fish oil from *Codex Allimentarius Commission* (CAC), *European Pharmacopeia Standard* (EP) and*Council of Responsible Nutrition* (CRN). These standards determine parameters for quality including acid value, free fatty acid content, peroxide value, anisidine value, total oxidation value, color, heavy metalsuch asiron, copper, and phospor[21].

Fish oil from by-product of fish canning and meal processing has inconsistent quality and different characteristics although from the same industries. These oils still contain non oil impurities such as phosphatides, dark color, and high free fatty acids and peroxides that makes these oils do not meet standard quality[22]. Non oily matters of fish oil should be removed to obtain edible fish oil[21]by several steps of refining, including degumming, neutralization,washing, and bleaching. During degumming, gum or mucilage that contains phosphatides isremoved. Degumming improves the quality of fish oil from by-product of fish meal manufacture[23].

Degumming primarily removesphospholipids and other mucilages from oil and quality of the degummed oil. If not removed effectively in the initial stage, these impurities may eventually interfere[24]. Oil degumming process plays a critical role in thephysical refining of edible oil[25]. Degumming has several methods, such as water degumming[26], enzymatic degumming[25], and ultrafiltration[27]. The main purpose of degumming is to remove phosphorus, because low phosphorus contents required for physicalrefining[25]. The presence of phospholipids orphosphatides or gums inoil cause a higher oil loss in theneutralization stage. The basis ofextraction of phosphatides is relied on theprinciple that phospholipids become swollenwhen treated by hydrating substances[26].

Acid and water degumming are the common methods in industries. In the water degumming process, thehydratable phospholipids are removed from the oil by treating them with water or vapour, usually at high temperature.The resulting hydrated phospholipids becomeimmiscible in the oil and are separated by centrifugation.During acid degumming, phospholipid hydration isincreased by the addition of phosphoric or citric acids[27]. Water has been used as a traditionalhydrating substance for separating hydratable phosphatides. Beside water, degumming also usually uses other hydrating agents such as phosphoric acid[26].

This study was aimed to compare some characteristics of fish oil from by-product of tuna and sardine canning and meal processing from several industries, before and after degumming.

2. Experimental

2.1. Materials

Fish oils were obtained from one sardine fish meal processing industry, one sardine canning processing industry, one tuna fish meal processing industry, and one tuna canning processing industry at East Java and Bali, Indonesia on April-June 2016. Fish oils were obtained from by-product of fish processing industries and the oil was separated from non oily materials such as water and other impurities by sedimentation. Separation process was prepared atthe fish processing industries. The oils were analyzed for phosphorus content by atomic absorption spectroscopy[28], free fatty acid[29], and oidation level that indicated by peroxide value[30], p-anisidine value[30], and totox value[28].

2.2. Degumming

Fish oil from was heated to reach 70ºC and then 1% (w/w) of phosphoric acid 85% was added. The mixture was stirredfor 30 min at 70ºC. The oil was cooled at ambient temperature. The oil (supernatant or upper layer) was seperated from hydrated gum (subnatant, lower layer) by centrifugation at 5000 rpm for 10 min and then anaylzed as the raw material fish oil. This experiment was replicated three times.

3. Results and Discussion

3.1. Phosphorus Content

Phosphorus content of fish oil before and after degumming is shown in Figure 1. Phosphorus content is

an indicator for phosphatides or phospholipids in oil. The degummed oil is generally judged by its phosphorus andtrace metal contents[24]. Phosphatides or phospholipids are the main constituents of gum in oil. Principally, degumming removes gum or phosphatidesand phosphorus content can be used as an indicator for the degumming[31]. Usually, vegetable oils have higher gum or phospatides than animal fats/oils.

Figure 1 shows that all of fish oil from by-product of fish processing has low phosphorus content. Although phosphorus represents phospholipids or phosphatides in oils, however the amount of phosphorus in phospholipids or phosphatides depends on the types of oil. Carelli *et al.*[31] evaluated phospholipid composition and phosphorus content of several crude and degummed sunflower oils and were measured in order to compare theoretical and experimental factors used to convert phosphorus content to phospholipid content.From fatty acid and phospholipid compositions, average theoretical conversion factors of 24.7 and 23.0 were found for crude and degummed sunflower oils, respectively.The relative phospholipid concentrations of oils depended on the method of extraction and the type of degumming. Therefore, theoritically the amount of phospholipids in fish oils was lower than 100 ppm. However, the phospholipids should be removed to get efficient neutralization after degumming. According to Dijkstra[32], water degumming is usually used for oils with phospholipids content less than 200 ppm.

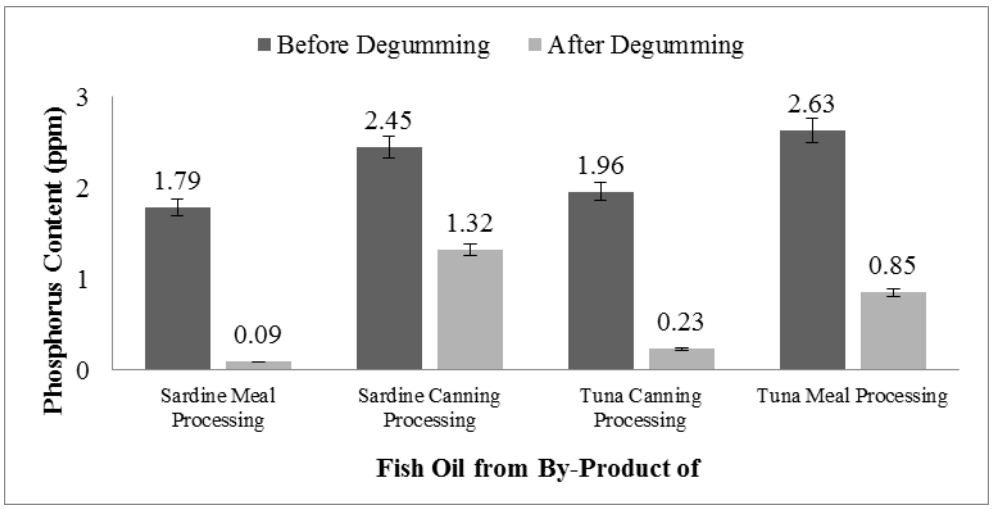

Figure 1. Phosphorus content of fish oil from by-product of sardine and tuna canning and meal processing industries before and after degumming

Figure 1 shows that fish oils from different processing had sligthly different phosphorus content. Variability might occur due to different type of fish as well as different source of oils. Oil from canning processing is obtained from pre-cooking that uses white flesh of fish. Meanwhile, oil from meal processing is obtained during steaming red flesh, head, tail, and viscera. Therefore, different type of raw materials results in different lipid composition and phospholipids, as well.

Fish oi from tuna meal processing had the highest phosphorus content, meanwhile the lowest was found in fish oil fom sardine meal processing. It means that although both oils were from by-product of meal processing, but the phopshorus content was not similar, depended on the type of fish. Tuna meal uses head, viscera, and red meat as raw materials, meanwhile sardine only uses head and viscera. Different raw materials implied on different phospholipid level that made different phosphorus content. Fish oil from canning processing of sardine showed higher phosphorus content than tuna. During sardine canning processing, there is no separation of red meat and flesh meat like in tuna canning. All of type of meat was processed that cause the phosphorus content of fish oil from sardine canning processing was higher. According to Wood *etal*.[33] red meat contained higher phospholipids than white meat.

Degumming reduced phosphorus content of fish oils for all oil types. The magnitude of reduction varied among fish oils. The highest reduction was found in fish oil from sardine meal processing, and the lowest was fish oil from sardine canning processing. Type of phosphatides presummably affectted the effectivity of degumming. Phospholipids present in oils are broadly classied as hydratable and non-hydratable types[24]. According to Carelli *etal*.[31] the existence of hydratable and non hydratable phosphatides affected

degumming. In this study, method of degumming was water degumming that based on the hydration of phosphatides in fish oil. Different type of fish possibly had different composition of hydratable and non hydratable phosphatides that implied on different degree of phosphorus removal. According to Dijkstra[32], dilute acid decomposed non hydratable phosphatides in oils into hydratable phospholipids that could be removed by hydration. However, phosphoric acid is not soluble in oils, therefore toroughly mixingis required to achieve desiredresult. In this study, it seemed that the occurance of hydratable and non hydratable phospholipidsin fish oil might affect the degree of phosphorus reduction.

3.2. Free Fatty Acids

Free fatty acid content is one indicator of fish oil quality[21]. Free fatty acid content of fish oil from by-product of sardine and tuna canning and meal processing is shown in Figure 2. Actually, all oils had low free fatty acid content. Free fatty acid content in oil is from hydrolysis of triglycerides. Several factors affecting triglyceride hydrolysis such as water, fatty acid composition, and temperature[34]. All fish oils in this study had low level of moisture content (data not shown). Choe and Min[34] explained that hydrolysis is more preferable in oil with short and unsaturated fattyacids than oil with long and saturated fatty acids because short andunsaturated fatty acids aremore soluble in water than longandsaturatedfatty acids. Generally, long chain fatty acids are abundant in fish oil therefore they are not easy to hydrolyze. Figure 2 shows that tuna oil had higher free fatty acid than sardine oil. Handling of fish before processing as well as fish oil might affect free fatty acid content. Oil from by-product of fish processing is not the main products[35], therefore it does not usually handle carefully and properly. The risk of oil hydrolysis could occur during fish oil handling.

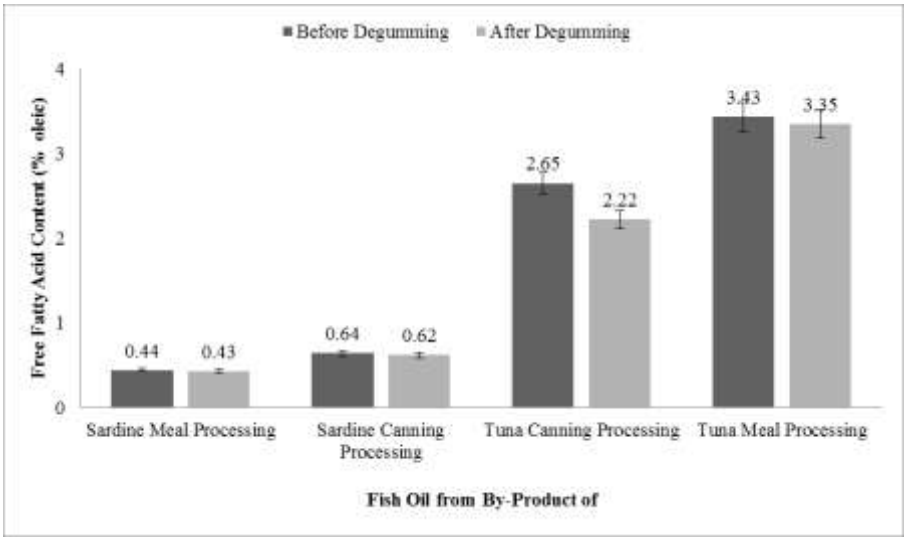

Figure 2. Free fatty acid content of fish oil from by-product of sardine and tuna canning and meal processing industries before and after degumming

Degumming did not affect free fatty acid content in all fish oil, although there was a slight reduction (Figure 2). Use of water during degumming increases the risk of oil hydrolysis. The study of Crexi *et al*.[23] showed that degumming increased free fatty acids from fish meal oil from carp (*Cyprinus carpio*) viscera. Carp is a fresh water fish, that fatty acid composition of fresh and sea water is different[36], that implied to oil hydrolysis resistance. Brevedan *et al*.[38] also showed a slight decrease in free fatty acids after degumming of sunflower oil.

3.3. Oxidation Level

Oxidation level is an indicator of the safety of edible fish oil. Oxidation level was represented by peroxide value as an indicator for primary oxidation product or recent oxidation, p-anisidine value as an indicator for secondary oxidation products or past oxidation, and total oxidation as an indicator for recent and past oxidation. All fish oil had high level of peroxide value. Fish oil is susceptible to oxidation due to high unsaturation. Oxidation might occur during fish preparation for canning and meal as well as fish oil handling.

Generally, peroxide value of fish oil from meal processing is higher than fish oil from canning processing (Figure 3). Fishmeal uses viscera, red flesh, and head as raw materials that contained heme pigment. According to Maqsood and Benjakul[38], heme pigment and trace amount of metalic ion in dark flesh fatty fish leads to prone to oxidation. Tuna oil tended to have higher peroxide level than sardine oil. Degree of fatty acid unsaturation of tuna was higher than sardine oil (data not shown). According to Khoddami[39], tuna waste lipid had higher DHA than *Sardinellalemuru*.

Degumming altered peroxide value of fish oil. Generally, peroxide value decreased after degumming. Peroxide value is an indicator of peroxidation products that formed due to the reaction of fatty acid with oxygen. According to Girotti[40], hydroperoxide is more polar then parent lipids, therefore during degumming they were possibly soluble in water. The decrease of peroxide value was observed in all fish oil.

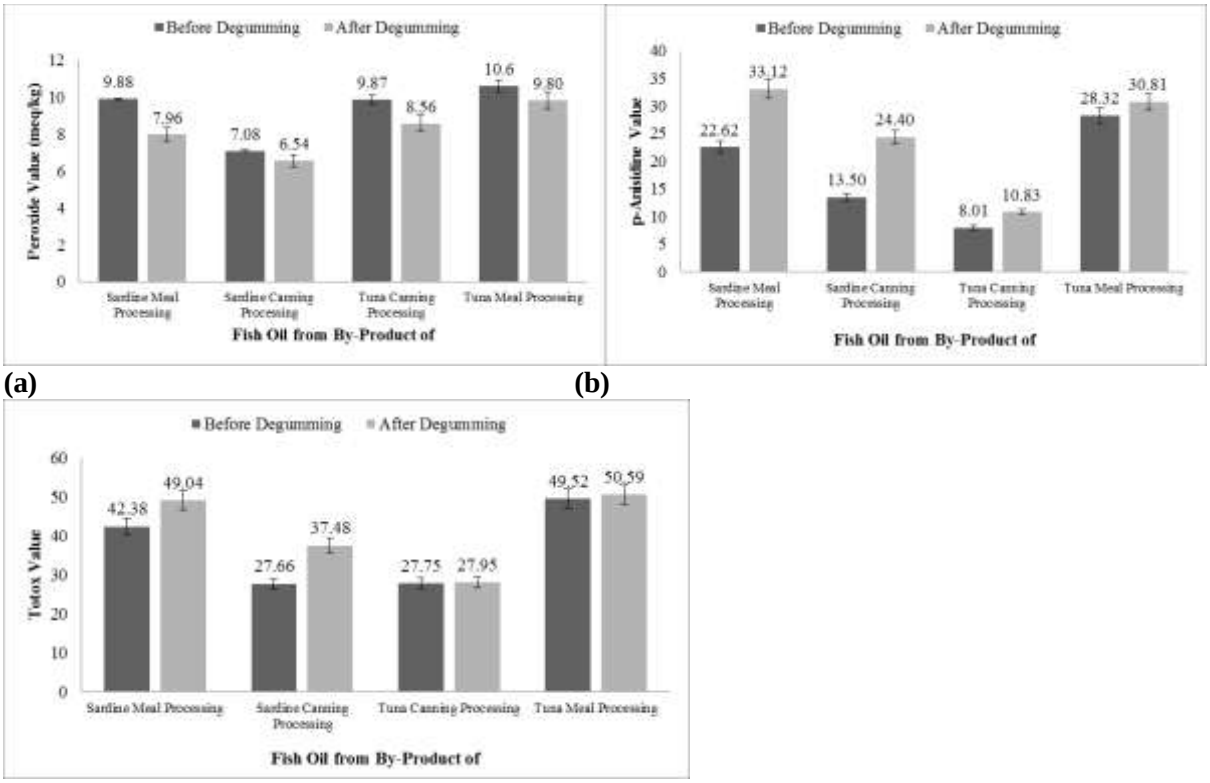

Figure 3. Oxidation of fish oil from by-product of sardine and tuna canning and meal processing industries before and after degumming. (a) peroxide value, (b) p-anisidine value, (c) total oxidation value

Anisidine value is an indicator of decomposition of hydroperoxides into low molecular weight compounds. The hydroperoxides arevery unstable and decompose to form secondaryreaction products, such as aldehyde, ketones, alcohols, and acids, which cause off-odors andoff-flavors, and affect the quality of the oil. Anisidine value measured secondary changes and was an an indicator of the aldehydecontent (mainly as 2-alkenals and 2,4-dienals)[41].

Anisidine value of fish oil from by-product of meal processing was higher than from canning processing. Deterioration of fish during meal processing was supposed to be more intensive than during canning processing. Fish meal uses viscera, liver, red flesh, and head as raw materials and they are also as solid waste of canning processing. Time for production of oil for meal processing was longer than canning processing that imply to more oxidation occured. Different degree of secondary oxidation between tuna and sardine oil was related to degree of unsaturation. Tuna oil from canning processing was the lowest secondary oxidation products, because this oil was from high quality white flesh. Red and white flesh are not separated during sardine canning processing. Therefore initial raw material for sardine canning might have higher degree of oxidation.

Degumming increased anisidine value of all fish oil from all by-products. Degumming used temperature 70ºC to hydrate gum effectively. Elevated temperature was supposed to decompose hydroperoxide into secondary oxidation products. High increase of anisidine value after degumming was found in sardine oil either from by-product canning or meal processing. Meanwhile a slight increase was found in tuna oil. This difference presumably related to the peroxide value of both oil. Initial and degummed tuna oil from by-product of canning and meal processing had higher peroxide value than sardine oil. Decomposition of hydroperoxide presumably more excessive in degummed sardine oil that indicated by high increase in anisidine value after degumming.

Totox value is and indicator of total oxidation that calculated using the equation of totox value = 2PV + p-AV[42]. Figure 3c shows that degumming significantly increased totox value of sardine oil, and in tuna oil slightly increased. Although degummed sardine oil had less peroxide value, but higher anisidine value of this oil made a significant increase in totox value. Totox value of initial and degummed tuna oil was almost similar or increased only slightly. No significant alteration in totox value before and after degumming in tuna oil might relate to only slight increase of peroxide and anisidine values after degumming.

4. Conclusion

Degumming of fish oil by water degumming with phosphoric acid successfully reduced phosphorus content as an indicator of phosphatidic compounds in all fish oils. Free fatty acid remained unchanged before and after degumming in all fish oils. Peroxide value as an indicator of recent oxidation decreased after degumming, meanwhile anisidine value as an indicator of hydroperoxide decomposition increased in all fish oilswith the high increase was found in sardine oil. Total oxidation increased in sardine oils both from by-products of canning and meal processing, but both tuna oils did not show significant increase of total oxidation. Water degumming is suitable to use for removal phosphatidic compounds of fish oil from by-products of canning and meal processing. The changes of fish oil characteristics after degumming is affected by type of fish oils

Acknowledgement

All authors are very grateful and greatly appreciate to Ministry of Research, Technology, and Higher Education for funding this research through PUPT scheme with contract no. 137/SP2H/LT/DRPM/III/2016.

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