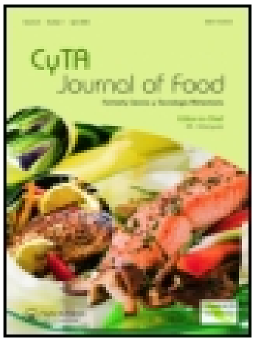

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REVIEW

Ready-to-eat products elaborated with mechanically separated fish meat from waste processing: challenges and chemical quality

Alimentos listos para comer elaborados con carne de pescado mecànicamente separada de residuos de procesado: retos y calidad química

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Both the worldwide demand for fish and aquaculture production have increased. Nevertheless, an extensive amount of fish production is destined for animal feed. Fish represents a rich source of nutrients necessary for good health, but it is highly perishable. This review contains descriptions of the relevance of the use of mechanically separated fish meat, which is considered a waste processing, for the manufacturing of semi- and ready-to-eat (RTE) products for human consumption and an evaluation of their chemical stability. Currently, consumers request nontraditional foods without risk to their health. Therefore, the development of innovative and healthy foods has been a challenge, mainly due to lack of knowledge and technology transfer to the industry.

Keywords: innovative foods; value-added; physicochemical parameters; quality evaluation; sustainability

Tanto la demanda mundial de pescado como la producción de la acuicultura ha aumentado en los últimos años. Sin embargo, una gran cantidad de la producción de pescado se destina a la alimentación animal. El pescado representa una rica fuente de nutrientes necesarios para una buena salud, pero es altamente perecedero. Esta revisión contiene descripciones de la pertinencia de la utilización de carne de pescado separada mecánicamente, que son considerados residuos de producción, para la fabricación de productos semi-listos y listo para consumo humano y una evaluación de su estabilidad química. Actualmente, los consumidores desean alimentos no tradicionales y sin riesgo para su salud. Por lo tanto, el desarrollo de alimentos innovadores y saludables ha sido un desafío, debido principalmente a la escasez de conocimiento y transferencia de tecnología a la industria.

Palabras clave: alimentos innovadores; valor agregado; parámetros fisicoquímicos; evaluación de la calidad; sostenibilidad

Introduction

The world fish production has grown steadily in the last five decades. In 2011, the fish production increased by 5% in relation to 2010 (from an average of 148.1 million tons in 2010 to 155.7 million tons in 2011), with a provisional estimate of 158.0 million tons in 2012 (increase of 1.5% in relation to 2011). The world per capita fish consumption increased from an average of 9.9 kg in the 1960s to 18.9 kg in 2010, with preliminary estimates of 19.2 kg for 2012. In 2010, the per capita fish consumption by continent was 9.7 kg per capita in Africa and 21.6 kg in Asia, of which 16.1 kg was consumed outside China. Moreover, in 2010, the per capita fish consumption values in Oceania, North America, Europe, and Latin America and the Caribbean were 25.4 kg, 21.8 kg, 22.0 kg and 9.7 kg, respectively (Food and Agriculture Organization [FAO], 2014).

The population growth, urbanization and growing concerns over healthy eating habits in developed countries as well as the increase in the purchasing power of developing countries have contributed to an increase in the worldwide fish demand (Food and Agriculture Organization [FAO], 2012). China has been the country mostly responsible for the increase in world per capita fish consumption, owing to a substantial increase in fish production, particularly from aquaculture. However, in 2012, 136.2 million tons (86%) of the estimated world fish production was used for direct human consumption, whereas the remaining 21.7 million tons (14%) was destined for nonfood uses, such as fish meal and fish oil (FAO, 2014). These latter uses constitute the major aquatic protein and lipid sources available for aquaculture feeds (Tibaldi et al., 2015). This has led to an increasing demand for these products and, consequently, an increase in their prices (Tacon & Metian, 2008).

Regarding their nutritive value, fish and fishery products represent a very valuable source of protein and essential micronutrients for balanced nutrition and good health. Regarding lipid fraction, fish represents a significant source of polyunsaturated fatty acids (PUFAs), especially the eicosapentaenoic (EPA-C20:5 ω-3) and docosahexaenoic (DHA-C22:6 ω-3) acids. These two fatty acids are supplied solely by the diet (i.e., they cannot be synthesized by the human body) and reduce risk factors associated with cardiovascular disease, hypertension, general inflammation, asthma, arthritis, psoriasis and various types of cancer (Calder & Yaqoob, 2009; Hooper et al., 2006). Nevertheless, the fatty acid composition is directly related to the processing and storage conditions due to the instability of unsaturated lipids (Taheri, Motallebi, Fazlara, Aghababyan, & Aftabsavar, 2012). These authors observed that increasing time in frozen storage decreased the nutritional value of Cobia fish. The PUFAs, especially EPA and DHA, were decreased due to oxidation of the lipids during 6 months in frozen storage.

Fish farming has increased considerably in several countries. However, some barriers should be overcome to make aquaculture

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more productive. These include the heterogeneity of fish weight, which now leads to their discard due to the lack of economic value in the market, and lack of standardization on the feed supplied, which increases the production cost. Moreover, technological deficiency in various processing steps, including the rational use of waste, makes the development of new products more difficult (Guttormsen, Myrland, & Tveteras, 2011; Moran, 2007).

Therefore, an improvement in the management of wastes destined for nonfood uses is urgently needed to maintain the continuous growth of aquaculture and to meet consumer demand. On the one hand, it becomes important to encourage research related to strategic replacements for fish feed to stimulate the continued growth of aquaculture production (Tacon & Metian, 2008). It is clear that technological alternatives must be found for the transformation of fish wastes in ready-to-eat (RTE) products or partially processed foods with added value for human consumption (Ferraro et al., 2010; Monteiro, Mársico, Viriato, Lima de Souza, & Conte Junior, 2012; Monteiro et al., 2014).

Nevertheless, fish are highly perishable, making it important to evaluate their chemical stability with the aim of improving quality monitoring and to provide safe food to consumers. Among several compounds, the thiobarbituric acid-reactive substances (TBARS) indicate quality loss related to lipid oxidation as well as pH and biogenic amines (BAs) refer to quality loss related to protein degradation; alkaline substances from microbial activity and endogenous enzymes; and bacterial decarboxylation of the amino acids that naturally compose the food, respectively (Lázaro & Conte-Junior, 2013; Rodrigues et al., 2013). Moreover, malonaldehyde (MDA) (secondary compound from lipid oxidation) and BAs are considered harmful compounds for human health, which emphasizes the greater need for monitoring.

In this context, the aim of this review was to evaluate the possibilities for the use of mechanically separated fish meat from waste processing for the manufacture of semi-RTE and RTE products destined for human consumption and the physicochemical parameters necessary to determine the product quality.

Fish wastes

In 2012, 21.7 million tons from fish production was destined for nonfood uses, representing an increase of approximately 9% in relation to that in 2010. Among the products not intended for human consumption (nonfood uses), the manufacture of fishmeal and fish oil is more prevalent (FAO, 2014; Tacon & Metian, 2008).

Fishmeal is the crude flour obtained after the milling and drying of fish or fish parts, and fish oil is oil derived from the tissues of oily fish. In addition, an important source of raw material for the production of fishmeal and fish oil is the waste from processing commercial fish species used for human consumption (FAO, 2012). Both fish meal and fish oil constitute the major available aquatic protein and lipid sources for aquaculture feeds, mainly carnivorous finfish and marine shrimp. These two ingredients are energy resources, which is important because fish tend to inefficiently convert carbohydrates to energy. Fish meal and fish oil also supply essential amino acids (such as lysine and methionine) that are deficient in plant proteins, and the fatty acids (eicosapentaenoic acid – EPA, and docosahexaenoic acid – DHA) that are not found in vegetable oils (Li, Rezaei, Li, & Wu, 2011; Tibaldi et al., 2015).

Historically, fishmeal was used in swine and poultry feeds as well as in aquaculture diets. In 1988, 80% of the world's fishmeal production was used in feed for swine and poultry, while only 10% was destined for aquaculture feed. Nevertheless, by 2010, the consumption of fishmeal for aquaculture, swine, chickens and others was 73%, 20%, 5% and 2%, respectively. During the 1980s, fish oil became the lipid source of choice due to the early growth of the farming of salmonids, and 20% of the supply was thus consumed in 1990 (FAO, 2012).

However, the increasing demand for fishmeal and fish oil for aquafeeds has been raising the price of fish meal and fish oil, which then led to steady declines in the average inclusion levels in compound fish feeds (Tacon & Metian, 2008). The cost of feed is the largest production cost for commercial aquaculture and the increases in fish meal and fish oil prices can decrease the profitability of many aquaculture enterprises (Rajkumar, Rahman, Prabha, & Phukan, 2013). Therefore, fishmeal and fish oil should no longer be regarded as low-value products due to their increased prices (Olsen, Toppe, & Karunasagar, 2014). According to the Food and Agriculture Organization, between January 2005 and January 2013, the price of fish meal increased by 206%. Therefore, lower percentage of fishmeal and fish oil is being used in compound feeds (FAO, 2014).

Therefore, strategic alternatives must be found by replacing fish meal and fish oil with vegetable meal and vegetable oil, respectively, in fish feed. This in turn will enable aquaculture production to continue to grow (FAO, 2012; Tacon & Metian, 2008). Although options have been established for fishmeal and fish oil replacers, as shown in Table 1 (Tacon, Hasan, & Metian, 2011), some studies (Bell et al., 2010; Brinker & Reiter, 2011; Salze, McLean, Battle, Schwarz, & Craig, 2010; Tibaldi et al., 2015; Trushenski et al., 2011) have been performed to determine the fishmeal and fish oil replacers that are more appropriate for various fish species.

The authors evaluated the decreasing fishmeal situation and the complete replacement of fish oil in farmed Atlantic salmon over the seawater production phase. They concluded that this is possible without any detriment to growth and feed conversion (Bell et al., 2010). Researchers tested the replacement of up to 94% of the fish meal and fish oil by soy protein concentrate in

Table 1. Feed ingredient usage for major aquaculture species and species groups.

Tabla 1. Ingredientes de alimentos usados para las principales especies acuícolas y grupos de especies.

Feed ingredients	Inclusion level in compound aquafeed *(Percentage)*
Plant protein meal	
Soybean meal	3–60
Wheat gluten meal	2–13
Corn gluten meal	2–40
Rapeseed/canola meal	2–40
Cottonseed meal	1–25
Groundnut/peanut meal	~30
Mustard oil cake	~10
Lupin kernel meal	5–30
Sunflower seed meal	5–9
Canola protein concentrate	10–15
Broad bean meal	5–8
Field pea meal	3–10
Plant oil	
Rapeseed/canola oil	5–15
Soybean oil	1–10

Source: FAO (2012). Adapted from Taconet al. (2011).

Fuente: FAO (2012). Adaptado de Tacon et al. (2011).

aquafeeds for juvenile cobia and obtained successful results. However, some ingredients (minerals and vitamin mixes) were added to the feed formulation that may compromise the feasibility and sustainability of such diets with regard to the economic aspects (Salze et al., 2010). Other authors reported no changes in the production performance of cobia with replacement of a substantial amount of fish oil with soybean oil. Nevertheless, even at low levels of fish oil replacement, the fatty acid composition was significantly altered, possibly because the juvenile cobia exhibits a particular requirement for intact long-chain PUFAs. These findings were explained by several apparent distinctions in fatty acid metabolism in this species. This has potential importance for both feed formulation and the composition and quality of fish tissue and merits further research (Trushenski et al., 2011). Researchers observed that high levels of plant protein lead to inferior results in both feed conversion and growth, but these are offset by some remarkable potential improvements in flesh quality and the health of the fish. Although as of yet such diets may not quite meet the target of maximized profits, these authors reported that it seems possible to produce rainbow trout competitively on a pure plant protein basis (Brinker & Reiter, 2011).

It is important to report that the inclusion rates of fishmeal and fish oil replacements depend on a number of factors. These include the specific differences among different fish species such as their biological requirements, nutritional knowledge and the production systems employed (stocking density, water management, feed management, natural food availability), and differences regarding the feeds used (local feed ingredient availability, quality and cost). In addition, different national legislative controls exist regarding imports and/or ingredient use (including subsidies and incentives) and the intended market and market value of the cultured species (Tacon & Metian, 2008). Therefore, specific studies related to decreasing the use of fishmeal and fish oil in aquafeeds must be encouraged. This is extremely important because the use of commodity-traded plant-protein sources as alternatives to fish meal represents the only practical avenue to true environmental and economic sustainability in the global aquaculture industry (Salze et al., 2010).

Simultaneously, the increase in value-added fishery products for human consumption results in even more wastes. These wastes are often discarded into the environment, leading to negative impacts on environmental quality. To avoid the use of fish wastes directly as fertilizer and in the manufacture of organic fertilizer or their improper discharge into rivers and estuaries, several technological strategies have been studied such as the production of functional ingredients and RTE and semi-RTE products (Chalamaiah, Kumar, Hemalatha, & Jyothirmayi, 2012; Monteiro et al., 2014; Nielsen & Jacobsen, 2013). The edible proportion of fish represents approximately 45% of the total fish weight; therefore, 55% of the fish can be considered as fish waste from processing including head, guts, bones, skin, fins, frame and meat adhered to bones and skin (Arvanitoyannis & Tserkezou, 2014). In general, head, guts, bones, skin, fins and frame are used for the production of biologically active protein hydrolysates, which serve as functional food ingredients due to their great nutritional composition, amino acid profile and antioxidant activities (Chalamaiah et al., 2012; Dekkers, Raghavan, Kristinsson, & Marshall, 2011). On the other hand, the meat adhered to head, bones and skin (mechanically separated fish meat) from commercial fish processing and fishes not acceptable such as fillets and whole fishes with noncommercial size are considered fish wastes, which can be consumed by human and, therefore, are used for the manufacturing of semi-RTE and RTE products for human consumption (Adeleke & Odedeji, 2010; Fabrício et al., 2013; Fuchs, Ribeiro, Bona, & Matsushita, 2013; Monteiro, Mársico, Viriato, et al., 2012; Monteiro et al., 2014; Nielsen & Jacobsen, 2013; Stevanato et al., 2007), which were the main focus of this review.

Several RTE and semi-RTE products have been developed such as soup (Stevanato et al., 2007), fish burgers (Marengoni et al., 2009), bread fortified with fish flour (Adeleke & Odedeji, 2010), surimi (Mello et al., 2010), sausage (Oliveira Filho, Fávaro-Trindade, Trindade, Balieiro, & Viegas, 2010), fish bouillon cubes (Fabrício et al., 2013), croquette (Fuchs et al., 2013), pâté (Lobo et al., 2015; Nielsen & Jacobsen, 2013) and instant soup (Monteiro, Mársico, Viriato, et al., 2012; Monteiro et al., 2014). However, there have been shifts in some points such as consumer preferences, in processing and in the general fisheries industry. In this context, the processors of traditional products have been losing their market share. This is an incentive for innovation in providing differentiated products for human consumption. Therefore, the current trend has been towards the technological improvement in food processing and packaging to increase the efficiency, effectiveness and profit from the utilization of raw materials, ensuring the standardized and sustainable development of the aquaculture sector (FAO, 2014).

Manufacturing of RTE products from mechanically separated fish meat

Product effectiveness is represented by two strong indicators: product innovativeness and process speed. Product innovativeness is defined by the degree of novelty and generative capacity regarding market needs (Hristov & Reynolds, 2015). However, the failure rate of new products has been high. Therefore, companies are focused on enhancing both product innovativeness (the presence of competing characteristics) and speeding up the development process (the time spent from the initial development until the introduction of the product into the marketplace) (Hristov & Reynolds, 2015; Lisboa, Skarmeas, & Lages, 2011).

Regarding the nutritive value of fish, it represents a rich source of high-quality protein, a range of micronutrients and essential fatty acids that have beneficial effects on human health including decreased cardiovascular disease risk, positive effects on the development of the brain and anti-inflammatory and anti-carcinogenic effects mainly in the most common cancers such as colorectal, prostate and even possibly thyroid cancer (Huang, Rose, & Hoffmann, 2012; Linseisen et al., 2011; Lund, Belshaw, Elliott, & Johnson, 2011; Stevanato et al., 2010; Tacon & Metian, 2013). Nevertheless, the time required for their preparation can discourage some consumers from purchasing fish, leading to a preference for RTE fish products (Brunsø, Verbeke, Olsen, & Jeppesen, 2009). On the other hand, RTE products are costly, which still appears to be a great barrier to consumption. However, it was proven that the current consumers would willingly pay more for RTE blue fish, mainly in sales channels (fast food and snack bars), suggesting a new point of view for these products. However, the lack of knowledge and technology transfer to the industries represent difficulties for the development of new products (Cosmina et al., 2012).

In this context, due to changing consumer tastes and advances in technology, packaging, logistics and transport, the use and processing of fish have significantly diversified. Currently, great importance has been attached to meeting the consumer demand based on social, environmental and economic aspects. Therefore, current innovation in value addition is converging on convenience foods such as fresh, frozen, breaded, smoked or canned forms of fish (FAO, 2014).

Several studies (Cavenaghi-Altemio, Alcade, & Fonseca, 2013; Mello et al., 2010; Monteiro, Társico, Viriato, et al., 2012; Monteiro et al., 2014; Monteiro, Társico, Canto, et al., 2015, Monteiro, Társico, Lázaro, et al., 2015; Nielsen & Jacobsen, 2013; Oliveira, Lourenço, Sousa, Joele, & Ribeiro, 2015; Palmeira, Rodrigues, et al., 2014; Stevanato et al., 2008; Takano et al., 2012) have been directed towards the manufacturing of nutritious and healthy foods by using fish wastes. Stevanato et al. (2008) evaluated flour manufactured from tilapia heads and found high nutritive value due to their protein and ash (minerals) contents. In addition, the lipid fraction exhibited a satisfactory content of omega-3 fatty acids, PUFA/SFA and the n-6/n-3 ratios. Mello et al. (2010) found great protein and lipid levels as well as compliance with appropriate microbiological standards in pulp and surimi from tilapia. These authors concluded that these products have potential for recovering a protein source for the development of value-added products destined for human consumption.

Monteiro, Társico, Viriato, et al. (2012) concluded that the processing of tilapia heads and carcasses in the form of pulp and flour produces high nutritive value foods with suitable protein content. Instant soup prepared from these raw materials exhibited low lipid levels with excellent protein and mineral contents. Moreover, pulp, flour and instant soup presented satisfactory microbiological quality. Takano et al. (2012) manufactured a fish sauce using soy sauce koji mold produced from the wastes of kamaboko processing. These authors reported that this represented a high-quality product, retaining only low levels of food additives derived from the original kamaboko (sorbic acid and ß-carotene). Moreover, the fish sauce evaluated by Takano et al. (2012) exhibited favorable characteristics such as very low off-flavor (fishy odor), high umami taste and agreeable soy sauce-like flavor. Nielsen and Jacobsen (2013) produced a fish pâté made from cod and enriched with fish oil (5%). These authors obtained a product with good sensory properties and a shelf life of 8 weeks. Cavenaghi-Altemio et al. (2013) manufactured frankfurter-type sausages from mechanically separated tilapia surimi and found promising characteristics for commercial applications. Lobo et al. (2015) observed a great potential for mechanically separated meat (MSM) of cachapinta (*Pseudoplatystoma* sp) for production of pâté.

Palmeira, Rodrigues, et al. (2014) used noncommercial-size trout fillets to produce restructured products with partial replacement of sodium chloride with potassium chloride and starch addition as well as the use of microbial transglutaminase (MTG) and MTG associated with soy protein. These products exhibited desirable sensory attributes and could represent a viable alternative to the manufacture of innovative fish products. Monteiro, Társico, Viriato, et al. (2012) concluded that flours and instant soup from tilapia wastes possessed great nutritious and technological potential. These products could be used in the food industry for the development and introduction of new alternative value-added foods to the market. In addition, the flours can be used as replacements in current food products made from conventional flour sources. This would produce a healthy impact on the consumers, but sensorial evaluation must be performed to define the final product acceptance. Monteiro, Társico, Lázaro, et al. (2015) evaluated different levels of MTG (0.0–0.8%) in restructured tilapia steak prepared from noncommercial-sized fillets. The MTG steaks were well-accepted and demonstrated better consumer preference than steaks without MTG. In addition, MTG maintained the proximate composition as well as improved the cooking yield, sensorial (salty taste, succulence and tenderness) attributes and textural parameters (instrumental hardness and chewiness) of the product. These authors affirmed that these advantages were achieved by using a low concentration of MTG (0.5%) in the product formulation, thus showing the use of MTG to be a viable tool for the food industry. Monteiro, Társico, Canto, et al. (2015) tested different salt levels by using sodium replacers in restructured tilapia steak prepared from sub-ideal weight fillets. The replacement of 50% of NaCl by KCl slightly increased the bitter taste but did not change the acceptability or color attributes, whereas the replacement of 50% of NaCl by $MgCl_2$ slightly decreased the cooking yield. However, the tri-salt blend (KCl, $MgCl_2$ and NaCl at a 1:1:2 ratio) resulted in higher acceptability and consumer preference. Therefore, the authors concluded that the NaCl replacement strategy is a good alternative to help decrease sodium consumption and to increase the added value of noncommercial-size tilapia fillets.

Oliveira et al. (2015) reported that the MSM from Brazilian catfish contains palmitic, oleic, stearic, palmitoleic, myristic, EPA and DHA fatty acids. Regarding its amino acid profile, these authors found higher concentrations of glutamic and aspartic acids, arginine, lysine and leucine. Moreover, the flour manufactured from Brazilian catfish wastes exhibited a high nutrient value with appropriate physicochemical and microbiological characteristics. This flour may be considered a product with environmental, economic, scientific and technological importance.

The application of fish flour produced from MSM in convenience foods has also been investigated, e.g., Persian ice cream (Shaviklo, Thorkelsson, Sveinsdottir, & Rafipour, 2011), extruded corn snacks (Shaviklo, Dehkordi, & Zangeneh, 2014), bread (Adeleke & Odedeji, 2010) and instant soup (Monteiro, Társico, Viriato, et al., 2012; Monteiro et al., 2014).

Based on findings from the literature, the use of fish wastes for human consumption can be a viable alternative to produce innovative foods (semi-RTE and RTE products), thereby decreasing the environmental impact, adding value to fish wastes, increasing industry profits and providing easy-to-prepare and nutritious foods for consumers. Nevertheless, studies of chemical-quality parameters are needed due to the high perishability of fish products (Rodrigues et al., 2012).

Chemical parameters for the quality evaluation of convenience fish products

Hydrogen potential

The pH is an important index for determining the fish quality (Okeyo, Lokuruka, & Matofari, 2009). The pH changes in fish occur by bacterial and enzymatic activity that affects the concentration of free hydrogen and promotes the decomposition of molecules (Ogawa & Maia, 1999). Therefore, an increased pH value indicates metabolite accumulation such as ammonia and some organic bases from microbial action and endogenous enzymes (Rodrigues et al., 2012). In general, the pH of live fish muscle ranges from 6.0 to 7.1 (Pacheco-Aguilar, Lugo-Sanchez, & Robles-Burgueno, 2000). After death, the pH of muscle will decrease, conforming to the amount of glycogen present, which is converted anaerobically to lactic acid during the pre-rigor period. The rigor period is characterized by the total exhaustion of glycogen (Bermejo-Pozaa et al., 2015). However, fish contain only small amounts of carbohydrate compared to foods of plant origin. This fact can be disregarded in nutritional terms, but directly influences fish quality during shelf life (Jeya Sree, Parulekar, Wahidulla, & Kamat, 1994) because the amount of glycogen is correlated with the length and severity of rigor (Bermejo-Pozaa et al., 2015). A higher glycogen reserve in live fish may be responsible for the lowered pH (Raoofi, Ojagh, Shabanpour, & Eighani, 2015). Generally, fish presents relatively lower residual glycogen levels than mammals. This leads to pH values close to neutrality during the rigor period, accelerating the action of enzymes and bacteria. The post-rigor period is characterized by the degradation of actomyosin by proteolytic enzyme action such as cathepsins, starting the process of degradation (production of peptides and free amino acids). This favors the quick action of endogenous and exogenous microorganisms, resulting in volatile nitrogenous substances and thus an increase in pH (Pacheco, Dias, Baldini, Tanikawa, & Sgarbieri, 2005). These changes are progressive during storage and significantly affect fish quality and consumer acceptance (Monteiro, Mársico, Teixeira, et al., 2012; Rodrigues et al., 2013).

Nevertheless, the methods of catch, processing and storage directly influence the pH values from fish (Aursand et al., 2009; Carneiro et al., 2013; Esaiassen et al., 2004; Gökoğlu & Yerlikaya, 2015; Karl, Lehmann, Rehbein, & Schubring, 2010; Lopes et al., 2004; Lyu, Huang, Liu, Zhou, & Ding, 2015; Rebouças, Rodrigues, Castro, & Vieira, 2012). The catching method significantly affected the pH during ice storage of *Rutilus kutum* in which the pH from fish caught by beach seine was lower than the pH of fish caught by gillnet (Raoofi et al., 2015). Regarding processing, the asphyxia in ice water method for slaughtering fish resulted in a higher pH and consequently exhibited a delayed rigor mortis, whereas the fish slaughtered by the stunning fish heads and asphyxia in air methods entered more rapidly into rigor mortis (Lyu et al., 2015). In addition, the type of raw materials also influences the pH values. Mechanically separated fish presents high moisture content, resulting in a higher pH and greater perishability compared to fish fillets (Rebouças et al., 2012). On the other hand, preservation methods such as packaging, temperature and additives have a direct influence on the pH of fish products. The modified atmosphere packaging (MAP) containing carbon dioxide (CO_2) leads to carbonic acid (H_2CO_3) formation (dissolution of CO_2 in the water from food) and a decreased pH (Lopes et al., 2004). Moreover, frozen temperatures (less than −30°C) enable greater pH stability during storage due to unfavorable conditions for microbial growth and occurrence of enzymatic reactions. Nevertheless, monitoring of the frozen fish product is important because a proportion of the water still remains in the unfrozen state and is mainly available for enzymatic reactions (Gökoğlu & Yerlikaya, 2015). The addition of salt (NaCl) increases the electrostatic repulsion between proteins, resulting in water-holding capacity (WHC) and an increased pH. This phenomenon also occurs with polyphosphate addition (Aursand et al., 2009; Carneiro et al., 2013), which is commonly carried out during the processing of conventionally farmed fish prior to freezing (Karl et al., 2010).

In this context, the increase in pH values during the storage period may be attributed to the accumulation of alkaline compounds (e.g., ammonia and trimethylamine), mainly derived from microbial action, which suggests a loss in fish quality. However, it is an important attempt to a product that will be evaluated (origin of fish, processing to which the product was submitted and storage conditions). As there is a lack of official parameters for the pH of each fish product or product groups, the pH analysis is generally used as supporting information. In general, the pH value is interpreted in association with the other quality parameters or compared with similar studies described in the literature (Okeyo et al., 2009; Rodrigues et al., 2012).

Monteiro, Mársico, Lázaro, et al. (2015) evaluated pH values in restructured tilapia steak prepared with sub-optimal-sized fillets and different MTG levels (0.0–0.8%) during frozen storage for 45 days. This parameter was not affected by the storage period for each treatment. However, the pH values were greater for products containing MTG (6.04–6.17) than those products without MTG (5.99–6.06) regardless of the storage time. These authors attributed this result to the chemical reactions catalyzed by MTG involving water molecules in the food matrix. This enzyme promotes increasing swell and binds water or induces the formation of a gel sieve entrapping the water molecules, thereby improving the water-holding capacity of proteins (Ionescu, Aprodu, Daraba, & Porneala, 2008). Moreover, in the absence of amine substrates, transglutaminase is capable of catalyzing the deamination of glutamine residues, where water is used as a nucleophile and ammonia is liberated, resulting in alkalization of the medium (Macedo, Cavallieri, Cunha, & Sato, 2010).

Monteiro et al. (2014) found no statistically significant difference between the pH values of flour made from fish heads (6.12), carcasses (6.08) and heads and carcasses together (6.07) manufactured from tilapia wastes. Nevertheless, the pH values were lower in instant soup (5.71) than all flours produced, probably due to the addition of ingredients such as maltodextrin, onion and garlic powder, which tend to make the products more acidic. Palmeira, Mársico, et al. (2014) manufactured a meatball-type product prepared with rainbow trout (*Onchorynchus mykiss*) waste with added starch, transglutaminase (MTG), textured soy protein (TSP) and having part of the sodium chloride replaced with potassium chloride (75%/25%). These meatball-type products made from rainbow trout waste were evaluated during frozen storage (−25°C) and the authors found no difference in pH values between 1 day (6.00–6.10) and 60 days (6.08–6.19). Oliveira et al. (2015) found a pH value of 5.73 in MSM from Brazilian catfish.

Based on the variation in pH values, studies should be more specific to form a database and/or encourage the creation of an official limit for this parameter in fish products or for product groups.

Thiobarbituric acid-reactive substances

Oxidative rancidity is a critical factor that limits the fish shelf-life during storage (Dellarosa, Laghi, Martinsdóttir, Jónsdóttir, & Sveinsdóttir, 2015; Karlsdottir et al., 2014). The lipids represent a potent (9 kcal/g) non-carbohydrate source of energy and are widely distributed in both the intra- and extracellular spaces of food (Pichard & Kudsk, 2002). Moreover, when compared to other food products from vegetable and animal origins, the lipid content in fish is considered to be an important constituent in the human diet. This fact is mainly due to the high levels of PUFAs, low levels of linoleic acid (C18:2n6) and linolenic acid (C18:3n3) and high levels of the long-chain n-3 PUFAs

(C20:5n3) and DHA (C22:6n3). These latter two have the potential to prevent human coronary artery disease, improve retina and brain development, and have anti-inflammatory and anti-carcinogenic effects (Huang et al., 2012; Linseisen et al., 2011; Lund et al., 2011; Stevanato et al., 2010; Tacon & Metian, 2013).

However, the unsaturated fatty acids are more prone to the oxidation process due to their chemical instability, especially during handling and storage (Chaijan, 2008; Karlsdottir et al., 2014; Mapiye et al., 2012). In this case, muscle lipoxygenase (LOX) is the main endogenous enzyme related to fatty acid oxidation. It is important to note that endogenous LOXs have activity at low temperatures (at least −20°C) (Abreu, Losada, Maroto, & Cruz, 2010). In addition, the distributions of unsaturated fatty acids, processing and storage conditions are considered some of the factors that directly affect the rate of lipid oxidation in foods, which influences the end quality and shelf life of the product (Karlsdottir et al., 2014).

With regard to processing, the addition of salt promotes moisture loss and an increase in muscle dry matter as well as intense lipolysis and lipid oxidation, which leads to a significant decrease in the total lipid content during the salting period (Jin et al., 2010). The lipid oxidation from salting occurs due to the promotion of oxidant action by the NaCl and the great reduction in water activity (Jittrepotch, Rojsuntornkitti, & Kongbangkerd, 2015). Vidal, Goicoechea, Manzanos, and Guillén (2015) reported that salting methods decrease the oxidative stability of sea bass lipids.

Lipid oxidation is a chain reaction with the production of free radicals that consists of three steps: initiation, propagation and termination (Chaijan, 2008; Mapiye et al., 2012). The initiation stage requires low activation energies to produce free radicals, where the energy source can be heat, light or high-energy radiation or metal ions (e.g., copper ions) (Pegg & Shahidi, 2012). The final product of the initiation reaction is the fatty acid (alkyl) radical (R•) that reacts with oxygen to form peroxy radicals (ROO•). These compounds then react with unsaturated fatty acids to form hydroperoxides (ROOH), which characterizes the propagation step (Chaijan, 2008; Mapiye et al., 2012). The termination stage is determined by hydroperoxide decomposition, which results in secondary compounds such as aldehydes, alkanes and conjugated dienes, which lead to undesirable effects on the sensory properties of the foods (volatile aromatic compounds), and others resulting in deleterious health effects (e.g., malondialdehyde) (Chaijan, 2008; Zaki, El-Bassyouni, Kamal, El-Gammal, & Youness, 2014).

Hydroperoxide formation can occur by three different mechanisms: the free radical route (described above), the LOX route and the photo-oxidation route. In the LOX route, this enzyme and/or peroxidase enzymes catalyze oxidative reactions on the double bonds of unsaturated fatty acids. This process results in a chain reaction (propagation step), which produces a wide variety of degradation products. In the photo-oxidation route, photosensitive compounds (e.g., riboflavin, chlorophyll, myoglobin, erythrosine and heavy metal ions) are excited to a high-energy state by absorbing light. This energy reacts with the normal triplet ground state of oxygen atoms to form a metastable singlet state, which is very reactive (singlet oxygen attacks double bonds 1500 times faster than the triplet-state molecule) (Pegg & Shahidi, 2012).

Regardless of the mechanism, the oxidation of lipids has negative effects both on food properties and on human health such as rancid odor, off-flavor development, drip losses, discoloration, loss of nutrient value, decrease in shelf life and the accumulation of toxic compounds (Chaijan, 2008; Mapiye et al., 2012). Aldehydes have been associated with atherosclerosis, putative mutagens and cancer formation (Duthie, Campbell, Bestwick, Stephen, & Russell, 2013). Moreover, Zaki et al. (2014) reported that an increase in MDA leads to a lower paraoxonase (PON1) level. This fact might contribute to the greater risk of dyslipidemia, insulin resistance and high blood pressure. These are considered important components in the pathogenesis of the metabolic syndrome, mainly in obese adolescents.

Therefore, the monitoring of lipid oxidation is highly relevant. One of the most common methods of measuring lipid oxidation in foods is the quantification of MDA. In this assay, one molecule of MDA reacts with two molecules of 2-thiobarbituric acid (TBA) to form a stable pink chromophore. This test is called the TBARS test due to other secondary compounds that also react with TBA. However, the results are expressed as μmol of MDA per 1 kg of sample because it is considered the main secondary compound from decomposition of PUFAs (Karlsdottir et al., 2014).

Regardless of the importance of this parameter, there are no limits established by legislation, and MDA values are variable within the scientific community. Al-Kahtani et al. (1996) affirmed that tilapia and Spanish mackerel with values below 3.0 mg of MDA□kg^{-1} should be considered in good condition. On the other hand, Ozer and Sariçoban (2010) reported that values above 1.59 mg of MDA·kg^{-1} sample can cause harm to the health of consumers. Monteiro, Mársico, Teixeira, et al. (2012) found 1.27 mg of MDA·kg^{-1} in tilapia fillets in ice storage when the samples presented undesirable sensory characteristics.

There are few articles about the TBARS values for fish products manufactured with processing wastes. Palmeira, Mársico, et al. (2014) manufactured a meatball product with rainbow trout waste with added starch, transglutaminase (MTG), TSP and having part of the sodium chloride replaced with potassium chloride (75%/25%). These authors found no difference among TBARS values during frozen storage (−25°C) of these products (on day 1 = 0.12–0.25 mg of MDA·kg^{-1}; on day 60 = 0.10–0.23 mg of MDA·kg^{-1}), except in the formulation with starch added. In this product, the authors reported higher TBARS on the 60th day (0.60 mg of MDA·kg^{-1}) than on the 1st day of storage (0.27 mg of MDA·kg^{-1}) and attributed this result to the presence of substances (ketones, amino acids, oxidized proteins, carbohydrates, pyridines, esters, sugars) that can react with TBA in addition to MDA. Oliveira et al. (2015) found 0.035 mg of MDA□kg^{-1} of TBARS in fresh MSM from Brazilian catfish. Nielsen and Jacobsen (2013) reported no difference in the TBARS values of enriched fish pâtés made from cod without fish oil addition during storage for 12 weeks at room temperature. However, when this product had fish oil (5%) added, the TBARS values increased (day 0 = 0.50 mg of MDA·kg^{-1}; after 12 weeks = 1.01 mg of MDA·kg^{-1}). Stevanato et al. (2010) observed an increase in the MDA values in tilapia head flour throughout its storage time at room temperature. The values found were 0.74, 1.52, 2.39 and 3.87 mg of MDA·kg^{-1} of flour at 0, 30, 60 and 90 days, respectively. Based on the limit proposed by Al-Kahtani et al. (1996), the tilapia head flour exhibited acceptable values up to 60 days. This may possibly be due to the high level of unsaturated lipids in this product, which might have contributed to the increase in the MDA values.

In this context, more studies should be performed to encourage the creation of an official limit for fish products due to the relevance of the MDA value to both the shelf life and human health.

Biogenic amines

The biogenic amines (BAs) represent a special category of basic nitrogenous compounds with low molecular weights that are produced by the metabolism of plants, animals and microorganisms. These amines can be formed by four different mechanisms: transamination of aldehydes and ketones, hydrolysis of nitrogen compounds, thermal decomposition or decarboxylation of amino acids (the main route of BA formation) (Chong, Abu Bakar, Russly, Jamilah, & Mahyudin, 2011; Halász, Baráth, Simon-Sarkadi, & Holzapfel, 1994). The amino acid decarboxylation may occur by the action of endogenous decarboxylase enzymes (enzymes naturally present in food) or by exogenous decarboxylase enzymes (produced by microorganisms). These enzymes remove the α-carboxyl group from the structure of a specific amino acid resulting in the corresponding amine, e.g., histidine in histamine and lysine in cadaverine (Shalaby, 1996).

BAs can be found in a wide range of foods (fresh and processed foods) such as alcoholic beverages, beef, chocolate, cheeses, fish, pork, poultry and fermented products (Cunha et al., 2012; Hernández-Jover, Izquierdo-Pulido, Veciana-Nogués, & Vidal-Carou, 1996; Lázaro et al., 2014, 2015; Palmeira, Mársico, et al., 2014; Rodrigues et al., 2013; Shalaby, 1996). The human intestine contains amine oxidases that rapidly detoxify the amines. Therefore, the low levels of BAs in aquatic products do not present a serious risk to human health. However, the ingestion of aquatic foods containing high levels of BAs may result in severe toxicological symptoms (Mohamed, Abd El-Hameed, Nezam El-Din, & El-Din, 2010; Muñoz-Atienza et al., 2011). In general, the toxin effects of BAs are related to headache, rash, redness, itching, dizziness, burning, urticaria, edema, local inflammation, nausea, vomiting, diarrhea, abdominal pain, indigestion, hypotension, cardiac palpitations and even death (Juneja & Sofos, 2010; Muñoz-Atienza et al., 2011; Shalaby, 1996). Moreover, BAs are considered potentially carcinogenic due to their reaction with nitrates resulting in nitrosamines, which are carcinogenic compounds (Juneja & Sofos, 2010).

The BA levels may strongly be influenced by the freshness of raw materials, good manufacturing practices and storage conditions, especially temperature and time. In this context, BAs may be considered as markers of microbial contamination and spoilage of fish and aquatic products (Cunha et al., 2013; Hernández-Jover et al., 1996). In addition, the BA accumulation in foods depends on the availability of the precursor amino acids, presence of microorganisms with decarboxylase activity on amino acids (from natural composition or introduced before, during or after food processing) and extrinsic characteristics such as handling and storage temperature. Moreover, BAs are basic nitrogenous compounds which are of the utmost importance to ensure that fish and fish products can be consumed without health risk (Rodtong, Nawong, & Yongsawatdigul, 2005).

Several analytical methods can be used to detect, semi-quantify and quantify the BAs in fish and fish products such as Thin-Layer Chromatography (TLC), Gas Chromatography (GC), Capillary Electrophoresis (CE), High-Performance Liquid Chromatography (HPLC), HPLC-mass spectrometry (HPLC/MS) and Ultra-performance liquid chromatography-electrospray ionization tandem mass spectrometry (UPLC-MS) (Gosetti, Mazzucco, Gennaro, & Marengo, 2013; Li et al., 2013; Monteiro, Mársico, & Vital, 2010; Önal, 2007; Pombo et al., 2009; Schutz, Chang, & Bjedanes, 1976).

Among the several chromatography methods, HPLC is most often used for the analysis of BAs due to its reliability and high sensitivity for the detection and quantification of various BAs (European Food Safety Authority [EFSA], 2011). Currently, studies have been performed to develop and validate new methods for the detection and quantification of BAs in several food matrices by HPLC (Baptista et al., 2014; Cunha et al., 2012; Lázaro et al., 2013), including fish (Palmeira, Mársico, et al., 2014; Rodrigues et al., 2013). However, the TLC must be considered for use in routine laboratories due to a number of advantages such as its practicality, faster results and effectiveness, low cost, and simultaneous determination of substances (Fuchs, Süb, Nimptsch, & Schiller, 2009). Moreover, due to the risk from BAs, mainly histamine, rapid tests are needed at the raw material receiving stage and also the subsequent steps of processing. Köse et al. (2011) have been evaluating four commercial test kits against an EU-accepted HPLC method for detecting histamine in several traditional fish products. These authors concluded that each test kit exhibited a different performance depending on the product type; therefore, new commercial test kits should be evaluated against an approved analytical method to help monitor histamine formation in fresh fish and fisheries products.

Regarding regulations and legal requirements, maximum limits of BAs in aquatic products, mainly histamine and tyramine, have been suggested and established by many countries and international organizations. This is due to the toxicological effects of BAs on human health (Kim et al., 2011). The Food and Drug Administration (FDA) recommends 50 mg·kg^{-1} as the limit for histamine in fish (Food and Drug Administration [FDA], 1996). Additionally, the FDA establishes 100 mg·kg^{-1} of tyramine and 1000 mg·kg^{-1} of total BAs as tolerance levels in fish (Food and Drug Administration [FDA], 2011). The Brazilian legislation recommends 10 mg·100 g^{-1} as the maximum level of histamine in muscle of fish species from Scombridae, Scombresocidae, Clupeidae and Coryphaenidae (Ministry of Agriculture, Livestock and Supply, 1997). Although there is no limit to other BAs, the Brazilian legislation establishes analytical methodologies for the quantification of histamine, cadaverine, putrescine, spermidine and spermine (Ministry of Agriculture, Livestock and Supply, 2011). In the European Union (EU), the maximum levels of histamine and total BAs in fish and fish products from Scombridae should be less than 100 mg·kg^{-1} and 300 mg·kg^{-1}, respectively (Conformite Europeene [CE], 1991).

The BAs, produced by microbiological spoilage, mainly mesophilic and psychrophilic bacteria, are considered quality indicators of fish or fish products (Brink, Damink, Joosten, & Veld, 1990; Lázaro & Conte-Junior, 2013; Moini et al., 2012; Palmeira, Mársico, et al., 2014; Rodrigues et al., 2013), including products thermally processed because these substances are heat-stable compounds (cooking or prolonged exposure to heat does not eliminate the toxin) (Gonzaga, Lescano, Huamán, Salmn-Mulanovic, & Blazes, 2009). Moreover, the fish and fish products differ in relation to their amino acid composition, ingredients in the formulation, processing and storage. In this context, many studies have been conducted to verify the BA concentrations in several fish and/or fishery products (Hu, Huang, Li, & Yang, 2012; Jiang, Xu, Li, Dong, & Wang, 2014; Koral et al., 2013; Palmeira, Mársico, et al., 2014; Park et al., 2010; Rodrigues et al., 2013; Zhai et al., 2012).

Rodrigues et al. (2013) reported that putrescine and cadaverine may be considered suitable indicators of the degradation process of rainbow trout meat. Palmeira, Mársico, et al. (2014) evaluated BAs in a meatball-type product prepared with rainbow trout waste. These authors affirmed that BAs may be a promising quality parameter, mainly in those products with soy protein added, which influenced the presence of some BAs (putrescine, cadaverine, agmatine, spermine and spermidine). This fact may be attributed to the high levels of arginine, lysine, proline and tyrosine in soybeans, precursor amino acids of the above-mentioned BAs (Hui, 2006). Moreover, Palmeira, Mársico, et al. (2014) reported that some ingredients such as salt and their replacers may influence the BA formation. Therefore, BAs should be carefully evaluated, taking into account the product formulation. The salt (NaCl) decreases the bacterial growth, which affects the activity of endogenous and exogenous proteolytic enzymes, thereby inhibiting the formation of free amino acids and consequently decreasing the BA formation (Virgili, Saccani, Gabba, Tanzi, & Soresi Bordini, 2007).

Hu et al. (2012) found more than 100 mg□kg^{-1} of total BAs in blue scad, octopus, golden thread, yellow porgy and belt fish. Regarding histamine and tyramine, these authors reported that the majority of samples exhibited less than 50 and 100 mg·kg^{-1}, respectively, except blue scad (577 mg·kg^{-1} of histamine). In addition, these authors concluded that putrescine, cadaverine, histamine and tyramine are more suitable as indicators of freshness of the species evaluated. These amines increased in blue scad, golden thread, belt fish and octopus during storage at 4 and 25°C, while freezing (−20°C) effectively prevented the BA formation in aquatic products.

Zhai et al. (2012) evaluated the BA concentration in various fish species and fish products consumed in southern China. Most of the samples presented lower levels of BA than the maximum accepted values. On the other hand, 12.24% of fermented fish products and packaged fish products exhibited high levels of total BAs (466.35 mg·kg^{-1} in lightly cured horse mackerel and 116.28 mg·kg^{-1} in packaged eel) and 2-phenylethylamine (2-PHE) (in excess of 30 mg·kg^{-1}). Moreover, lightly cured horse mackerel samples presented high levels of cadaverine (244.41 mg□kg^{-1}), 2-PHE (57.61 mg·kg^{-1}) and tyramine (62.85 mg□kg^{-1}), indicating that these products require careful monitoring to ensure their safety for human consumption.

Park et al. (2010) reported that the histamine and tyramine levels were less than the EU acceptable level in fish (mackerel, herring, spotted mackerel, salmon, gizzard-shad, anchovy, mackerel pike, tuna, cuttlefish, redlip croaker, flatfish, Atlantic cutlassfish and Alaska pollack) and fish products (salted mackerel, canned mackerel, canned mackerel pike, canned tuna and canned salmon). On the other hand, Pombo et al. (2009) reported that most fish cured by salting and fermentation presented histamine levels above the limits of the FDA, EU and Brazilian regulations.

Koral et al. (2013) observed that the BA levels vary depending on the product type and salting methods. Most of the samples of various commercial salted fish products had histamine levels below the limits of the FDA and EU regulations. Nevertheless, approximately 9.1% of brined, 8.3% of dry salted and 15% of lakerda samples exceeded the permitted levels, where the maximum values found were 421.7, 229.1 and 293.2 mg·kg^{-1}, respectively.

Jiang et al. (2014) evaluated seven BAs in 35 Yulu samples, which is a traditional condiment (fermented fish sauce) widely commercialized in China. The authors concluded that the BA content should be monitored in these products; approximately 57% of Chinese fermented fish sauce exhibited higher histamine levels than the limit established by the FDA for seafood products (50 mg·kg^{-1}). Moreover, 60% of the samples presented more than 100 mg·kg^{-1} tyramine, whereas approximately 29% had more than 1000 mg·kg^{-1} total BAs.

In this context, the BAs in aquatic products should be more closely monitored and efforts should be made to prevent the formation of BAs due to their toxicological effects and serious health risks.

Conclusions

Based on findings from the literature, less-expensive aquafeed alternatives must be found to allow the continued growth of aquaculture production. Moreover, new fish products can be developed with mechanically separated fish meat from waste processing, which represents a viable alternative to manufacture semi-RTE and RTE products for human consumption, taking into account social, economic and environmental benefits. Nevertheless, the current consumers request nontraditional products without risk to human health. Therefore, the development of innovative and healthy products has been a challenge to the industrial sector, mainly due to lack of knowledge and technology transfer to the industry. In addition, the evaluation and establishment of the chemical parameters for each fish product or product groups are fundamental to aid the fishery industries and government agencies to ensure product quality and consumer health.

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