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COMPARISON AND EVALUATION OF THE QUALITY OF FISH OIL AND FISHMEAL EXTRACTED FROM THE HEADS OF YELLOWFIN TUNA (*Thunnus albacares*) AND ALBACORE TUNA (*Thunnus alalunga*)

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ABSTRACT

This study focuses on the utilization of tuna heads and exploring its efficiency. Fish oil and fish meal were extracted from the heads of two tuna species, albacore tuna (*Thunnus alalunga*) and yellowfin tuna (*Thunnus albacares*), using an experimental method performed under laboratory conditions. These by-products were investigated for proximate composition and quality analysis. The crude fish oil and semi-refined fish oil extracted from both species had a similar yield of 2% and 1% respectively. The fishmeal also had a somewhat similar yield around 23% from both species. The fatty acid composition of the oil was analyzed and the saturated fatty acid, mono-unsaturated fatty acid and poly-unsaturated fatty acid that had been detected ranged from 1.67-37.99%, 3.17-38.34%, and 0.70-34.99% respectively. Palmitic acid, oleic acid and DHA were the dominant fatty acids in both oils. The albacore tuna liquid phase and semi-refined oil had lower oxidation by-product values and higher omega-3 fatty acids than the yellowfin tuna, but an extremely low lipid content and a very high moisture content, which would make it unacceptable for the consumer despite the desired fatty acid profile and required quality factors. The overall composition and quality factors of the yellowfin tuna oil were within the standard range and is according to these parameters considered an acceptable edible fish oil. The level of Hg, Pb and Cd was similar and within acceptable levels, whereas As had high levels in the tunas. The fishmeal protein content was 59.1% for albacore tuna and 56.2% for yellowfin tuna.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

One of the main fish processing and export companies in Suriname is Suvveb N.V. located on the Cevihas complex at Bethesda alongside the Suriname River, which is a central fish landing site for industrial fishing vessels with its own jetty and ice production. The company processes marine fish and some coastal fish, but the focus is on tuna processing. About 150 tons/month of tuna is sent to the EU and the US as fresh loins and fresh headless/gutted product. The tuna production mainly consists of yellowfin tuna (*Thunnus albacares*) and some albacore tuna (*Thunnus alalunga*). The company produces a lot of rest raw material (RRM) from the tuna processing. The RRM includes skin, viscera, bones, heads, tails, trimmings, belly flaps, and dark meat. Currently, little to no utilization of these tuna RRM is done. Sometimes the dark meat can be sold as dog food. The RRM is dumped in the Suriname River, near the landing site. The total RRM of the tuna headless/gutted production is around 15% and that of the tuna loin production is around 40% of the tuna processing. Tuna heads are estimated to be 8% of the whole tuna (estimates are obtained from the company, Suvveb NV).

Surinamese fish processors try to make up the most value from their primary products, neglecting to extract more value from RRM. This results in missed economic return from this secondary resource due to underinvestment in equipment and knowledge that add value to by-products. In addition to this missed opportunity, disposal of RRM often has a direct financial and environmental cost. These products could be processed for the food, feed and pharmaceutical products.
Tuna oil is a special kind of marine oil, because it has the highest content of the omega-3 poly-unsaturated fatty acid called docosahexaenoic acid, compared to the other marine oils. The utilization of the tuna heads and trimmings processed into oil could be of great value for Suriname considering the health benefits, high demand and high prices of this oil.

The meal production in Suriname includes vegetable flour types (for human consumption) and some vegetable based meal used to formulate animal feeds (for chickens, ducks, pigs, cows). Fishmeal or fish feed production is not done in Suriname. There are aquaculture farms that need to import their fish feed. The fishmeal production could be a viable option to make fish feed for aquaculture or as an additional protein used in the animal feed.

This study focuses on the utilization of tuna heads for oil and fishmeal and exploring its efficiency which could help maximize profits and reduce environmental problems.

The main goal of this study was to determine if extracting oil and fishmeal from the tuna heads is a viable utilization for the tuna processing industry in Suriname.

The objectives of this study were:

- to determine and compare the yield of the oil extracted from the heads of the yellowfin tuna and the albacore tuna.
- to investigate the fatty acid composition and compare the quality and safety of the tuna oil.
- to determine the composition of the fishmeal extracted from the tuna heads.
- to generate knowledge and experience on methods used to extract oil and fishmeal out of fish rest raw material.

2 LITERATURE REVIEW

2.1 Characteristics and distribution of yellowfin and albacore tuna

Yellowfin (YF) tuna (*Thunnus albacares*) is a highly migratory species distributed mainly in the tropical and subtropical waters of the three oceans, but absent from the Mediterranean Sea (Figure 1). Yellowfin tuna are torpedo-shaped with dark metallic blue backs, yellow sides, and a silver belly. They have very long anal and dorsal fins and finlets that are bright yellow (WWF, 2016). yellowfin can live up to six or seven years. The sizes range from 30 cm to 170 cm forklength (FL); maturity occurs at about 100 cm FL (Froese & Pauly, 2016). They form schools with other tunas like skipjack and bigeye, and are also known to associate with dolphins.

Albacore (AL) tuna (*Thunnus alalunga*) is also a cosmopolitan species distributed mainly in tropical and temperate waters of all oceans including the Mediterranean Sea (Figure 1). They are bullet-shaped with a dark blue back and lighter blue-grey sides and belly (WWF, 2016). AL tuna also have very long pectoral fins and live for around 12 years. The average length and the maximum length of a mature AL tuna are respectively 85 cm and 140 cm FL (Froese & Pauly, 2016). Albacore tuna swim in single species schools, without the level of mixing seen in other species.

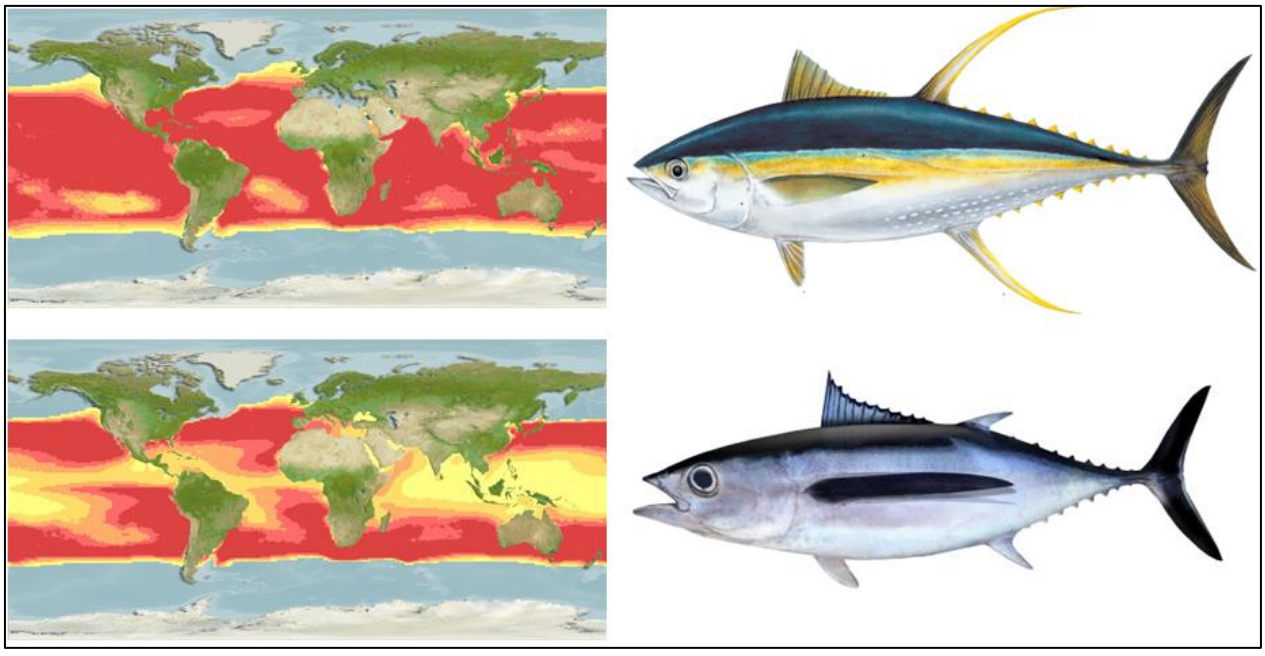

Figure 1: Fish body profile and distribution of the yellowfin and the albacore tuna (www.fishbase.org). The distribution (left) and fish body profile (right) of yellowfin tuna is shown in the upper figures. The distribution (left) and fish body profile (right) of albacore tuna is shown in the lower figures.

2.2 Tuna rest raw material

The global catch of the principal tuna species (albacore, bigeye, bluefin, skipjack and yellowfin) in 2010 was 4.3 million tons and they contributed to about 8% of global fish trade (FAO, 2013). Tuna is generally processed as raw fillets and marketed as loins/steaks or as a canned food.

Tuna RRM are commonly viewed as a low-value resource with negligible market value. However, the recognition of limited biological resources and increasing environmental pollution has emphasized the need for better utilization of RRM from fisheries. Thus, efficient recovery and use of such products is very important to reduce environmental problems and to maximize economic benefits. Tuna RRM are currently used to produce fish oil, fishmeal, fertilizer, pet food, and fish silage (Herpandi *et al.*, 2011).

YF tuna heads have a proximate composition of 59% moisture, 13.5% fat and 14.8% protein (Nguyen, 2011; Nguyen, 2013). According to Ali (2013) the YF tuna migrating to Oman's southeastern coast of the Arabian peninsula has a higher moisture, ash and fat content in the edible flesh during the summer than in the autumn. This indicates seasonal variability of the proximate composition of tuna.

Most tuna processing companies in Suriname only process fresh and frozen loins and headless/gutted tuna products. The tuna production in Suriname mainly consists of YF, skipjack and some AL tunas. The total catch of tuna (albacore, skipjack and yellowfin tuna) in Suriname in the period 2012-2014 ranged between 2500 and 4000 tons in a year (Figure 2)

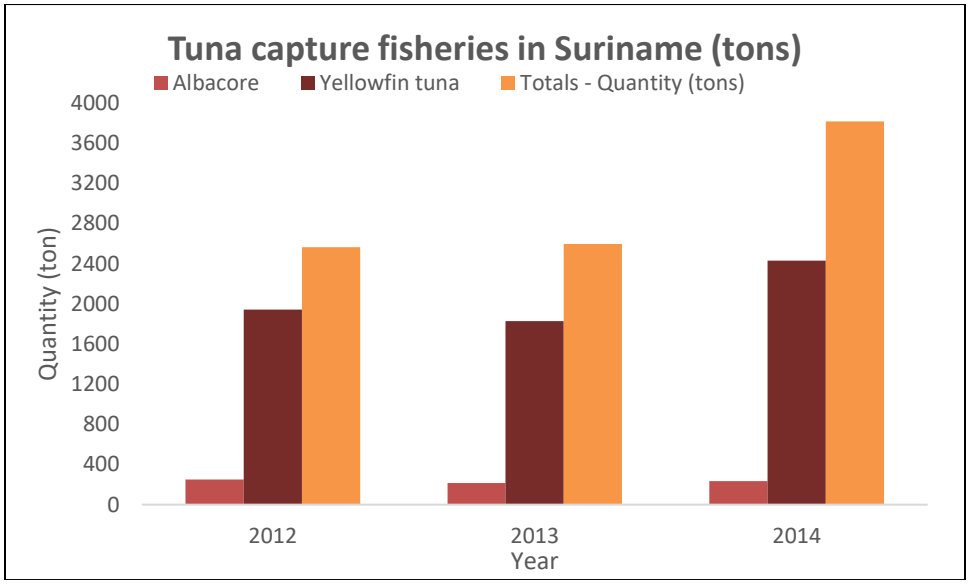

Figure 2: Tuna capture fisheries in Suriname (FishStat 2014).

Suvveb NV processes the most of tuna caught in Suriname (Figure 3). The YF capture is slowly on the rise whereas the AL tuna production is stable. The total RRM of the YF and AL tuna headless/gutted production is around 15% (±332 tons in 2016) and that of the tuna loin production is around 40% (±885 tons in 2016). The production of YF and AL tuna heads (8% of the whole tuna) are estimated at 177 tons in 2016 (estimates obtained from Suvveb NV).

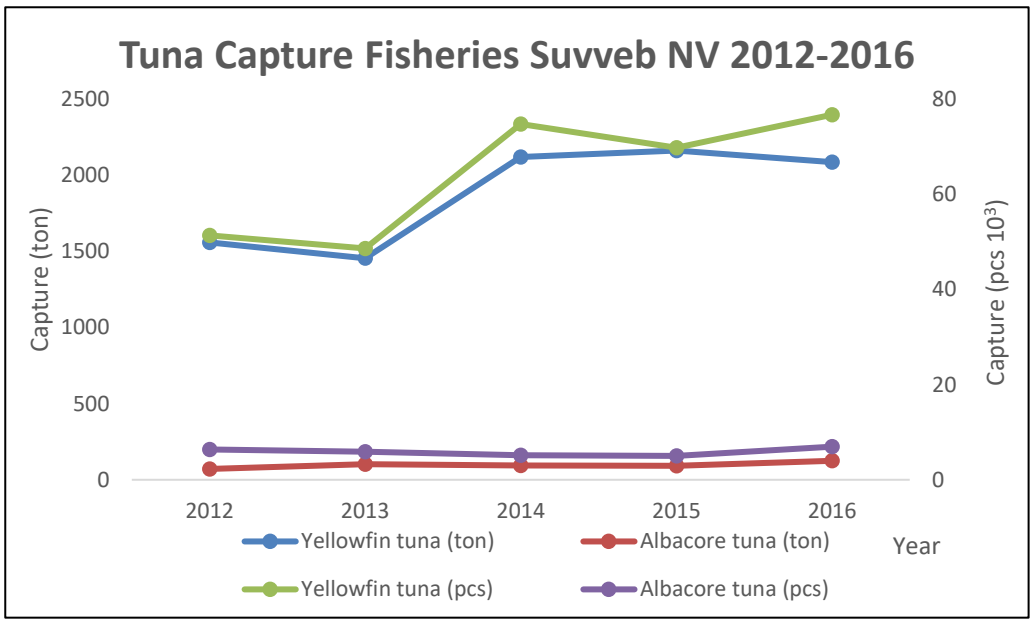

Figure 3: Tuna capture fisheries in tons and pieces Suvveb NV

The tuna processing produces a substantial amount of RRM which includes skin, viscera, gills, bones, heads, tails, trimmings, belly flaps, and dark meat (Figure 4).

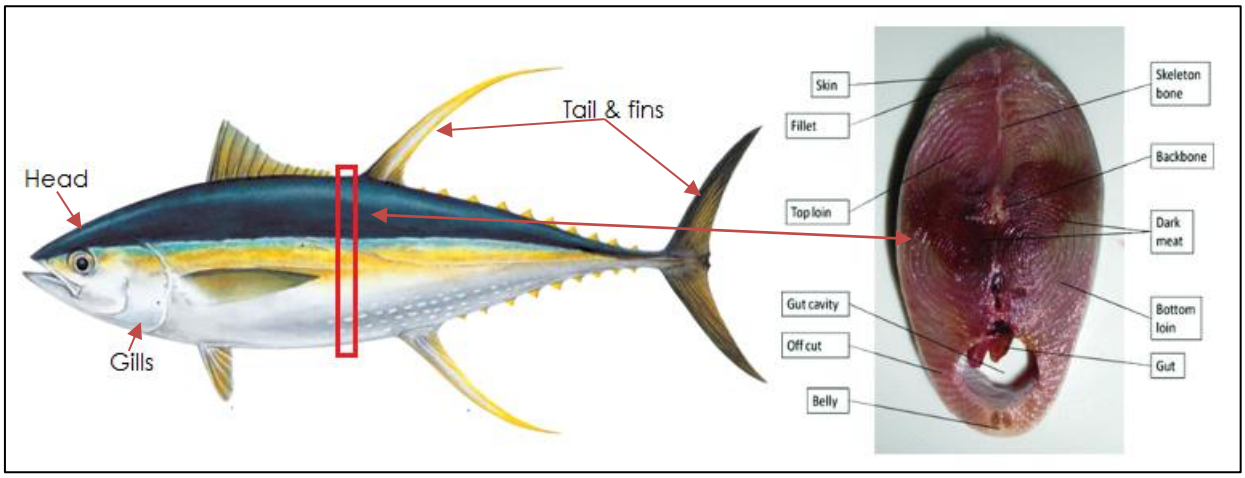

Figure 4: Rest raw materials from tuna (Herpandi *et al.*, 2011)

2.3 Fish lipids and health aspects

2.3.1 Fish lipids

Marine lean fish usually have a flesh lipid content of 0.1-1%, while the flesh lipid content of marine fatty fish varies from 2-30% with considerable variation depending on the type of species, dietary, geographic, environmental, reproductive and seasonal variations (Kim & Mendis, 2006; Macrae, 1993).

Fish oils are liquid at room temperature but generally solidify below 15^{o}-10^{o}C (Pike & Jackson, 2010). The fatty acid composition of the oils contains saturated fatty acids (SFAs), mono-unsaturated fatty acids (MUFAs) and polyunsaturated fatty acids (PUFAs) and fatty acid composition varies widely with fish species and the time of year. There are certain PUFAs that are obligatory nutrients for mammals, because their body requires them for good health but cannot synthesize them, and these PUFAs are called the essential fatty acids (EFA). There are two series of EFAs derived from linoleic (18:2 n6) and α-linolenic (18:3 n3) which are also known as omega-6 fatty acids and omega-3 fatty acids respectively (Macrae, 1993). Composition of fish oil is different from that of other oils as they contain high proportions (5-30% of the fatty acids) of two omega-3 fatty acids, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), which are predominantly found in many marine animals including cold-water fish species with a high unsaturated fat content (Kim & Mendis, 2006). The more unsaturated fish oils with a higher content of long chain omega-3 fatty acids also have a higher content of SFAs such as myristic and palmitic acid. Fish lipids mainly consist of triglycerides and phospholipids (PL). In most cases PLs have been found to be higher in their content of PUFAs like EPA and DHA than the triglycerides from the same fish. The oils also contain small but variable amounts of unsaponifiable components, such as hydrocarbons, fatty alcohols, waxes and ethers, and these also influence the properties of the oils to some extent (FAO, 1986).

2.3.2 Health aspects of fish oil

Intake of fish oil has been linked to promotion of human health to fight against numerous diseases. Absence of EFAs from the diet of animals leads to poor growth rate and impaired energy utilization, as well as structural and functional abnormalities in many tissues. The latter include impaired function of the transepidermal water barrier, a scaly dermatitis, electro-physiological abnormalities in the heart and retina, impaired cell-mediated immunity, platelet aggregation and reproduction (Macrae, 1993).

EPA is believed to especially help cardiovascular health; maintain a healthy heart by improving circulation, lowering homocysteine levels and improving immune function. DHA is being heavily studied for its effects on the improvement of memory and cognitive function as well as its role in infant brain development.

Most of the recommendations for omega-3 fatty acids are for a daily intake in the range of 0.25 g to 0.5 g (Pike & Jackson, 2010). Of all known dietary factors, long-chain omega 3 fatty acids may be the most protective against death from coronary heart disease. By increasing the n-3 omega intake of an individual with coronary artery disease by approximately 1 g/day may prevent death caused by this disease (GOED, 2014). It has also been proposed that an intake of 0.25 to 1.8 g of

omega 3 fatty acids such as EPA and DHA per day in the form of fatty fish or supplements is adequate to elicit desirable benefits such as reducing platelet aggregation and lowering plasma triglycerides (Gogus & Smith, 2010).

In Suriname cardiovascular diseases is the number one leading cause of death occurring primarily among men (Ori, 2014; WHO, 2014). Promoting the health benefits of fish oil to the Surinamese population could be of great importance.

2.3.3 Tuna oil

With depleting marine fisheries resources, it is not encouraged to only catch fish for their oil. Therefore, a large amount of fish RRM generated from processing, would be a potential source to produce good quality fish oil for human consumption, especially from the processing of fatty fish like tuna.

Tuna oil is a special marine oil, because it contains higher DHA content than other marine lipids (Ferdosh *et al.*, 2014). Usually the head, meat, and bones are used in tuna oil production. The crude tuna oil is produced from tuna RRM by steam followed by purification. This 1st-stage oil is a darker colour than that of the finished product. The product is then shipped to a refinery to undergo a process that involves neutralization, bleaching, and winterizing to remove crystallized fats, followed by a deodorizing process to remove odour-causing contaminants. The oil then is either shipped in bulk or packaged and sent to end users, including the pharmaceutical industry and other manufacturers (Herpandi *et al.*, 2011).

The fatty acid profile of tuna includes a wide range of SFAs, MUFAs and PUFAs (Table 1). The DHA level of tuna species is mostly within the high range of 21.0-42.5%. The level of EPA has a lower value range of 2.5-9.0% which is comparable with the salmon oil that has a range of 2.0-9.5% (FAO/WHO Codex Alimentarius Commission, 2015).

2.4 Quality indicators and contaminants of marine lipids

2.4.1 Oxidation of marine lipids

MUFAs and PUFAs are susceptible to oxidation. Fish oils contain high levels of PUFAs and must be protected against oxidation. PUFAs in foods like fish oils are more sensitive to oxidation than those rich in MUFAs in foods like animal fats. Oil oxidation is an undesirable series of chemical reactions by which oxygen is added, or hydrogen or electrons are withdrawn that degrades the quality of an oil. The principal negative effect of oxidation in foods is that flavour quality is lost, giving rise to the defect often referred to as rancidity. In addition, functional, colour and nutritional qualities of food components can be lost because of oxidation in foods. Therefore, quality parameters must be measured in order to know at what stage of oxidation the oil is. Methods of detecting and quantifying the extent of oxidation in fish oil involve measuring oxidative breakdown products, such as aldehydes and peroxides. The peroxides are usually measured using the peroxide value (PV) and aldehydes by anisidine value (AV). The PV is a standard oxidative quality

Table 1: Fatty acid composition (FAC) of named tuna fish oil as determined by gas liquid chromatography (expressed as percentage of total fatty acids) (FAO/WHO Codex Alimentarius Commission, 2015)

Formula	Name	Tuna %
C14:0	Myristic acid	2.0-5.0
C15:0	Pentadecanoic acid	≤0.05-2.0
C16:0	Palmitic acid	14.0-24.0
C16:1 (n-7)	Palmitoleic acid	1.0-12.5
C17:0	Heptadecanoic acid	1.0-3.0
C18:0	Stearic acid	1.0-7.5
C18:1 (n-7)	Vaccenic acid	2.0 – 7.0
C18:1 (n-9)	Oleic acid	10.0-25.0
C18:2 (n-6)	Linoleic acid	≤0.05-3.0
C18:3 (n-3)	Linolenic acid	≤0.05-2.0
C18:3 (n-6)	γ-Linolenic acid	≤0.05-4.0
C18:4 (n-3)	Stearidonic acid	≤0.05-2.0
C20:0	Arachidic acid	≤0.05-2.5
C20:1 (n-9)	Eicosenoic acid	≤0.05-2.5
C20:1 (n:11)	Eicosenoic acid	≤0.05-3.0
C20:4 (n-6)	Arachidonic acid	≤0.05-3.0
C20:4 (n-3)	Eicosatetraenoic acid	≤0.05-1.0
C20:5 (n-3)	Eicosapentaenoic acid	2.5-9.0
C21:5 (n-3)	Heneicosapentaenoic acid	≤0.05-0.5
C22:1 (n-9)	Erucic acid	≤0.05-1.0
C22:1(n-11)	Cetoleic acid	≤0.05-1.0
C22:5 (n-3)	Docosapentaenoic acid	≤0.05-3.0
C22:6 (n-3)	Docosahexaenoic acid	21.0-42.5

parameter based on measurements of the primary oxidation products and the AV is one of the standard oxidative quality parameters based on measurements of the secondary oxidation products. These compounds, with others resulting from further decomposition, are responsible for the rancid flavours that develops. The lipid oxidation is a sequential process. Following an initial raise of PV, the AV rises (Figure 5). To prevent having both oxidation products at maximum level in the same oil, total oxidation (ToTox) of oil should be established (FAO/WHO Codex Alimentarius Commission, 2015).

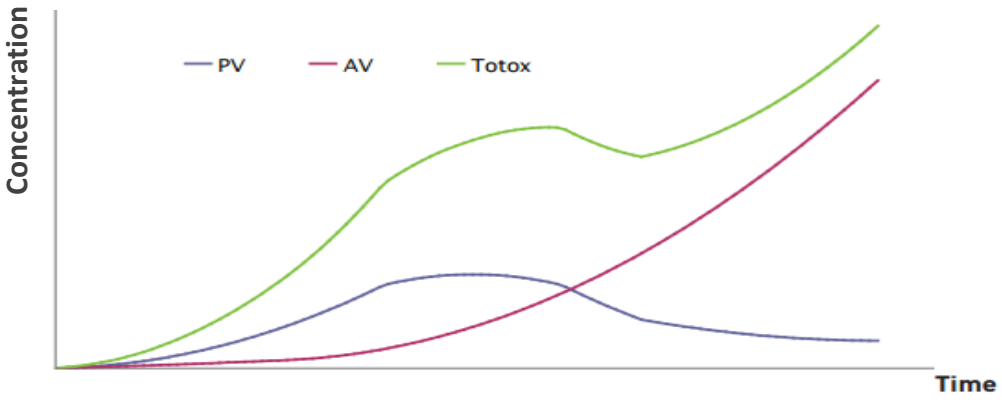

Figure 5: The oxidation of oil over time as measured by peroxide value, anisidine value and the ToTox value (AV + 2PV). PV can decrease over time so AV and/or ToTox calculation is needed to appreciate the whole oxidation story

It is important to produce fish oil from fresh fish. RRMs are especially vulnerable to spoilage and degradation e.g. the blood and the viscera have a high number of indigenous enzymes. Lipase and phospholipase are enzymes that catalyse the hydrolysis of triglycerides to yield glycerol and fatty acids (free fatty acids). Free fatty acids (FFA) are more prone to oxidation and rancidity. Thus, FFA is the most reliable parameter for oil quality and yield assessment. The level of FFA depends on time, temperature and moisture content because the oils and fats are exposed to various environments such as storage, processing, heating or frying (Mahesar *et al.*, 2014). The FFA value for crude fish oil should be within the range of 1-7% oleic (Bimbo, 1998). The maximum moisture content for crude oil is on usual basis 0.5 up to 1% and for refined oils it is 0.20% (Bimbo, 1998). Table 2 characterizes the typical chemical properties of fish oil obtained from the proposed draft codex standards for fish.

Table 2: Quality parameters (FAO/WHO Codex Alimentarius Commission, 2015)

Fish oils quality parameters	
FFA (Acid value)	≤ 3 mg KOH/g
PV	5 meq oxygen/kg oil
AV	≤ 20
ToTox value (2PV + AV)	≤ 26
Fish oils with high phospholipid concentration	
FFA (Acid value)	≤ 30 mg KOH/g
PV	5 meq oxygen/kg oil

The quality of the oil depends on the sorting, storage and handling of the raw material. Several different factors can be controlled to reduce the amount of oxidation that occurs in the oil. Oxygen exposure (in the air) will be a catalyst for production of free radicals. To reduce oxidation, all containers with the smallest possible headspace need to be sealed, the area of the oil in contact with air needs to be reduced and/or the oil needs to be covered with an inert gas (like nitrogen) or in vacuum at all possible points. Generally, as the temperature increases, the rate of oxidation reactions also increases. The rate can be doubled for every rise of 10^{o}C (Macrae, 1993). The temperature should be kept as low as possible throughout processing, shipping and manufacturing.

Light (UV) can trigger photo-oxidative processes. The oil should not be exposed to direct light which can be reduced by using brown glass/plastic containers or black plastic bags. Moisture in combination with these other factors can accelerate oxidation. As water activity increases, rates of oxidation increase probably due to increased mobility and activity of catalysts. Transition metals like iron and copper, can act as pro-oxidants. Changing of metal equipment (e.g. no brass valves) is necessary and contact with transition metals from the oil should be limited and/or eliminated to reduce oxidation (Miller, 2016). The oils are often also treated with antioxidants, such as butylated hydroxyl-toluene (BHT) (Pike & Jackson, 2010).

2.4.2 Contaminants

Environmental contaminants are harmful chemicals that enter the ecosystem because of industrial activity. These compounds accumulate in the fatty tissues of fish, albeit in minute proportions, meaning that oil derived from these tissues may contain excess concentrations of contaminants. Contaminants commonly detected in fish oil include heavy metals (e.g., mercury, lead, arsenic, cadmium) PCBs, dioxins, furans and dioxin-like PCBs (IFOS, 2016). Most of these contaminants can be removed or reduced in the refining step of oil extraction. Like other large marine fish, tuna is known for having higher than average amount of mercury. This is of concern for young children, whose nervous system, brain, heart, kidneys and lungs are all susceptible to the harmful effects of mercury, which is highly toxic. The presence of contaminants in food is controlled by legislation to protect consumers. There are some standards regarding the contaminants in seafood, like the Commission Regulation (EC) No 1881/2006 that set maximum levels for certain contaminants in foodstuff (Table 3) and the Codex General Standard for contaminants and toxins in food and feed.

Table 3: Maximum levels in contaminants

Contaminants	Tuna
Hg (mg/kg) in muscle	1
Pb (mg/kg) in muscle and edible fat and oil	0.1
Cd (mg/kg) in muscle	0.1
As (mg/kg) in edible oil	0.1

2.5 Fishmeal and nutrient composition

Fishmeal is a brown powder which normally contains a high quality balanced amount of all essential amino acids, energy, vitamins, minerals, and trace elements for optimum development, growth and reproduction. Fishmeal is an important source of protein and is often used in the feeds of poultry, pigs, ruminants, farmed fish, crustaceans and pets because it increases productivity and improves feed efficiency.

Freshness of raw material is an extremely important criterion since the profitability of feed use can vary with the freshness of raw material used. As a guide to freshness of raw material the content of total volatile nitrogen in the fish can be measured. It should be less than 80 mg-N per 100 g raw material (FAO, 1986). The colour of the meal is often thought to be related to fish meal quality. This is only partly true as several factors can affect the colour, such as fish species, particle size, fat and moisture content, and the food on which the live fish had been feeding prior to capture. However, a very dark brown colour may be the result of overheating during production or storage.

Severe heating to a blackish/brown colour does not affect the protein content, but will damage the protein quality (Barlow & Windsor, 1984).

Fishmeal typically contains 60% - 72% protein, 10% - 20% ash and 5% - 12% fat (IFFO, 2016). A desirable composition usually depends on the requirements of the buyer. A whole meal made from fatty fish like herring might contain about 72% protein, 9% fat, 8% water and 10% ash, whereas a meal made mainly from white fish and white fish offal and dried to the same extent will contain about 65% protein, 5% fat, 10% water and 20% ash (Table 4).

Table 4: Average values of the proximate composition from different species (FAO, 1986)

	Proximate analysis (%)		
	White fish meal	Herring type fish meals	S. American type fish meals
Moisture	10.0	8.0	10.0
Crude protein	65.0	72.0	65.0
Crude fat	5.0	9.0	9.0
Crude ash	20.0	10.0	16.0

The meal should be allowed to cool gradually with air circulation, that is, controlled "curing" after leaving the dryer. Use of an antioxidant such as ethoxyquin at 700 ppm is desirable for oily fish species, especially in hot climates, for stabilizing the oil in the fish meal by preventing oxidation. Rapid oxidation in fish meal can result in overheating in the stored product. Use of antioxidant is required by the International Maritime Organization if fish meal is to be shipped in a low hazard category. Correct "curing" and/or antioxidant treatment of fish meal will produce a product which can be stored indefinitely under dry conditions without deterioration. During cooking and drying, any harmful bacteria in fish are killed. Subsequently, contamination of fish meal is possible; good hygiene is necessary at all stages in handling and storage if this is to be avoided (FAO, 1986).

Aquaculture has been growing at an annual rate of 15.75% since 1988 (Bimbo, 2012). With the rise of aquaculture production, aquaculture is the major market for both fish meal and fish oil. Fish meal also provides a valuable outlet to recycle trimmings from the food fish processing sector which would otherwise be dumped at considerable cost to the environment. The protein in fish meal has a high biological value in diets for animals, as it is rich in essential amino acids, particularly lysine. All the energy in fishmeal comes from its protein and fat content. The quantity of fat present in fish meal depends on several factors including the fish species, season of catching, feeding of the fish, processing, and whether antioxidant was used (Barlow & Windsor, 1984).

2.6 Fish oil and fishmeal processing

2.6.1 Fish oil and fishmeal production

According to the Food and Agriculture Organization (FAO, 1986), raw material used for the production of fishmeal and fish oil falls into several categories: fish caught specifically for reduction to fishmeal and fish oil such as menhaden, anchovy, capelin and sardines; incidental or by-catch from another fishery; fish RRM from the edible fisheries such as cuttings from filleting operations, fish cannery waste, roe fishery waste and more recently surimi processing waste (Bimbo, 2011). Traditionally the yield of fishmeal and fish oil obtained from raw material is 22.5% for fishmeal and 4-5% for fish oil (Shepherd & Jackson, 2013). Better utilization of marine fish

processing RRM could be achieved by converting these materials into fishmeal and fish oil. The most common extraction method used in the industries is the wet reduction process. In addition to the wet reduction process, which is the primary method for producing crude marine oils, there are other production methods that are being or have been used to produce these oils like hydrolysis (enzymatic), silage production (autolysis), dry rendering, solvent extraction and alkali-aided process. The processing techniques involved in commercial production of edible fats and oils vary according to the type of raw material (Figures 6 and 7). The fishmeal and fish oil production show slow decline but continues to be dominated by production in South America. Production in Europe has continued to decrease. The estimated use of fishmeal and fish oil by sector in the year 2010 for fishmeal were: aquaculture (73%), pigs (20%), chickens (5%) and others (2%) and for fish oil: hardened edible (2%), aquafeed (71%), industrial (3%), refined edible (24%) (Sheperd & Jackson, 2012).

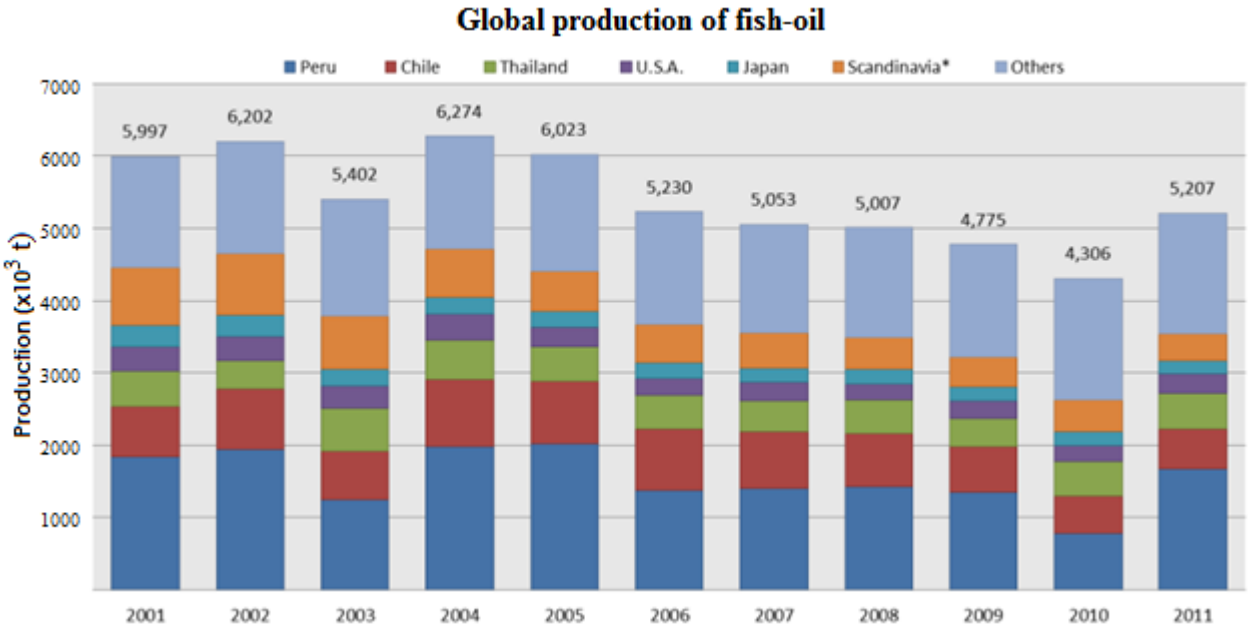

Figure 6: Global fish oil production 2001-2011 (Sheperd & Jackson, 2012)

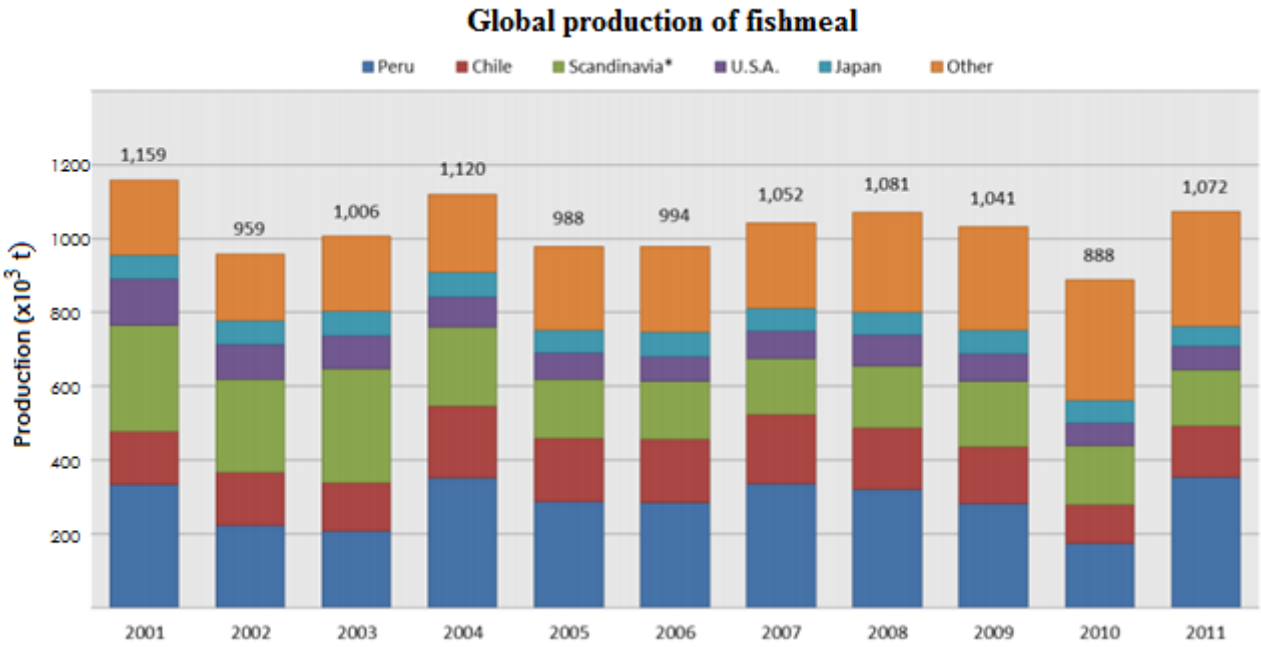

Figure 7: Global fish meal production 2001-2011 (Sheperd & Jackson, 2012).

2.6.2 The wet rendering process

The wet rendering process is universal, i.e. factories all over the world both on land and on ships employ it with slight differences in equipment type, but the major steps of cooking, pressing, separating, and drying are always present. Continuous processing from the time the fish are landed optimizes efficiency and maximizes product quality. Fish entering the process are cooked and pressed to separate the solids from the liquids. The solids eventually become fishmeal while the liquids undergo further processing first to recover suspended solids that might have escaped the press and then to separate and recover the oil. The water that is left after the fish oil is recovered is called stickwater. The composition of the fish meal depends both on the kind of raw material and on the type of process (Table 5).

The processing steps to produce fish oil and fishmeal from fish and fish cuttings (Figure 8) include (Bimbo, 2011; FAO, 1986):

1. *Cooking*: Steam cooking coagulates the protein, ruptures the fat deposits and liberates the oils. The most common practice of cooking is heating good raw material to 95-100^{o}C within 15-20 minutes.
2. *Draining*: The cooked fish mass is screened to separate free liquid from the solids
3. *Pressing (or centrifugation)*: Pressing mechanically removes a large fraction of the liquids from the solids producing a press liquor (oil and water) and a presscake (semi-moist meat and bones). Some factories use tricanters instead of pressers to separate solids, oil and water.
4. *Press liquor separation* is a three-step process: Decanters separate fine solids from the liquid fraction. Separators split the liquid fraction into oil and water (stickwater), and

polishing water washes the crude oil before it is pumped to storage. This step may be omitted if the oil content of the fish is less than 3%.

5. *Evaporation*: Stickwater is a mixture of water, suspended and dissolved solids, salts and fat. Generally, stickwater will contain about 8-10% total solids made up of approximately 5.6% protein, 0.6% fat, 1.8% ash and 92% moisture. If the factory uses steam dryers, then the waste heat from the dryer can be used to heat and evaporate the stickwater.
6. *Drying*: two stages: The solids from the decanter separation and the press cake are mixed and partially dried. The partially dried fishmeal is then mixed with the concentrated stickwater and the drying is completed to about 10% moisture. Factories use steam and indirect hot air dryers, but old factories still use the old direct fired hot air dryers.
7. *Grinding*: grinding of the meal into a desired particle size.
8. *Cooling and stabilization*: The fishmeal is cooled and antioxidant is added. Generally, ethoxyquin is the antioxidant of choice but for certain markets natural antioxidants based on tocopherols are used.
9. *Packaging*: The fishmeal is packed in 50 kg bags or 1000 kg totes. The fishmeal can also be stored in bulk piles or in silos.
10. *Optional fish oil carbon treatment*: If the crude fish oil is destined for the omega-3, animal feed, aquaculture or pet food market and if analysis indicate the presence of dioxins, furans and or polyaromatic hydrocarbons, it can be treated with activated carbon to reduce the levels of these compounds.

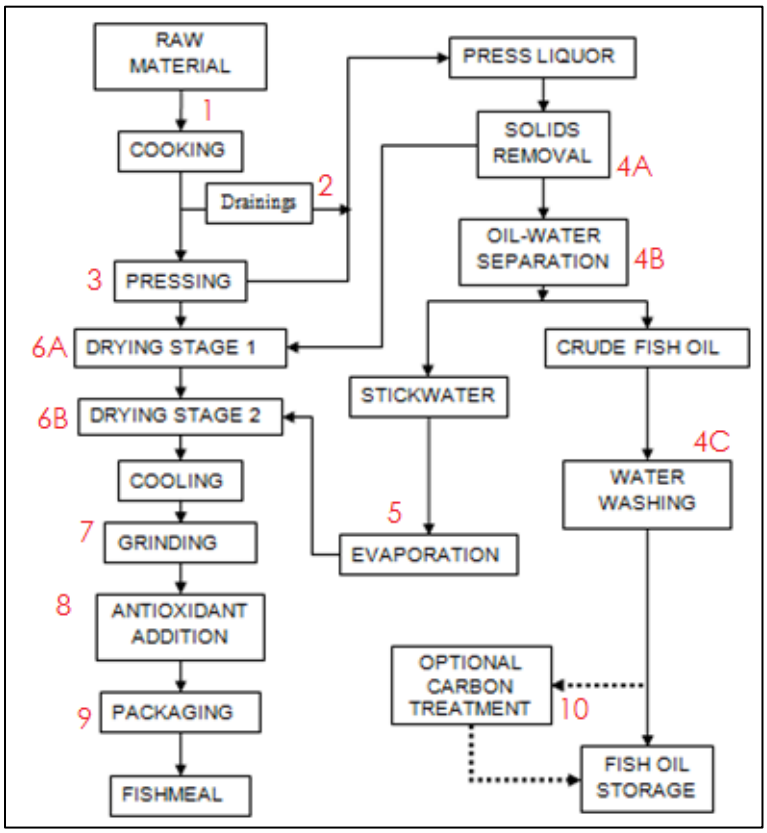

Figure 8: Wet reduction process to produce crude fish oil and fish meal (Bimbo, 2011)

Table 5: Proximate composition of products from the fish meal and oil processing

	Water	*Solids*	*Fat*
Material	***%***	***%***	***%***
Raw fish	70	18	12
Press cake	53	44	3
Press liquor	78	6	16
Dilute Stickwater	95	5	<1
Conc. Stickwater	65	33	2
Fish meal	9	85	6

2.6.3 Impurities in fish oil

Crude fish oil contains mono-, di- and triacylglycerols along with impurities (non-triglyceride substances), which need refining. The main objective of refining is to remove the contaminants that could affect the quality of the oil, thereby reducing the shelf life and consumer acceptance. The refining process should be tailored as the composition of crude oil and is highly variable depending upon the fish species, geographical location of the source and method of extraction (Vaisali *et al.*, 2015).

Non-triglyceride substances in fish oil can be classified according to their effects (Bimbo, 1998):

1. Hydrolytic – moisture, insoluble impurities, proteinaceous compounds, free fatty acids, phospholipids and soap;
2. Oxidative – trace metals, oxidation products, pigments and phospholipids;
3. Catalyst poisons (substances which inhibit the hydrogenation reaction) – phospholipids, oxidation products, and compounds containing nitrogen, sulphur, and halogens;
4. Miscellaneous – hydrocarbons, terpenes, resins, sterols, waxes, trace metals, and sugars, whose effect is not well-known but which can be classified as contaminants and also may have an effect on the final flavour of the oil.

Off flavours in fish oil can be divided into three categories (Bimbo, 1998):

a) Fishy off flavour – caused by residues of nitrogen containing substances, biogenic amines and their oxides, and protein degradation products;
b) Putrefied fish off-flavour – caused by residues of sulphur-containing substances such as mercaptans and sulphides;
c) Cod-liver oil-type off-flavour – caused by oxidation products from the n-3 fatty acids.

To make fish more acceptable for food use, all of these substances must be removed from the oil.

2.6.4 Oil refining process

To produce oils and fats from vegetable and marine sources with a bland and neutral taste is the challenge every edible oil industry faces today. To achieve such characteristics, harmful and flavour producing compounds have to be removed, while keeping some of the most desirable components. Undesirable compounds like FFA and PLs needs to be removed. FFA are derived from lipids by cleavage of ester bonds due to enzyme (lipase) action, heat and moisture, which happens after the harvesting of raw material for oil extraction. Normal values of free fatty acids are below 5% in most crude edible oils. Most FFAs are removed from crude edible oils during refining

because of the undesirable effects on flavour, and the reduction of the smoke point caused by FFA. A refined oil usually contains less than 0.1% FFA (Macrae, 1993). The PL content in commercial fish oils is important, because of the effects of these compounds as emulsifying agents in refining and as catalyst poisons in hydrogenation. The phosphorous content of fish oil is largely dependent on the efficiency of cleaning of the extracted oils (Young, 1986). An acceptable PL content in refined oils is <10 ppm (0.001%) (Vaisali *et al.*, 2015). Efficient final separation of water and protein from oil or a final water washing stage will ensure the removal from the oil of the bulk of the phosphatides.

The general refining steps (Figure 9) of crude marine oils may include (Bimbo, 1998; Vaisali *et al.*, 2015):

1. *Carbon treatment*: this treatment is optional and can be performed on the starting crude oil if the oil is to be sold on the non-industrial market. The treatment is to ensure the removal of dioxins, furans, and polyaromatic hydrocarbons (PAH).
2. *Oil storage:* insoluble impurities, trace moisture and some phospholipids will precipitate out in the tanks. The combination is known as "foots".
3. *Degumming*: this step removes phospholipids, sugars, resins, proteinaceous compounds and trace metals along with other slimy substances.
4. *Alkali refining*: alkali like sodium hydroxide is added to the degummed oil, thereby precipitating free fatty acids, pigments, phospholipids, oil insoluble material, water soluble material and trace metals as soap stocks which are removed by centrifugation or water washing.
5. *Water washing/silica treatment*: water is added to the oil, mixed and left to separate the water from the oil resulting in saturation of the water with contaminants like soaps, oxidation products and trace metals.
6. *Drying*: remove moisture from the oil
7. *Adsorptive bleaching & carbon treatment*: bleaching clays and/charcoal is added to the oil to remove many minor impurities like colour compounds, oxidation products, trace metals, phospholipid remains, sulphur compounds, dioxins, furans, PAH and possibly some PCB's.
8. *Winterization*: the process of winterization consists of a crystallization (or partial solidification) by cooling the oil, followed by a separation of solids (higher melting triglycerides, waxes) which can be scooped or filtered out. This is used to enhance the unsaturated triglycerides
9. *Deodorization*: is generally carried out by a conventional steam distillation process where compounds like free fatty acids, mono-diglycerides, aldehydes, ketones, chlorinated hydrocarbon and pigment decomposition products are removed. Based on the vapour pressure and volatility at high temperature (180^{o}C-220^{o}C) the components are stripped from the oil. This is usually the finishing step and results in a bland tasting oil.
10. *Vacuum stripping or thin film, molecular or short path distillation*: Removal of chlorinated hydrocarbons, fatty acids, oxidation products, PCB and free cholesterol. Sometimes this step is used as a replacement for the deodorization step.

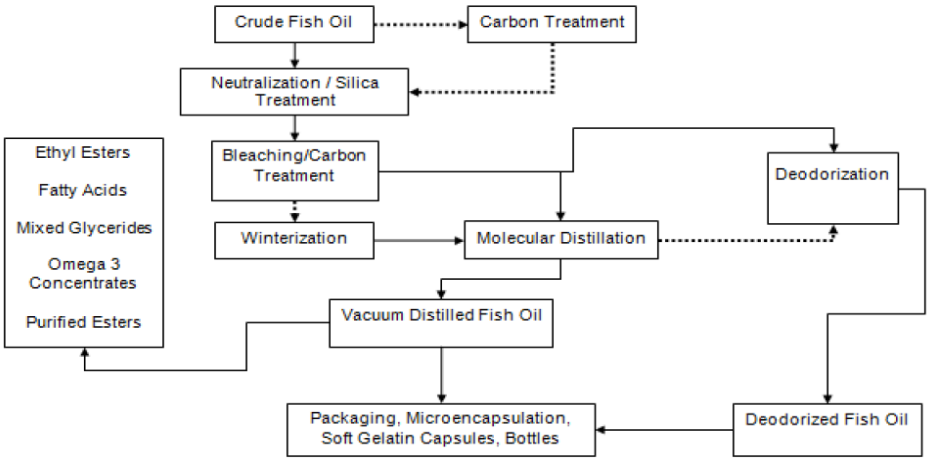

Figure 9: Production of edible and pharmaceutical grade fish oils and derivatives (Bimbo, 2011)

3 METHODOLOGY

3.1 Raw material collection and preparation

A total of 10 frozen YF tuna and 10 frozen AL tuna heads, were provided by the fish processing company Suvveb NV, Suriname. The tuna were caught by long line fishing boats in the fishing area FAO-31 in November 2016. The heads were cut in 2-4 pieces, put in plastic bags and stored in a blast freezer to freeze at a temperature of -35^{o}C. The frozen samples were then put in styrofoam boxes covered with gel packs and shipped to Iceland for 2-3 days under cooled conditions. The heads were stored in a freezer upon arrival. The fish was thawed at 4^{o}C overnight only to remove the gills and bones the next day. The first group of 10 heads (five YF and five AL) was prepared on December 21 and the second group was prepared a week after. The muscle tissues, eyes and skin parts were stored in the freezer again at -24^{o}C. For the preparation of the oil extraction, the samples were thawed overnight at 4^{o}C.

3.2 Extraction of fish oil and fish meal

The extraction method used in this research was based on the wet reduction method with some modifications performed at the Matis laboratory. A trial was carried out with blue whiting liver to test out the modified extracting and refining method of oil. It was performed to see if any modifications should be made for the extraction of the tuna oil.

The oil and fishmeal were extracted from the YF and AL tunas, 10 heads of each species. First the deboned samples were minced in a silent cutter machine. The slurry was then cooked with water at a temperature around 95^{o}C for 5-7 minutes. The slurry was then poured in centrifuge containers for centrifugation at 6000 rpm for 20 minutes at 9^{o}C. This step separated the slurry in two fractions: solid phase and the liquid phase (which includes stickwater and oil). The liquid phase was collected and stored at 4^{o}C until the alkali treatment. Before the alkalinisation step, the liquid phase was heated in an incubator at 65^{o}C to dissolve the liquid as it hardened at 4^{o}C. Sodium hydroxide was

added to mix with the liquid phase to reach a pH of 8.5 under a temperature of 65°C before the mixture was centrifuged. The upper layer was collected and stored at 4°C until the rinsing step. For the bleaching process, the oil was heated to 60°C and a mixture of 1% highly active bleaching earth (TONSIL SUPREME 112 FF) (Clariant, 2014) and 0.5% activated carbon (Norit SA 4 PAH) (Norit Digital Library, 2009) was added to the oil until it was homogenized. The mixture was then placed in a Rotavapor for 30 minutes at 95°C. The mixture was then filtered (Whatmann glass fibre filter) under vacuum. The filtered product was the finished oil. The mixture of the gathered solids was put in aluminium containers and stored in a freezer at -24°C. A part of the samples was taken for the freeze-drying process. The freeze dryer, CHRIST-ALPHA 2-4 LSC plus, was set to -85°C at 0.02 mbar for 67 hours, with a second drying step at 30°C for 30 minutes for the removal of remaining water. After the drying it was grinded resulting in a finished fishmeal product (Figure 10).

3.3 Determination of the yield

A mass balance was done for the experiment of the fish oil and the meal extraction. The yield of oil was expressed as the percentage of either crude or finished oil product extracted from minced raw material. The yield of fishmeal was expressed as percentage of fishmeal extracted from minced raw material. Yield was calculated as follows:

$$\%\ oil\ Yield = \frac{wt{:}\ of\ crude\ or\ refined\ oil \times 100}{wt{:}\ of\ minced\ tuna\ heads}$$

$$\%\ meal\ Yield = \frac{wt{:}\ of\ fishmeal \times 100}{wt{:}\ of\ minced\ tuna\ heads}$$

3.4 Proximate composition

The lipid content was determined on samples obtained from the raw minced material, crude oil, stickwater, semi-refined oil and the tuna meal according to the method of Bligh & Dyer (1959). The moisture content was measured on the raw minced material, liquid phase, semi-refined oil, stickwater and fishmeal, and was measured according to ISO 6496 (1999). The protein content of the raw material, stickwater and the fishmeal was also measured according to the ISO 5983-2 (2005). The ash content of the fishmeal was measured according to ISO 5984 (2002). Data was expressed as percent of wet weight.

3.5 Fatty acid composition

The fatty acid composition analysis was based on the AOCS official method Ce 1b-89 with some minor adjustments and the readings were done by Matis chemical analysts. This method determines the fatty acid composition of marine oils and marine oil esters by capillary column gas-liquid chromatography.

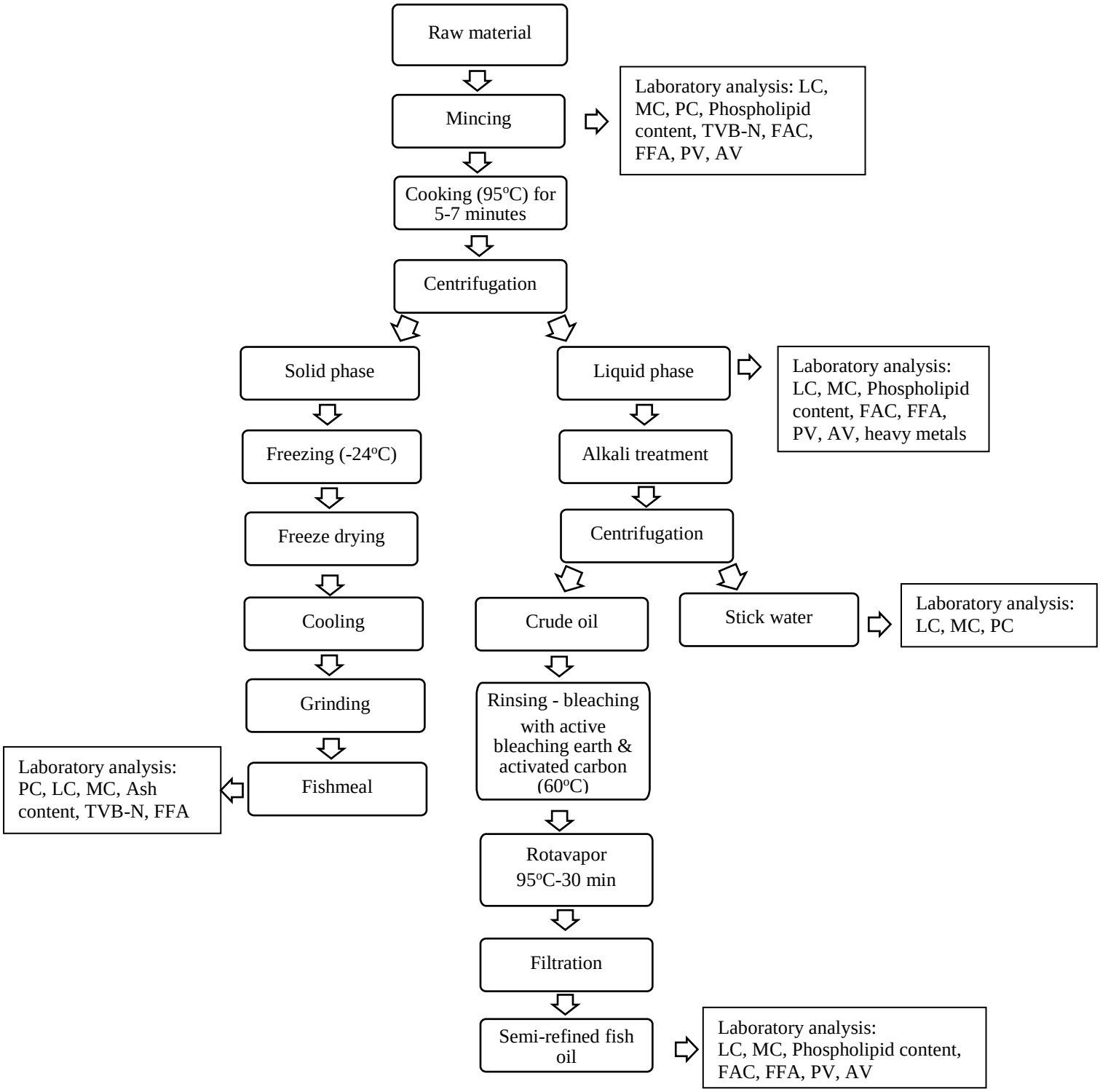

Figure 10: Flow chart of the process of making and extracting oil and meal out of yellowfin and albacore tuna heads.

3.6 Oxidation and contaminant measurements of the fish oil

Regarding the oxidation of the fatty acid profile, measurements of the free fatty acids (Lowry & Tinsley, 1976), peroxide value (PV) (Shanta & Decker, 1994) and anisidine value (AV) ((IUPAC II.D.26, 1979)) were carried out on most of the products. The FFA value (% oleic acid) was converted to acid value (mg/g) by multiplying it with 1.99 (IFFO, 1987). The peroxide value was converted from mmol/kg to meq oxygen/kg by multiplying it with 2 (ISO 3960:2007). PL content of lipid extracts was measured by the colorimetric method of Stewart based on the formation of a complex between PLs and ammonium ferrothiocyanate (Stewart, 1980). Heavy metals (arsenic, mercury and lead) analysis was measured on the liquid phase to give an indication of the safety of the products according to the modified method of NMKL 186 (2007).

3.7 Quality parameters of the fishmeal

The total volatile base nitrogen (TVB-N) of the raw material and of the fish meal was performed to evaluate the spoilage of the products according to the method of Malle & Poumeyrol (1989). FFA measurements on the fish meal were also executed to measure the oxidation of the fishmeal.

4 RESULTS AND DISCUSSION

4.1 Proximate composition

The data on the proximate chemical composition, namely lipid, moisture, protein and ash content (in %) of YF and AL tuna in different stages are presented in Table 6. The last column shows the phospholipid content of the raw material, liquid phase and semi-refined oil stages in the AL and YF tuna species.

Moisture in oil acts like a pro-oxidant and is an undesirable compound that needs to be removed during the refining step. The moisture content of the raw material was around 70% for both species. During the processing of the AL tuna from raw material to refined oil, the moisture content slightly increased in the liquid phase and then decreased in the refined oil. The high moisture levels in the liquid phase and semi-refined oil of the AL tuna could imply errors that took place during oil extraction. For the YF tuna, the moisture content decreased throughout the whole experiment, from raw material to refined oil by 99.7%. The stickwater of both species had a somewhat similar moisture content (91.8% for AL tuna and 90.1% for YF tuna) and close to the average stickwater level of 92% (FAO, 1986). The moisture level of the fishmeal was around 0.3% for both species and was far below the fatty fish meal level of 8-9%. The general fishmeal composition normally contains the gathered concentrated stickwater, which increases the moisture content (FAO, 1986). In this experiment the stickwater was not added to the fishmeal, which might have resulted in the low moisture level of the fishmeal. Also, the drying method that was carried out, in this case the freeze drying method, was not the conventional fishmeal drying method and this could have had some impact on the moisture level of the fishmeal.

The lipid content in the raw material was slightly higher in the YF tuna (13.25%) than in the AL tuna (12.24%). The lipid content of the AL tuna decreased during the processing stage from raw material to liquid phase and increased in the refined oil. The lipid content of the refined oil of the AL tuna is 22.01%, which is unacceptably low. This could be linked to the increased moisture level in the liquid phase of the AL tuna. Continuous increase of the lipid content occurred during the processing stages of the YF tuna from the raw material to the refined oil. A slightly higher lipid content was measured in the stickwater of the YF tuna than in the AL tuna and both were higher than the general lipid content of 1% in the stickwater. The lipid content in the fishmeal for both species was considerably higher than the maximum value of 12%. This could mean that the lipid release during the cooking stage was not very efficient and that there was still a lot of lipid left in the solid phase after the centrifugation step. A longer cooking time might have increased lipid release from the flesh.

The PL content in the liquid phase of AL tuna was within the crude oil range of 0.01-0.05%, but higher in the YF tuna (0.077%). The PL content of the YF tuna refined oil (0.001) was close to the maximum acceptable PL content in refined oils of <10 ppm (<0.001%), whereas the AL tuna refined oil was higher (0.015%). The removal of the PL in AL was not sufficient.

The protein content for the raw material and fishmeal in AL tuna was somewhat higher than in the YF tuna, and was for both species below the minimum value of 60% protein content required in fishmeal. This result could be associated with the low moisture content and the high lipid content. The proximate composition of a product is usually used as an indicator of nutritional value. The proximate composition results for the raw YF tuna heads were similar found by Huang (2011, 2013) which was around the average of 14.8% for lipid content and 13.5% for protein content, except for the moisture content which was much higher than 59% compared to around 70% found in this present study. The results from the albacore in this study show lower lipid content, and a higher moisture content and higher protein content than what Huang (2013) found for yellowfin tuna.

The proximate content in the fishmeal of both AL tuna and YF tuna were somewhat lower than the minimum value of 60% protein content, lower than the minimum of 10% ash content and higher than the maximum of 12% lipid content (FAO, 1986). Seasonal variability and environmental changes may have affected the proximate composition (Ali *et al.*, 2013; Goñi, 2010; Rani *et al.*, 2016). In the industry, these standard values could sometimes be different than the requirements set out by the fishmeal buyer. A tuna meal and oil factory (Mazinsa) in Mexico adopts product specifications for fishmeal which are 10% moisture, 10% fat and 59-62% protein (Mazinsa, 2017a) of which only applies to the protein level of AL tuna meal.

Table 6: Proximate composition (%)

Product	Lipid content %	Moisture %	Protein %	Ash %	Phospholipids %
Raw material					
albacore [a]	12.24	70.40	15.5	1.9[b]	0.982
yellowfin	13.25	70.55	14.7	1.5 [b]	0.994
Liquid phase (crude oil+ stickwater)					
albacore [a]	7.98	78.80	-	-	0.031
yellowfin	27.26	63.10	-	-	0.077
Stickwater					
albacore	1.70	91.80	4.0	2.5[b]	-
yellowfin	3.07	90.10	4.9	1.9[b]	-
Semi refined oil					
albacore [a]	22.01	12.40	-	-	0.015
yellowfin	94.88	0.20	-	-	0.001
Fishmeal					
albacore	34.24	0.35	59.1	7.4	-
yellowfin	31.19	0.30	56.2	7.3	-

Sample group contains 10 heads for each species, unless mentioned otherwise.

[a] batch contained five heads

[b] ash content calculated from 100-(LC+MC+PC)

4.2 Material balance (yield)

Yields of the freeze dried meal, stickwater, crude oil and semi-refined oil of the AL and the YF tuna after the fishmeal and oil extraction are shown in the material balance (Figure 11). The yield is expressed as product weight divided by minced weight (grey area). The total weights were also recorded from raw material to end product of both species and are expressed as grams in the mass balance.

The experiment had several complications and losses. Losses of oil occurred during mincing, centrifugation, transferring, sampling and filtering resulting in low yield. After the centrifugation step, some of the bottles from the AL group sucked in and were difficult to remove the oil (upper layer), which lead to only a small amount of semi-refined oil being collected after the refining and filtering. The yield of the fishmeal of the AL tuna (23%) and YF tuna (24%) was slightly above the average fishmeal yield of 22.5% (Figure 11). The yield of the crude oil was 2% for both species and was much lower than the average oil yield of 4-5% (Shepherd & Jackson, 2013) and according to a research done on skipjack tuna (Chantachum, 2000) which yielded 4.8% crude oil from non-precooked samples. This low oil yield was a result of all the losses that occurred throughout the experiment. The yield of the semi-refined oil (1%) was half the yield of the crude oil. The estimated production of crude fish-oil and fishmeal would have been 3.5+ tons and 41.5+ tons respectively, according to the results of the fish oil and fishmeal yield numbers and the estimated YF and AL tuna head production of 177 tons in 2016 (numbers obtained from SUVVEB NV), which is an extremely low production rate.

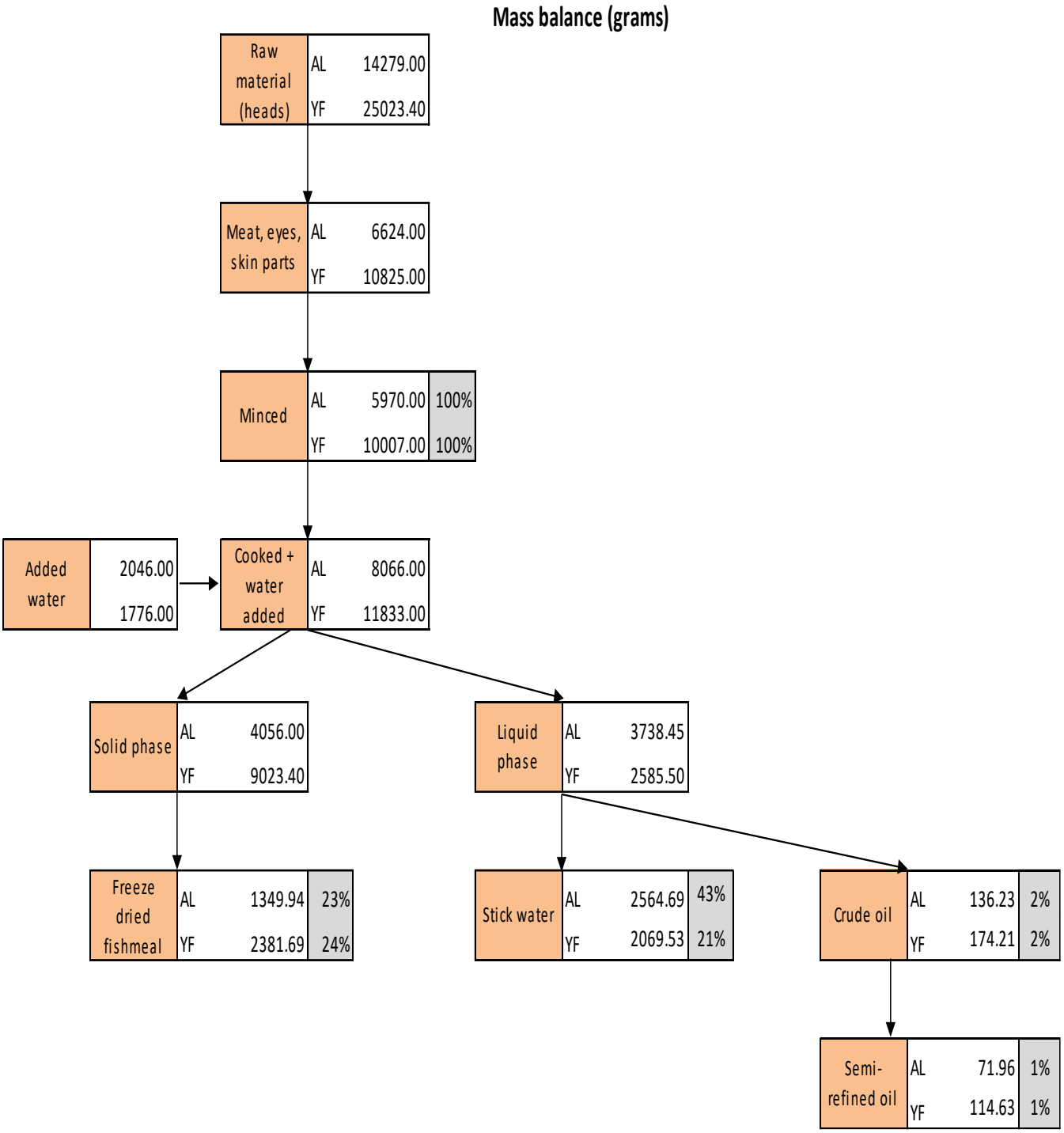

Figure 11: Material balance of the fish oil and fish meal extraction experiment on albacore tuna (AL) and yellowfin tuna (YF).

4.3 Fatty acid profile

The fatty acid profile included several SFA, MUFA and the PUFA of the YF and AL tuna in the three stages which were raw material, liquid phase and the semi-refined oil (Table 7). The last column is the general fatty acid profile range of tuna obtained from FAO/WHO Codex Alimentarius Commission (2015) which was used as a reference and compared with the results from the different stages.

The fatty acid profile of the two species were similar at all stages of the processing. The SFA and the PUFA levels were more dominant in the AL tuna than the YF tuna in all stages, with the palmitic acid (>17%) being the highest among the SFAs and the DHA (27%) the highest among the PUFAs. The semi-refined oil had a SFA level of 27.6% and 25.3%, a MUFA level of 25.8% and 28.5% and a PUFA level of 43.4% and 41.8% for AL tuna and YF tuna respectively. Both the EPA and DHA levels in AL tuna were higher than the YF tuna in all stages, except for the AL tuna liquid phase. The C20-PUFAs in the AL tuna liquid phase contained differences between all stages including EPA. These C20-PUFAs might have been altered during the analysis or the readings might have been inaccurate. The most abundant MUFAs in the YF tuna were oleic acid (±17%). Fatty acid composition of the tuna heads showed high content of palmitic acid, oleic acid and DHA. The fatty acid composition of both species was in agreement with the range from the FAO/WHO Codex Alimentarius Commission (2015). According to a study done by Erlinda (2002) on RRM of raw yellowfin tuna, which had EPA and DHA levels of 5.3% and 26.8% respectively are slightly lower than the EPA and DHA levels of the YF tuna raw material of 5.7% and 27.5% collected from this research. The EPA and DHA levels of the semi-refined oil of AL tuna and YF tuna were 35.2% and 33.3% respectively, with AL tuna oil containing the highest omega-3 fatty acids. The omega-3 PUFA are important throughout life and are a dietary necessity found predominantly in fish and fish-oil supplements.

4.4 Lipid oxidation

The results of the oxidation analysis on FFA, PV, AV and ToTox value are presented in Table 8. The analysis was performed on the YF and AL tuna in the raw material, liquid phase and semi-refined oil for both species. Only the FFA content was measured for the fishmeal obtained from both tuna species.

Unsaturated fatty acids are susceptible to oxidation and quality control of fish oil should determine the degree of oxidation. Optimal removal of FFA occurred during the refining. The FFA value decreased after the cooking and centrifugation step and in the semi-refined oil by 70% in the AL tuna oil and 95% in the YF tuna oil (Table 8). The FFA content of AL tuna was higher than the YF tuna in all stages. All the values were below the standard level for refined oil of 3 mg/g (FAO/WHO Codex Alimentarius Commission, 2015).

During the oil extraction the PV increased both after the centrifugation step and the refining step, while the AV decreased in both steps. The PV from the AL tuna was lower than the YF tuna in all stages, especially in the liquid phase. The low but increased PV in the liquid phase and the semi-refined oil might indicate that the two stages were still in the primary oxidation phase. All PV levels were lower than the maximum PV of 5 meq oxygen/kg oil according to the FAO/WHO Codex Alimentarius Comission (2015). The high AV and the low PV in the raw material may imply

Table 7: Fatty acid profile of YF and AL

Formula	Name	Raw material		Liquid phase		Semi-refined oil		Tuna oil (FAO/CAC 2015)
		AL	YF	AL	YF	AL	YF	
C14:0	Myristic acid	2.7	2.3	2.6	2.2	2.6	2.2	2.0-5.0
C15:0	Pentadecanoic acid	0.8	0.7	0.8	0.7	0.8	0.7	≤0.05-2.0
C16:0	Palmitic acid	19.5	17.4	19.6	17.3	19.1	17.2	14.0-24.0
C17:0	Heptadecanoic acid	0.8	0.6	0.8	0.6	0.7	0.6	1.0-3.0
C18:0	Stearic acid	4.3	4.3	4.3	4.3	4.1	4.3	1.0-7.5
C20:0	Arachidic acid	0.3	0.3	0.3	0.3	0.3	0.3	≤0.05-2.5
C14:1		0.1	0.1	0.1	0.1	0.1	0.1	
C16:1n7	Palmitoleic acid	5.3	5.4	5.2	5.3	5.2	5.3	1.0-12.5
C17:1		0.7	0.8	0.7	0.8	0.7	0.8	
C18:1n9	Oleic acid	13.8	17.4	13.8	17.2	13.9	17.1	10.0-25.0
C18:1n7	Vaccenic acid	2.1	2.3	2.1	2.3	2.2	2.3	2.0 – 7.0
C20:1n11	Eicosenoic acid	1.8	1.5	2	1.5	2	1.5	≤0.05-3.0
C20:1n9	Eicosenoic acid	0.1	0.1	0.2	0.1	0.1	0.1	≤0.05-2.5
C22:1n11	Cetoleic acid	0.5	0.2	0.5	0.2	0.6	0.2	≤0.05-1.0
C22:1n9	Erucic acid	0.3	0.2	0.3	0.2	0.3	0.2	≤0.05-2.0
C24:1n9		0.7	0.9	0.7	0.8	0.7	0.8	
C16:2n4		0.1	0.1	0.1	0.1	0.1	0.1	
C16:3n4		0.9	0.9	1	0.9	0.9	0.9	
C18:2n6	Linoleic acid	0.9	1	0.9	1	0.9	1	≤0.05-3.0
C18:3n6	γ-Linolenic acid	0.2	0.2	0.2	0.2	0.2	0.2	≤0.05-4.0
C18:3n4		0.2	0.2	0.2	0.2	0.2	0.1	
C18:3n3	Linolenic acid	0.5	0.5	0.5	0.5	0.5	0.5	≤0.05-2.0
C18:4n3	Stearidonic acid	0.5	0.3	0.5	0.3	0.5	0.3	≤0.05-2.0
C20:2		0.3	0.3	0.2	0.3	0.3	0.3	
C20:3n6		0.1	0.1	1.1	0.1	0.1	0.1	
C20:4n6	Arachidonic acid	2.2	2.5	1.3	2.4	2.1	2.4	≤0.05-3.0
C20:4n3	Eicosatetraenoic acid	0.5	0.4	3.6	0.4	0.5	0.4	≤0.05-1.0
C20:5n3	**Eicosapentaenoic acid (EPA)**	6.7	5.7	3.5	5.7	6.9	5.8	2.5-9.0
C22:2		0.1	0.1	0.2	0.1	0.2	0.1	
C22:4n6		0.3	0.4	0.1	0.4	0.2	0.5	
C22:5n3	Docosapentaenoic acid	1.4	1.8	1.5	1.8	1.5	1.8	≤0.05-3.0
C22:6n3	**Docosahexaenoic acid (DHA)**	27.7	27.5	27.7	27.6	28.3	27.5	21.0-42.5
Saturated fatty acid (SFA)		28.3	25.6	28.4	25.5	27.6	25.3	
Mono-unsaturated fatty acid (MUFA)		25.4	28.9	25.6	28.6	25.8	28.5	
Poly-unsaturated fatty acid (PUFA)		42.6	41.9	42.5	42.0	43.4	41.8	
EPA+DHA		34.4	33.3	31.2	33.3	35.2	33.3	
Total omega-3		37.3	36.3	37.2	36.4	38.2	36.3	

Table 8: Results of the oxidation products: FFA, PV, AV and ToTox.

Product	FFA mg/g	PV meq/kg	AV	ToTox
Raw material				
Albacore [a]	1.26	0.08	76.26	76.42
Yellowfin	1.44	0.09	116.90	117.08
Liquid phase (crude oil+ stickwater)				
Albacore [a]	0.87	0.53	-	-
Yellowfin	0.38	0.91	23.31	25.13
Semi refined oil				
Albacore [a]	0.38	1.37	-	-
Yellowfin	0.07	1.40	16.71	19.51
Fishmeal				
Albacore	0.44	-	-	-
Yellowfin	0.41	-	-	-

Sample group contains 10 heads for each species, unless mentioned otherwise.
[a] batch contained five heads

that the solids in the raw material contained more secondary oxidation products. The AV could not be measured for the AL tuna, because the oil sample was not large enough to perform the analysis. Because of the high AV in the raw material the ToTox value also increased. The YF tuna liquid phase (which contains crude oil) had an AV and ToTox value of 23.31 and 25.14 respectively, and was in agreement with the quality guidelines obtained from Bimbo (1998) which is 4-60 for AV and 10-60 ToTox value for crude marine oils. The refined oil from the YF tuna also had acceptable levels in the AV (16.17) and ToTox value (19.59), which were less than 20 for the AV and less than 26 for the ToTox value (FAO/WHO Codex Alimentarius Comission, 2015). With these levels the lipid oxidation products can be considered acceptable. Some impurities might have remained after the refining step. The oil has been heated several times during the whole oil extraction process. The samples were also exposed to light for a short period before laboratory analysis.

4.5 Heavy metals

Hg, Pb, Cd and As analysis was carried out on the AL and YF tuna liquid phase (Table 9). The liquid phase was an extraction from the 10 heads of each species. The levels for Hg, Pb and Cd in the YF and the AL tuna were similar and lower than the corresponding limits according to the Commission Regulation (EC) No 1881/2006. The As levels in the liquid phase of both species were high. As there are no statutory limits for arsenic levels in food at EU level, arsenic does not fall within the scope of this Commission Regulation (EC) No 1881/2006. However, according to the Codex General Standard for Contaminants and Toxins in Food and Feed (1995), the As level in both species was higher than the maximum level of 0.1 mg/kg in edible oil, with YF tuna having the highest level. No measurements of the semi-refined oil were performed to monitor the possible reduction during the refining stage.

Table 9: Heavy metal results of AL and YF tuna in the liquid phase.

Liquid phase	Hg (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	As (mg/kg)
AL	<0.06	<0.03	<0.04	1.018
YF	<0.06	<0.03	<0.04	1.707

4.6 Total volatile base nitrogen (TVB-N)

The total volatile base nitrogen (TVB-N) must be performed to evaluate the spoilage of the products. Table 10 shows the TVB-N levels obtained from the raw material and the fishmeal in the AL and YF tuna expressed in mg N/100g. The TVB-N value of the AL tuna raw material was slightly higher than that of the YF tuna and both species were below the average value of 80 mg N/100 g required for raw material used to produce fishmeal (FAO, 1986). This resulted in a relatively low TVB-N value in the fishmeal (<42 mg N/100g). The levels for TVB-N in fishmeal usually must meet the requirements of the buyers. The factory in Mexico mentioned earlier (Mazinsa, 2017b), produces tuna meal and one of the specifications is a TVB-N value of lower than 120 mg N/100g, which is in line with the TVB-N levels of the fishmeal in both species. The raw material is considered to be appropriate fresh material intended for fishmeal production.

Table 10: TVB-N in raw material and fishmeal

	TVB-N (mg N/100g)	
Product	AL	YF
Raw material	14.9[a]	13.3
Fishmeal	32.0	40.8

Sample group contains 10 heads for each species unless mentioned otherwise.
[a] batch contained five heads

5 CONCLUSIONS AND RECOMMENDATIONS

The experiment had many complications due to inexperience of the extraction method performed under laboratory conditions. The relatively low yield of the tuna oil and the high lipid content in the fish meal might be an indication that the minced meat was not sufficiently cooked to liberate most of the lipids from the muscles. The temperature and the cooking time should be modified for future experiments. The AL tuna liquid phase and semi-refined oil had low oxidation by-product values and high omega-3 fatty acids, but an extremely low lipid content and a very high moisture content, which would make it unacceptable for the consumer despite the desired fatty acid profile and required quality factors. The overall composition and quality factors of the YF tuna oil were within the standard range and is according to these parameters considered an acceptable edible fish oil. The heavy metal results were favourable, except for the As level, which exceeded the maximum level in edible oil. This was however only performed in the liquid phase (containing crude oil). Although As does not fall within the scope of the Commission Regulation (EC) No 1881/2006, measurement of the As level should be performed as it would be interesting to see changes of the As level during the refining stage. An advanced research on the seasonal variability of the proximate composition is necessary, especially to observe the lipid content of both species in Suriname considering the wide distribution of these tuna species. Further research on the other

RRMs like bones and the trimmings should be considered and/or business partnerships should be formed to collect more Tuna RRM from nearby countries, e.g. from the Caribbean region.

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APPENDICES

Appendix 1: Sample preparation of the YF and the AL tunas.

Date	Product	Species	
Batch 1: 21.12.16	Whole heads (kg)	yellowfin	albacore
	1	2.5440	1.3300
	2	1.7190	1.0460
	3	2.6690	1.6660
	4	3.5210	1.1240
	5	3.2220	1.3020
	Total whole heads	13.6750	6.4680
	Meat, eyes, skinparts	6.0720	3.4250
Batch 2: 28.12.16	whole heads (kg)	yellowfin	albacore
	1	2.4194	1.5330
	2	3.2950	1.4820
	3	1.7400	1.6690
	4	1.2710	1.4760
	5	2.6230	1.6510
	Total whole heads	11.3484	7.8110
	Meat, eyes, skinparts	4.7530	3.1990

Appendix 2: Material balance of the initial groups according to batch and species. The initial four groups: AL1 (21-12-2016), AL2(28-12-2016), YF1 (21-12-2016) and YF2 (28-12-2016).