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QUALITY ANALYSIS OF DRIED COD (*Gadus morhua*) HEADS ALONG THE VALUE CHAIN FROM ICELAND TO NIGERIA

Mutiat Motolani Salaudeen
Nigerian Institute for Oceanography and Marine Research
3, Wilmot point off Ahmadu Bello way, Victoria Island, Lagos, Nigeria. PMB 12729.
salaudeen06@yahoo.com

Supervisors: Arnljotur Bjarki Bergsson (arnljoturb@matis.is)
Sigurjon Arason (sigurjon@matis.is)
Gunnar Thordarson (gunnar.thordarson@matis.is)
Matis Ltd. – Icelandic Food and Biotechnology Research and Development

ABSTRACT

The effect of bleeding and storage conditions on the quality of dried cod heads were determined by changes in physicochemical and nutritional properties. Dried cod heads from cods that were bled alive (BA) and bled dead (BD) were produced using the Icelandic method of geothermal energy in a drying chamber. The dried cod heads were packed in jute bags and stored in simulated storage conditions similar to that of Nigeria, 65% relative humidity at 30ºC during the day and 85% relative humidity at 20ºC at night for six weeks, storage conditions were altered at 24hours intervals. Samples of dried cod heads were taken at predefined intervals for quality analyses. The bleeding method has significant (P> 0.05) effect on the colour has the bled alive dried cod heads were whiter than the bled dead cod heads. Bleeding has no significant effect on other parameters tested but they fluctuated due to fluctuation in the storage conditions. The rehydration properties of the dried cod heads decreased as the storage period increased. The water activity, pH, moisture and protein of the dried cod heads during storage were 0.4-0.6, 6.6-7.1, 12.0%-16.5% and 54.1%-60.5% respectively. Dried cod head is a good source of protein, mineral and marine lipids rich in polyunsaturated fatty acids especially omega-3 fatty acids. Drying has no significant effect on the fatty acids profile and composition of the dried cod heads. The saturated fatty acids, monounsaturated fatty acids and polyunsaturated fatty acids of the dried cod heads were 28.3%, 27.7% and 37.8% of the total fatty acids respectively. The storage conditions have significant effect on the freshness and spoilage indices tested. The free fatty acids (FFA), peroxide value (PV) and total volatile basic nitrogen (TVB-N) were (30.1-36.8) g FFA/100g of lipids, (13.3-74.7) meq. /kg and 74.7-185.7mgN/100g respectively during the storage.

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1 INTRODUCTION

The global market for seafood products continue to increase year by year. Food safety considerations are crucial in this sector, and high standards of quality are demanded as shipment of products increase with distances the products are transported around the world. Currently, a global focus on connections between health and diet induces growth within the industry and opens number of commercial opportunities at various fronts. Beneficial effects of marine functional compounds such as omega-3 polyunsaturated fatty acids meets increasing interest (Alasalvar *et al*., 2011).

Fisheries are an important part of food security. Food security is "a state of affairs where all people at all times have access to safe and nutritious food to maintain a healthy and active life" (UNEP, 2002). Fish is a perishable food commodity, the initial quality and the storage conditions under which it is kept affects its shelf life. The shelf life of fish species is affected by the type of the fishing method and subsequent handling practices. Improper bleeding, gutting and insufficient cleaning will also affects the quality of fish during processing and storage (Eunice, 2010).

“Value chain” is used to describe a range of activities which add value to a product at each stage along the chain, from sourcing, to production, delivery, and final consumption (Kaplinsky and Morris, 2001). In its simple form, a value chain can be narrowed to three main activities, with so-called “vertical linkages: Production-Marketing-Consumption’’ (UNDP, 2012).

Processing of a fish species involves a storage period for final product before marketing and consumption. As fish is composed of perishable nutrients, storage period should be minimised with adequate storage conditions provided in order to avoid deteriorative changes to occur through oxidative damage, microbial, insect or rodent infestation. Shelf life of fish is governed by the most important environmental factors; ambient temperature and humidity. Factors that determine the rate at which chemical changes take place (Daramola *et al.,* 2007).

Food crisis is the challenge of the 21st century. Estimation on future global population reach up to 9-10 billion; resources are scarce and up to a third of food is wasted or gets spoilt within a few days due to unavailability of effective storage methods.

Post-harvest losses in fish translate reduction in amounts of nutrients available to the consumer either by direct physical loss or nutritional loss. These factors influence consumer acceptability, commercial value and income of fish producers (Bostock *et al*., 1987).

Drying of fish has ancient roots within the field of processing technologies. It has been used for centuries to preserve, and is widely used for this purpose in the developing countries where up to 70% of the catch is smoked for preservation (Ward, 2003). Drying enhances flavour and increase utilisation of the fish. Nonetheless, deterioration and spoilage still occur in dried fish during storage due to conditions of storage and perhaps lack of control of these conditions (Daramola *et al*., 2007).

Dried cod heads have been used in Nigerian’s favourite soups for centuries. Little information is available about its functionality, processing and storage along the value chain, it is therefore pertinent to get data on dried cod heads quality along the value chain from Iceland to Nigeria.

2 LITERATURE REVIEW

2.1 Fish processing and handling

Fish processing refers to processes associated with transforming fish from raw material into product that is delivered to the consumer. A general concern of fish processing is to prevent fish from deteriorating to avoid it from harming the consumer. Fish handling is a subdivision of fish processing which is the preliminary processing of raw fish, and the production of fish products (FAO, 2005).

Fish is a highly perishable food, if long shelf life is demanded and that it retains good quality and nutritional value, good handling and preservation is necessary (FAO, 2005).

The spoilage rate of fish depends on handling during processing, species, mode of storage and temperature during transportation. Chemical breakdown of nutrients contribute to spoilage of fish (Clucas, 1982). Proper handling of fish is necessary as soon as it is harvested from its aquatic environment, this determines the nutritional properties and the quality of the fish product.

Improper bleeding or not bleeding fish can have negative impact on the overall quality of the end product. It affects shelf life, taste and appearance as previously mentioned results of chemical reactions (Clucas, 1982) that occur as a result of the residual blood in the tissues of the fish (Huss, 1995).

Ahimbisibwe *et al.,* (2010) also reported that hypoxanthine, volatile basic nitrogen (VBN) and trimythylamine (TMA) were higher in the un-bled muscle tissues of amberjack (*Seriola dumerili*) and red sea bream (*Pagrus major*) after one week of storage.

2.2 Production of dried cod heads

Drying means evaporation of water from a substance, usually by heating. The two things that are of primary importance during heating, i.e. heat transfer that causing evaporation of water and mass transfer of water evaporated through the substance and eventually removal of moisture from the substance itself. The purpose of drying is to extend the storage time of the product. Deterioration of food is caused either by microorganisms or chemical processes. In drying, these processes are retarded and halted depending on which extent the drying is done, with the exception, of oxidation. The species used for drying in Iceland are mostly cod, tusk and ling. When the market price of capelin, saithe, and haddock is favourable, these species are also purchased for drying. Generally, fish must be lean to be fit for drying and fat content better not exceed 5%. (Arason, 2003).

Traditionally in Iceland, cod heads have been dried by hanging on outdoor racks as shown in Figure 1, recently indoor drying is becoming more common among drying companies using geothermal energy. This has the benefit of reduction in drying time, production of dried fish all year, consistency of the dried product and prevention of flies and insects from contaminating the product (Arason *et al.*, 1982). Primary drying and secondary drying as in Figure 2 are the two stages involved in indoor drying of cod heads. Arason (1992) found out that the total drying time for splitted cod heads is about 120 hours and the yield is 21.2% while the total drying time for unthreaded cod heads is about 160 hours.

Fresh cod heads contain 82% water; after primary drying the water is down to 55% and, after secondary drying, it is 15%. Arason and others have discovered that the optimal parameters for drying cod heads are having air temperature at 25ºC, air speed at about 3 m/s and air humidity at about 45% (Arason, 2003).

Figure 1: Cod heads dried outdoor on racks.

Figure 2: Fish heads on racks in the primary drying unit on the left and secondary air-drying unit with geothermal pipes on the right.

2.3 Dried fish as healthy food

Specialist at Matis have investigated dried fish and its possibility to be categorized as health food as Jonsson *et al*. (2007) stated that diet greatly affects human health and this has influenced and created for a vast market of functional foods. Research has shown that fish is good for the health. Long chains of amino acids form different proteins, they have good effects on the health. Protein content in fish is 16-20% of the total weight. During the drying of fish,

about 70%-80% of moisture in the fish is evaporated living nutrients in its most natural form. For instance, the nutritional value of a kilogram of dried fish is the same as approximately five kilograms of fresh fish.

Fish is a complex material, hence has complex effect on the consumers. It has been reported that fish has improving effect on health (Gutt *et al*., 2007) since most consumers care about their health, this in turn stimulates fish consumption. The fat in fish is mostly liquid because it contains a relatively low percentage of saturated fatty acids. Fish is very rich in omega-3 polyunsaturated fatty acids such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) which have been shown to protect against several diseases, including heart disease (Lee and Hiramatsu, 2011).

Martin *et al*., (2006) reported that the ratio of omega-6 (n-6) to omega-3 (n-3) fatty acids of the human diet before the industrialization was around 1:1 to 2:1 due to the abundant consumption of vegetables and seafood high in n-3 fatty acids. Industrialization resulted in gradual increase in this ratio, mainly due to the consumption of refined oils from oleaginous seeds with a high content of linoleic acid (LA) and decrease in ingestion of fruit and vegetables. This led to consumption of diets with inadequate amounts of n-3 fatty acids. Recently, the average ingestion of n-6/n-3 fatty acids in several countries has been around 10:1 to 20:1, with reports of values up to 50:1. Some clinical studies have stressed the need to reduce the n-6/n-3 ratio in the last decade. Martin *et al*., (2006) also reported the benefits of a low n-6/n-3 ratio in the reduction of 70% in the mortality ratio in cardiovascular patients, the reduction of inflammation caused by rheumatoid arthritis, and the reduction of the symptoms of asthma.

2.4 Dried fish trade and consumption in Nigeria

Nigeria has a consuming potential for 2.66 million metric tons (MMT) of fish per annum with population of about 140 million, based on the 19 kg/head/annum recommended by food and agriculture organization (FAO). The total domestic fish production was put at 0.62 MMT and total fish importation at 0.74 MMT leaving a deficit of 1.34 MMT (FDF, 2008). Nigeria is staying a net importer for long due to insufficient domestic catches and aquaculture production. For this reason, dried fish products have become very popular and sought in the local fish markets of Nigeria.

Importation of dried fish into Nigeria markets in order to bridge the gap between fish supply and fish demand is mainly from Norway and Iceland. Dried fish products are also imported from Faroe Island and Greenland. In the 70's, Nigeria was importing about 30,000 tons per annum from Norway and the volume has dropped greatly. Norway has been the major exporter of whole dried fish (stockfish) to Nigeria. Importation of dried fish into Nigeria makets from Iceland has been placed at about eighteen thousand metric tons (18MT) annually (Statistics, Nigeria Foreign Trade Summary, 2010). In 2011, the value of export of stockfish and dried fish heads excluding other dried fish products are USD 46.03 million and USD 48.81 million from Norway and Iceland respectively. Today, in terms of volume, Iceland export almost twice of the volume of Norway, the value of export are almost the same because Iceland exports dried fish heads in bigger volume and Norway export more whole dried fish (stockfish) which is higher in value (Szabolcs and Dancs, 2012).

Currently about 5% of Iceland's aggregate seafood exports goes to Nigeria. The value of exports mainly from dried cod, haddock and saithe to Nigeria has, in fact, increased in the

last years from about 3.1 billion ISK (EUR 35 million/ USD 49 million) to the current level of 12.4 billion ISK (EUR 77 million / USD 107 million), making Nigeria one of the 10 largest buyers of Icelandic seafood products (Iceland, 2013).

Dried fish especially dried cod (whole fish, cutlets, heads, backbones) is extremely popular and is widely consumed by Nigerians. It is used in combination with other ingredients as condiment to flavour most of their soups. It is a stable part of Nigerian cooking and present in many recipes. Its consumption varies between regions, ethnic groups and social classes, the rich people buy the whole dried fish (stockfish), the middle class buy cuts and cutlets and the low class buy the dried heads and backbones.

2.5 Value addition and Value chain analysis

In general value addition means "any additional activity that in one way or the other change the nature of a product thus adding to its value at the time of sale''. Value addition is an expanding sector in the food processing industry, especially in export markets. Value addition to fish and fishery products is based on different market requirements.

Fish is processed industrially into a wide array of products to increase their economic value, allow the fishing industry and exporting countries to reap the full benefits of their aquatic resources. Value processes generate further employment and hard currency earnings. This is more important nowadays because of societal changes that have led to the development of outdoor catering, convenience products and food services requiring fish products ready to eat or requiring little preparation before serving. Despite the availability of technology, it is important to consider the economic feasibility of value addition, including distribution, marketing, quality assurance and trade barriers, before embarking on a value addition fish process (FAO, 2005).

A typical value chain diagram of dried cod heads and other dried fish products from Iceland/North Atlantic to Nigeria is represented in Figure 3. The value chain of dried fish products look simple on the part of Iceland/North Atlantic but complex on the part of Nigeria.

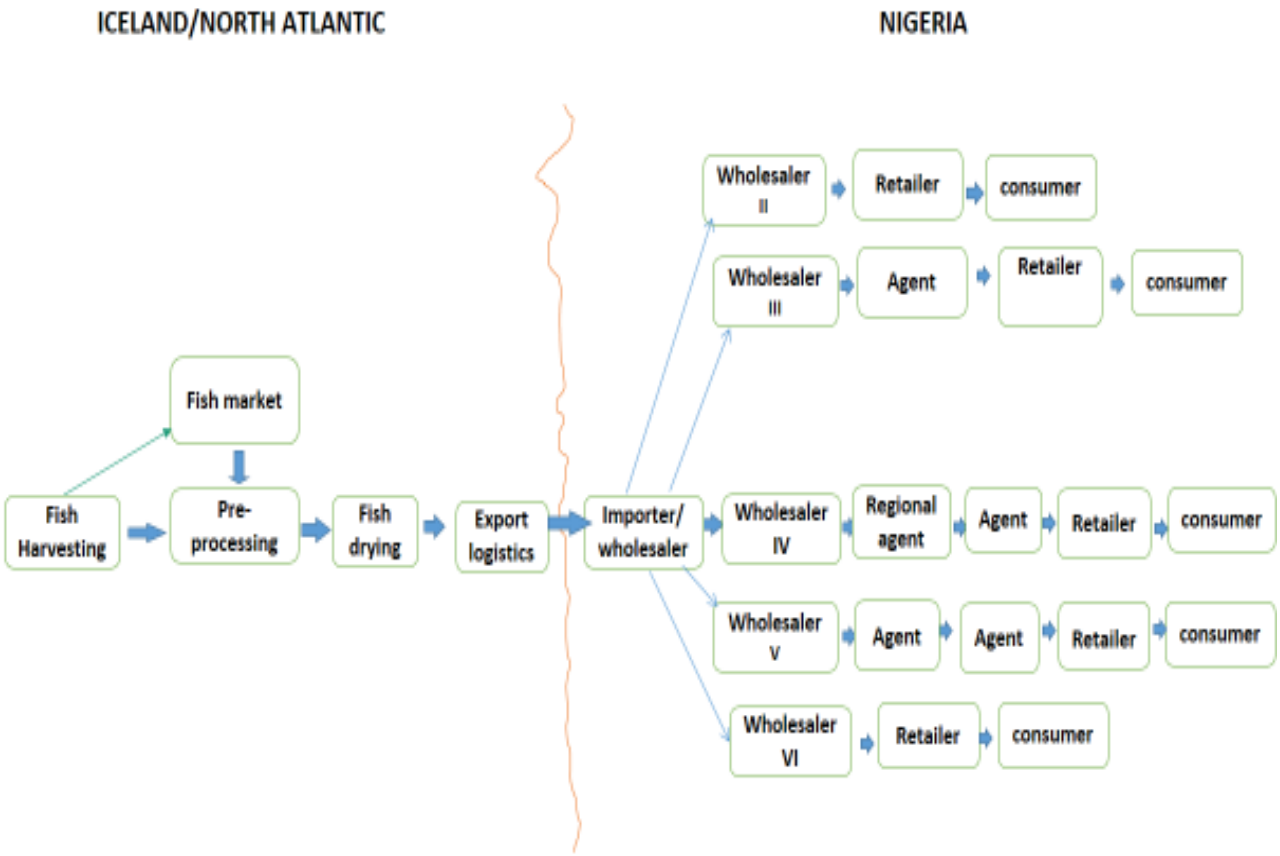

Figure 3: Value chain of dried cod heads from Iceland/North Atlantic to Nigeria.

2.6 Quality changes, spoilage of dried fish and quality indices

Freshness is an important factor in determining quality of all kinds of seafood products. It has been stated that no single method is reliable for the assessment of freshness and quality of seafood products. A range of methods have been proposed which can be objective, subjective and statistical. Each method has its own merits and demerits. Total volatile basic nitrogen (TVB-N), peroxide value (PV), free fatty acids (FFA) are some of the objective chemical methods for assessing fish product freshness. Electronic nose, nuclear magnetic resonance (NMR), water activity (Aw) and acidity (pH) are some of the physicochemical methods for assessing freshness and quality of seafood products (Alasalvar *et al*., 2011).

It is important to note that the raw material for drying must be fresh fish. Good product does not come from a bad raw material, and drying never makes bad fish good (Arason, 2003).

Percentage of water absorbed by dried fish at a certain temperature and time is called water rehydration (reconstitution). It is one of the most important physical parameters to assess the quality of the dried products (Shamima *et al.*, 2011).

3 MATERIALS AND METHODS

3.1 Cod heads drying, packaging and storage

Fresh cod heads from two bleeding methods were provided. The first bleeding method was fresh cods bled while still alive (bled alive) and the second bleeding method was fresh cods left to die before bleeding (bled dead).

Fifty-six pieces each of fresh cod heads from bled alive and bled dead cods were provided by Jakob Valgeir a fish processing company in Bolungarvik. Six pieces from each bleeding methods were taken for analysis before drying. Pre-process operations were carried out on the remaining cod heads and dried using Icelandic geothermal energy in the drying chamber of Klofningur a fish drying company at Sudureyri of Sugandafjordur in the municipality of Isafjardarbaer.

Dried cod heads from each bleeding methods were divided into two groups, group A and B. They were packed in jute bags and stored in a simulated storage conditions similar to that in Nigeria (65% relative humidity at 30^{o}C during the day (setting 1) and 85% relative humidity at 20^{o}C at night (setting 2) in a storage cabinet at Matis. Settings were adjusted at 24 hours intervals.

3.2 Sampling and homogenization

Three pieces of dried cod heads from each groups were pulled weekly and homogenised together. Several methods of homogenization were tried because of the biophysical nature of the heads; muscle, collagen, skin and bones. Combination of the methods were used to get an appreciable homogenous sample.

3.3 Physicochemical parameters

Physicochemical parameters were carried out on groups A and B of each of the two bleeding methods weekly and each analysis was done in duplicate.

3.3.1 Colour detection

The colour of the fresh samples was taken on three heads from each bleeding methods at the same point on the heads. Samples of the dried heads were also drawn weekly throughout storage period for the colour measurement using Minolta CR-300 Chroma meter (Minolta camera Co., Ltd; Osaka, Japan) in Lab* system. The instrument records the L* value, lightness on the scale of 0 to 100 from black to white (black 0, and light, 100); a* value, (+) red or (-) green b* value, (+) yellow or (-) blue. Whiteness was calculated based on L* values only. The a* and b* values were not used in the final analysis of the results, as the main emphasis of the analysis was to measure whiteness.

3.3.2 Water activity

An Aqua Lab water activity meter was used to measured water activity (aw) of the fresh and dried samples. About 2 g of samples was put into the instrument and water activity was measured automatically after starting the program.

3.3.3 Acidity (pH)

The pH of fresh and dried samples was measured by the method of Bragadottir *et al.,* (2007). 5 g of fresh samples was measured directly while 5 g of dried samples was mixed with 20 ml of deionised water, stirred for 5 mins prior to measurement with combined electrode SE 104- Mettler Toledo, Knick Berlin Germany connected to a portable pH meter Portamess 913, Knick, Berlin, Germany.

3.3.4 Rehydration

Two pieces each of the dried cod heads from the groups were pulled, cut into halves, weighed using Sartorius scale and rehydrate with tap water at ambient temperature of about 21ºC for 24 hours. The samples were taken out of the rehydrating medium (water), the surface water was removed with plotting paper and reweighed every one hour for six hours and lastly at 24 hours.

3.3.5 Moisture content

The moisture content of the samples was determined by electronic moisture analyser (Sartorius Moisture Analyser) Model MA35 that uses thermo gravimetric method.

3.3.6 Mineral content

The mineral content of the samples was determined using muffle furnace at 550ºC as described by (ISO, 2002).

3.3.7 Sodium chloride

The salt content of the fresh and dried cod heads was determined by weighing 5g of sample into the extraction bottle, 200 ml of deionised water was added, mixed using the shaker for 50 minutes. 20 ml of nitric acid was then added to 20 ml of the supernatant and titrated with silver nitrate (AOAC, 2000).

3.3.8 Protein

Protein was determined by Kjeldahl method. The organic matter was digested by sulphuric acid in the presence of a catalyst. The reaction product was rendered alkaline, then the liberated ammonia was distilled and titrated with hydrochloric acids (ISO, 2005).

3.3.9 Lipid

Lipid content was determined by Bligh and Dyer, 1959. The samples were weighed in 250ml FEP plastic bottles intended for organic solvents and water was added as necessary. 25ml of chloroform and 50 ml of methanol were added and homogenized for 2 minutes in ice bath with Ultra-turax T25 homogenizer. Additional 25 ml of chloroform was added and homogenized for 1 min followed by 25 ml 0.88% potassium chloride solution and homogenised for 1 min. Centrifuged for 20 minutes at 2500 rpm at 0-5^{o}C. The lower chloroform phase containing the lipids was then filtered via disodium sulphate on a glass filter under suction.

The suction flask was rinsed well and made up to mark in a 50 ml volumetric flask. The lipids was then calculated by evaporating the chloroform under nitrogen gas.

3.3.10 Fatty acids profile

Fat extraction from the samples was by (Bligh and Dyer, 1959). Methylation was carried out to convert the fats to their methyl esters based on (AOCS, 2009) with minor adjustment. Fatty acid methyl esters (FAME) were separated on a Varian 3900 GC equipped with a fused silica capillary column (HP-88, 100 m x 0.25 mm x 0.20µm film), split injector and flame ionisation detector as described by (AOAC, 1997).

3.3.11 Free fatty acids (FFA)

Method from Lowry and Tinsley (1976) with modification made by Bernardez *et al.*, (2005) was used to determine the free fatty acids of the fats extracted from samples by Bligh and Dyer (1959).

3.3.12 Peroxide value (PV)

Determination of the peroxide values, about 5 g of the fresh samples was weighed while 1 g of the dried samples was weighed into 50 ml centrifuge tubes and homogenised with 10 ml of ice cold solvent methanol: chloroform (1:1), chloroform was ethanol stabilised. 5 ml of sodium chloride was added, mixed using homogenizer and centrifuge at 5100 rpm for 5mins at 4^{o}C. 500 µl of the bottom layer was collected into Eppendorf tubes, 500 µl of solvent was added followed by 5 µl of ammonium thiocyanate and ferrous chloride solution (1:1). The mixture was left for 10 minutes at room temperature, 100 µl was pipetted into the microplate and read at 500 nm using Sunrise microplate reader, Tecan Austria GmbH, A-5082 Grödig, Austria. (Shantha and Decker, 1994).

3.3.13 Total volatile bases (TVB-N)

Total volatile basic nitrogen of the samples was determined by steam distillation method. 5 g of sample plus 3 g of magnesium oxide were weighed into distillation flask followed by addition of 100 ml distilled water. Distillation was done for 10 minutes, 50 ml of 1% boric acid in 500 ml receiver flask was used to collect the ammonia gas. The solution in the receiver flask was titrated using sulphuric acid (Malle and Poumeyrol, 1989)**.**

3.4 Shipment of cargo to Nigeria

In order to map the condition of dried fish head cargo in transport and assess the possible effect of transport on quality shipment of dried cod heads was monitored from Iceland to Nigeria with iButton loggers.

3.5 Statistical analysis

Microsoft Excel 2013 was used to calculate means, standard deviations and generate graphs. It was also used to test for significance using t-test, correlation and regression between the two bleeding methods and within each bleeding method over the storage periods. The statistical evaluation level was set at α=0.05.

4 RESULTS

The effect of two bleeding methods and storage conditions on the quality of fresh and stored dried cod heads were examined by changes in physicochemical and nutritional properties during storage.

4.1 Storage

The relative humidity (RH) and temperature (T) of the storage cabinet were alternated every 24 hours, The RH fluctuated between 66.2% and 85.2%, while T fluctuated between 20.3ºC and 31.3 ºC during the storage. The RH and T changes for each sampling days (Table 1).

Table 1: Changes in temperature (T) and relative humidity (RH) of the sampling days.

Storage Period (weeks)	T (°C)	RH (%)
0	20.3	83.3
1	30.8	67.0
2	20.5	82.9
3	30.0	68.8
4	20.5	83.8
5	31.3	66.2
6	21.2	85.2

4.2 Sample homogenization

A combination of methods were used to homogenise the fresh and dried cod heads, they were cut into pieces of approximately (2*2) cm for muscles and bones, less than (0.5*0.5) cm for skin with knives and scissors, after which they were pounded with laboratory mortar and pestle followed by grinding with warring laboratory blender, model 34BL99 at high speed for 10mins and finally with Bosch coffee blender for 2mins. 100% homogenous sample was not achieved by all the methods as shown in Figure 4.

Figure 4: Homogenized dried cod heads.

4.3 Physicochemical parameters

The average of the replicates (groups A and B) and duplicates values for all the analysis are presented for each of the two bleeding methods

4.3.1 Colour detection

The whiteness of fresh and dried cod heads was calculated by measuring lightness (ranging from black to white). The results show that the colour of fresh cod heads from bled alive cods (F-BA) was not significantly whiter than in the fresh cod heads bled dead (F-BD) as shown in Figure 6. The result also show fluctuations in the colour of dried cod heads bled alive and dried cod heads bled dead during storage, there was significant difference in the whiteness of just dried (week 0) cod heads and from 4th week of the storage period, the dried cod heads bled alive were significantly whiter than bled dead dried cod heads throughout the rest of the storage period as shown in Figures 5 and 6.

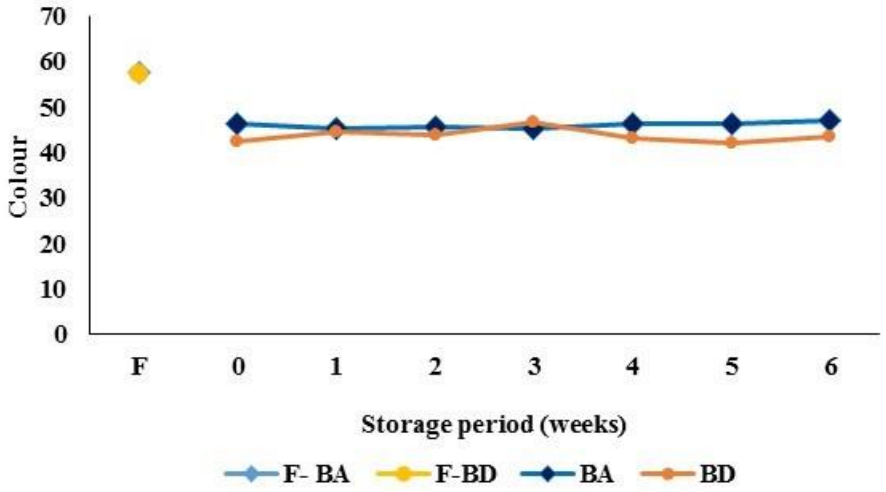

Figure 5: Changes in colour of dried cod heads during storage. F-BA = Fresh cod heads bled alive, F-BD = Fresh cod heads bled dead, BA = Dried cod heads bled alive, BD = Dried cod heads bled dead.

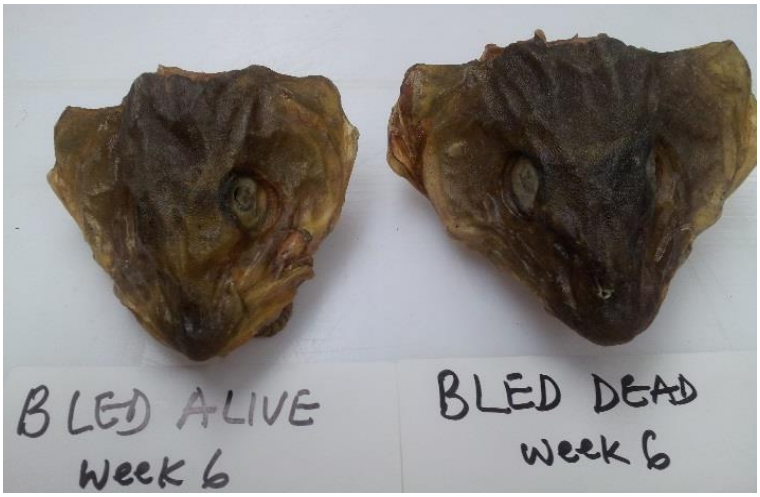

Figure 6: Colour difference of the dried cod heads with bled dead (BD) cod head darker.

4.3.2 Water activity (Aw)

The water activity of fresh cod heads bled dead and fresh cod heads bled alive was almost the same as the points overlap each other as shown in Figure 7. The water activity for the dried cod heads bled alive ranged between 0.4 and 0.6 while dried cod heads bled dead ranged between 0.4 and 0.63 as shown in Figure 7. There were no significance difference in water activity between the two bleeding methods each week of storage and no significance increase in water activity within each bleeding methods during the storage period.

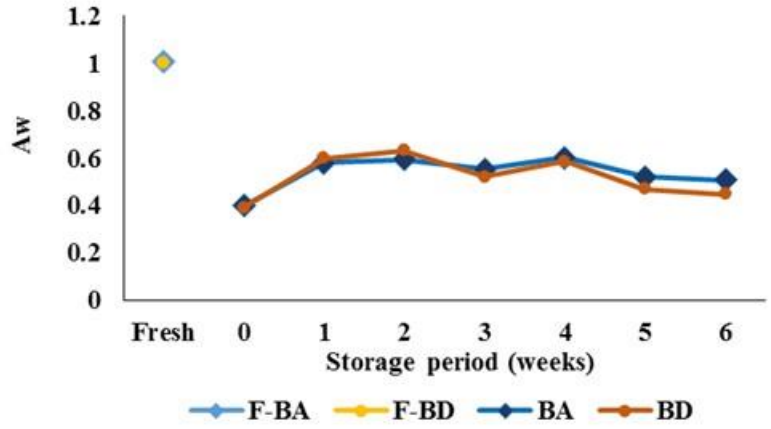

Figure 7: Changes in water activity of dried cod heads during storage. F-BA = Fresh cod heads bled alive, F-BD = Fresh cod heads bled dead, BA = Dried cod heads bled alive, BD = Dried cod heads bled dead.

4.3.3 Acidity (pH)

The acidity pH of the fresh bled alive cod heads and fresh bled dead cod heads was 7.30 and 7.34 respectively. The pH of the bled alive dried cods and bled dead dried cod heads ranged between 6.68-6.86 and 6.62-6.94 respectively as shown in Figure 8.

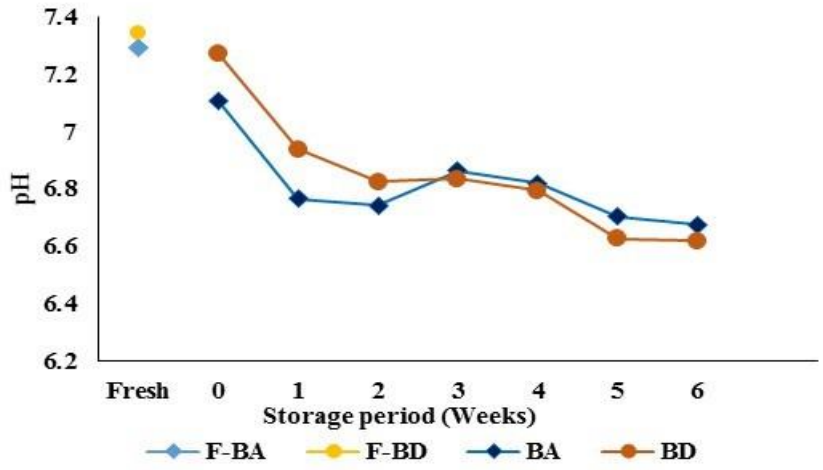

Figure 8: Changes in pH of dried cod heads during storage. F-BA = Fresh cod heads bled alive, F-BD = Fresh cod heads bled dead, BA = Dried cod heads bled alive, BD = Dried cod heads bled dead.

4.3.4 Rehydration

The rate of rehydration (reconstitution properties) of the dried cod heads for both bleeding methods was investigated using tap water at room temperature (24.5^{o}C) for 24 hours. The average rehydration percentage at different time interval and changes in rehydration percentage during the storage period for both bleeding methods are presented in Figure 9 and Figure 10 respectively.

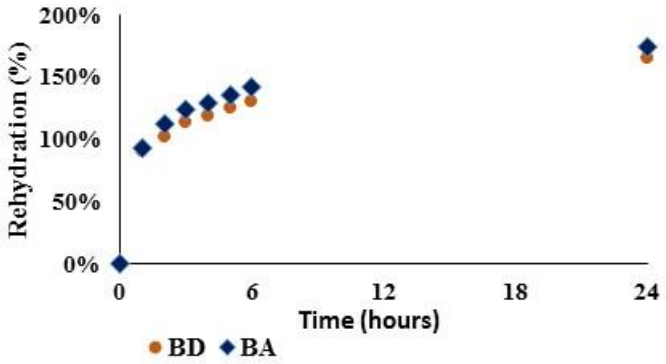

Figure 9: The rate of rehydration of dried cod heads.

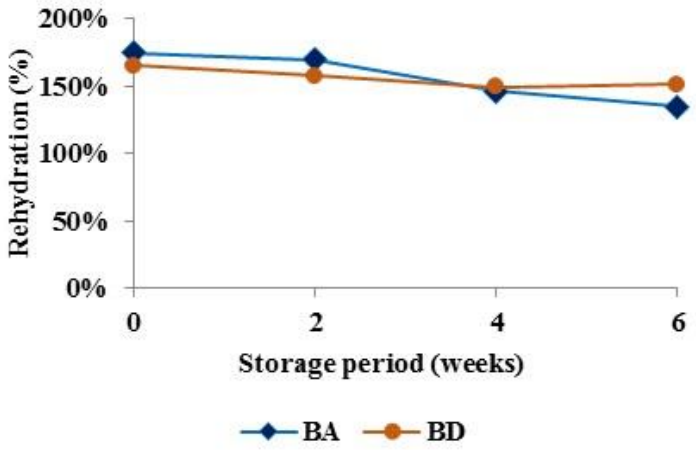

Figure 10: Changes in the rate of rehydration of dried cod heads during storage.

4.3.5 Moisture content

The moisture content of the fresh cod heads and dried cod heads during storage from the two bleeding methods was investigated and result presented in Table 2.

Table 2: Moisture content (%) of fresh and dried cod heads where BA (Bled Alive), BD (Bled Dead) and SD (Standard Deviation).

	Fresh cod heads	Storage period of dried cod heads (weeks)						
		0	1	2	3	4	5	6
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
BA	78.3 ± 0.8	12.2 ± 0.5	16.0 ± 0.3	16.3 ± 0.3	14.5 ± 0.6	16.4 ± 0.7	14.2 ± 0.5	14.2 ± 1.7
BD	78.7 ± 1.4	12.0 ± 0.1	16.3 ± 0.4	16.5 ± 0.4	14.6 ± 0.2	15.7 ± 0.4	13.76±0.34	14.2 ± 0.7

4.3.6 Mineral content

The mineral content of the fresh cod heads was determined, the mineral content of the dried cod heads during storage was investigated and presented in Table 3.

Table 3: Mineral content (%) of fresh and dried cod heads where BA (Bled Alive), BD (Bled Dead) and SD (Standard Deviation).

	Fresh cod heads	Storage period of dried cod heads (weeks)		
		0	3	6
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
BA	5.9 ± 1.4	26.7 ± 1.5	26.2 ± 2.5	24.5 ± 1.3
BD	5.8 ± 0.3	27.0 ± 3.6	25.9 ± 1.0	24.7 ± 1.9

4.3.7 Sodium chloride

The salt content (sodium chloride) of the fresh cod heads from the two bleeding methods was determined and the salt content of the dried cod heads from the two bleeding methods during storage were also investigated and presented in Table 4.

Table 4: Sodium chloride (salt) content (%) of fresh and dried cod heads where BA (Bled Alive), BD (Bled Dead) and SD (Standard Deviation).

	Fresh cod heads	Dried cod heads storage period (weeks)		
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
		0	3	6
BA	0.5 ± 0.0	2.8 ± 0.0	2.6 ± 0.1	2.5 ± 0.0
BD	0.6 ± 0.0	2.8 ± 0.1	2.6 ± 0.1	2.6 ± 0.1

4.3.8 Protein content

The protein content of the fresh cod heads from the two bleeding methods was determined before drying and the protein content of the dried cod heads during storage was investigated and reported in Table 5.

Table 5: Protein content (%) of fresh and dried cod heads where BA (Bled Alive), BD (Bled Dead) and SD (Standard Deviation).

	Fresh cod heads	Dried cod heads storage period (weeks)		
		0	3	6
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
BA	15.8 ± 1.4	56.8 ± 3.9	56.1 ± 3.3	59.2 ± 4.7
BD	15.8 ± 2.6	60.5 ± 2.8	54.1 ±0.8	55.1 ± 0.6

4.3.9 Lipid content

The lipid (fat) content of the fresh cod heads from the two bleeding methods was determined before drying and the lipid content of the dried cod heads during storage was investigated and reported in table 6.

Table 6: Lipid content (%) of fresh and dried cod heads where BA (Bled Alive), BD (Bled Dead) and SD (Standard Deviation).

	Fresh cod heads	Dried cod heads storage period (weeks)		
		0	3	6
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
BA	1.5 ± 0.1	3.1 ± 0.1	3.0 ± 0.4	3.0 ± 0.1
BD	1.4 ± 0.0	3.2 ± 0.1	3.0 ± 0.1	3.1 ± 0.0

4.3.10 Fatty acids profile

The fatty acids profile and their percentage composition of fresh and dried cod heads were analysed and result presented in Table 7 and Appendix 1.

Table 7: Fatty acids composition of fresh and dried cod heads where SD (Standard Deviation).

Fatty acids composition (%)	Fresh cod heads	Dried cod heads
	Mean ± SD	Mean± SD
Total Fatty acids composition	94.2 ± 1.8	93.9 ± 1.0
Saturated fatty acids (SFA)	26.5 ± 1.3	28.3 ± 0.6
Monounsaturated fatty acids (MUFA)	26.9 ± 0.3	27.7 ± 1.1
Polyunsaturated fatty acids (PUFA)	40.9 ± 0.5	37.8 ± 2.0
Eicosapentaenoic EPA	11.6 ± 0.5	10.4 ± 1.1
Docosahexaenoic DHA	21.7 ± 2.0	19.8 ± 1.4
∑EPA + DHA	33.3 ± 1.5	30.2 ± 2.4
n-3	39.4 ± 0.7	36.5 ± 2.3
n-6	0.8 ± 0.1	0.7 ± 0.2
n-6/n-3	0.02 ± 0.0	0.02 ± 0.0

4.3.11 Free fatty acids (FFA)

The free fatty acids of both the fresh and dried samples were investigated on the zero day (week 0) of drying, 3rd and 6th week of storage and result presented in Figure 11.

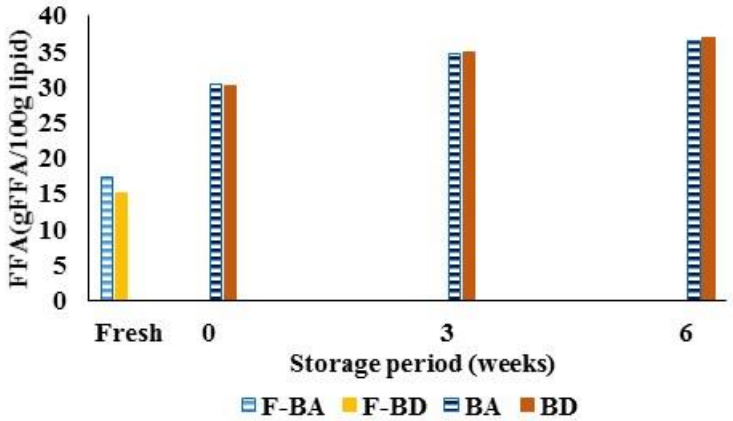

Figure 11: Changes in FFA of dried cod heads during storage. F-BA = Fresh cod heads bled alive, F-BD = Fresh cod heads bled dead, BA = Dried cod heads bled alive, BD = Dried cod heads bled dead.

4.3.12 Peroxide value (PV)

The peroxide value was determined in fresh cod heads from the two bleeding methods. It was also investigated in the dried cod heads from the two bleeding methods during storage as presented in Figure 12.

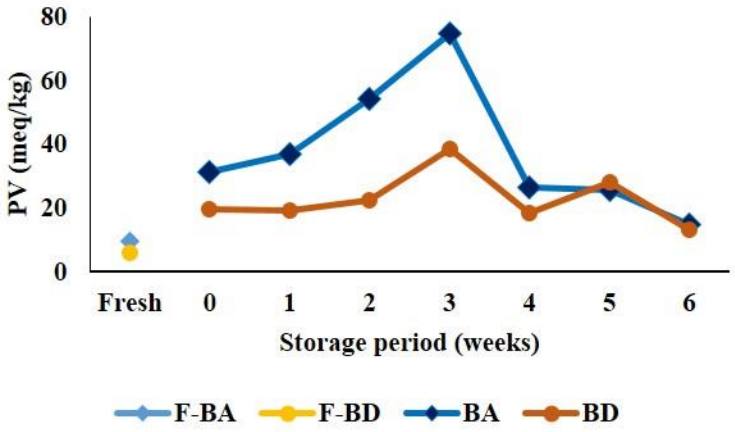

Figure 12: Changes in peroxide value of dried cod heads during storage. F-BA = Fresh cod heads bled alive, F-BD = Fresh cod heads bled dead, BA = Dried cod heads bled alive, BD = Dried cod heads bled dead.

4.3.13 Total volatile bases (TVB-N)

Total volatile basic nitrogen of the fresh samples and dried samples during storage was determined and presented in Figure 13.

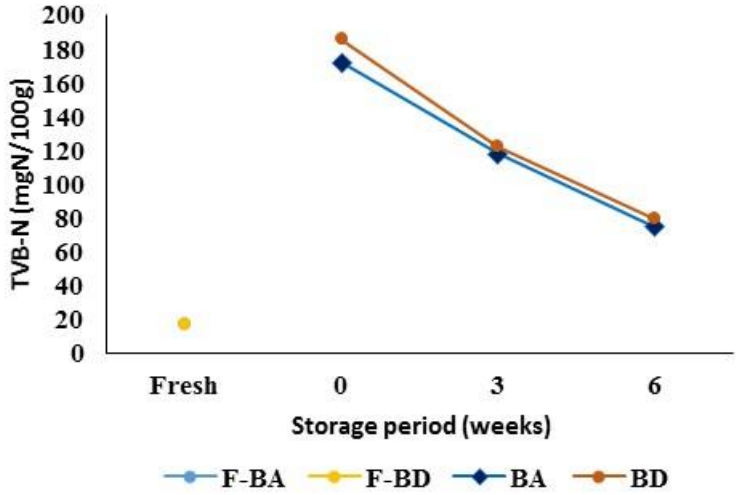

Figure 13: Changes in total volatile basic nitrogen (TVB-N) of dried cod heads during storage. F-BA = Fresh cod heads bled alive, F-BD = Fresh cod heads bled dead, BA = Dried cod heads bled alive, BD = Dried cod heads bled dead.

5 DISCUSSION

Fish handling at every stage of the value chain determines the quality of the fish. Erikson *et al.,* (1999) reported that bleeding significantly improves the quality in terms of appearance, odour and rancidity of fish flesh. This makes bleeding an important part of on-board handling of fish. The results of this study show that the colour of fresh cod heads from bled alive cods (F-BA) was not significantly whiter than in the fresh cod heads bled dead (F-BD). It also show fluctuations in the colour of dried cod heads bled alive and dried cod heads bled dead during storage, just dried (week 0) bled alive cod heads were significantly whiter than dried cod heads bled dead and from the 4^{th} week of the storage period the dried cod heads bled alive were significantly whiter than dried cod heads bled dead throughout the storage period.

Water activity is the measure of the amount of water in a food that is available for the growth of microorganisms, including pathogens. It determines the storage life of fish. The water activity of the dried cod heads for both bleeding methods fluctuates throughout the six weeks storage periods as a result of fluctuation in the storage conditions. The water activity for the dried cod heads bled alive ranged between 0.4 and 0.6 while dried cod heads bled dead ranged between 0.4 and 0.63. Generally, there is no microbial growth or toxic formation in food when the water activity is lower than 0.85. Dried fish products should have water activity around 0.6. According to rules from FDA from 2001. Water activity should be lower than 0.85 in food that are not stored in a refrigerator. Results of this study indicate that even though the heads were stored under fluctuating conditions for 6 weeks, the water activity of the dried cod heads complies with standards set by FDA.

The pH value is an indicator of the degree of freshness or spoilage of food. The pH of the fresh and dried cod heads in this study was quite neutral and dropped as the storage period increased. Nester *et al.,* (2007) reported that a high pH favours microbial growth and that most bacteria will grow best at neutral pH 7 although they can still tolerate ranges from pH 5 (acidic) to pH 8 (basic). The pH of the dried cod heads from both bleeding methods throughout the storage period fall in the range at which most spoilage bacteria will thrive.

Tunde-Akintunde, (2008) reported that rehydration of food products depend principally on the internal structure of the dried pieces, extent to which water holding components (e.g. protein and starch) have been damaged during drying. In this study, the dried cod heads from both bleeding methods absorbed water throughout the 24 hours soaking period. The rate of water absorption was more in the bled alive cod heads but not significantly higher ($p>0.05$) than the rate of water absorption by the bled dead cod heads. It was also found out that the optimum water was absorbed by the first hour of rehydration and soaking further than one hour is not necessary as this can cause more nutrients to be leached out into the soaking water, as absorption gradually increased for the next 23 hours, time elapsed/weight gained benefit is questionable with longer rehydration period than one hour. It was also found out that there was negative correlation between the water absorbed and the storage period, meaning that the amount of water absorbed decrease with increase in storage periods but not significantly different between the bleeding methods.

Moisture content is a determinant of the quality of dried food products. Clucas, (1982) reported that dried fish with 25% or more moisture is not sufficient to inhibit microbial growth whereas dried fish with 15% or less moisture is well enough to inhibit microbial growth. The water content of the cod-heads after drying is about 15%, or the product's water activity

must be lower than 0.6, which is achieved in about 3 days in the drying container (Arason, *et al*., 1992). In this study, moisture content of the fresh cod heads from both bleeding methods ranged between 78.3% and 78.7% and was reduced to between 12.04% and 12.23% after drying. It was observed that the moisture content fluctuates between 12.04% and 16.49% during the six weeks storage period as a result of fluctuation in the relative humidity and temperature of the storage conditions. There was no significant ($p>0.05$) effect of bleeding methods on the moisture content of the dried cod heads during storage. It was also observed that dried fish retains all the nutrients that are available in a fresh fish, but in concentrated form due to the drying process where moisture content is reduced.

Mineral (Ash) is the residue without water and volatile constituents. Total mineral content of the dried cod heads obtained in this study was higher than the total mineral content of the fresh cod heads as a result of moisture lost by the dried cod heads. There was no significant effect of bleeding methods and storage period for six weeks on the mineral content. The dried cod head is a good source of minerals, but this need further and more detailed analyses to be able to conclude.

The salt content of the dried cod heads was found to have increased from about 0.5% of the fresh cod heads to about 2.8% as a result of evaporation of water. Jonsson *et al.*, (2007) reported that the salt content for the dried fish products is around 1.5-2.0%. The salt content fluctuated as a result of fluctuation in the moisture content during storage.

It was observed that the crude protein formed the largest quantity of the dry matter in the dried cod heads which was in line with previous studies (Pannevis, 1993). The crude protein ranged between 54.1g and 60.5g/ 100g of dried cod heads, which makes dried cod head a good source of protein. There was no significant reduction in the percentage of crude protein of the dried cod heads during the period of storage. It was also observed that the bleeding methods has no significant effect on the percentage of the crude protein.

The mean percentage of lipid in the fresh cod heads was between 1.40% and 1.48%, it concentrated after drying to between 3.13% and 3.15% due to loss in moisture. It was observed that the lipid fluctuates during the storage period but a slightly higher amount of lipid was observed in the freshly stored dried cod heads. Fluctuation of the lipid could be attributed to fluctuation in the moisture content and lipid oxidation of the poly-unsaturated fatty acids (PUFA) contained in the dried cod heads. There was no significant difference in the lipid content of the bled alive and bled dead dried cod heads during the storage period.

Omega-3 and omega-6 fatty acids are unsaturated "Essential Fatty Acids" (EFAs) that need to be included in the diet because the human metabolism cannot create them from other fatty acids. It has been reported that highly unsaturated n-3 fatty acids, particularly (EPA) and (DHA), are important for human health and early development, and dieticians are advising increased consumption of foods that contain these fatty acids (Connor, 2000) and (Ruxton *et al.*, 2007). In this study, both fresh and dried cod heads are rich in fatty acids composition and drying has no significant effect on the fatty acids composition of the dried cod heads. The fresh and dried cod heads are excellent sources of polyunsaturated fatty acids which constitute 40.9% of the fresh cod heads and 37.8% of the dried cod heads fatty acids composition. The sum of the omega-3 fatty acids ∑EPA + DHA are 33.3% and 30.2% for fresh and dried cod heads respectively. The oil of both fresh and dried cod heads are richer in omega-3 fatty acids (∑EPA + DHA) than the omega-3 fatty acids in cod liver oil. It was reported that excessive amounts of omega-6 polyunsaturated fatty acids and a very high

omega-6/omega-3 ratio have been linked with pathogenesis of many diseases, including cardiovascular disease, cancer, and inflammatory and autoimmune diseases. The ratio of omega-6 to omega-3 in modern diets is approximately 15:1, whereas ratios of 2:1 to 4:1 have been associated with reduced mortality from cardiovascular disease, suppressed inflammation in patients with rheumatoid arthritis, and decreased risk of breast cancer http://www.scientificpsychic.com/fitness/fattyacids.html. The Health Department of England (HMSO, 2001) suggested a maximum intake ratio of omega-6 to omega-3 of 4. (Simopoulos, 1999) suggested that the ratio must be between 5 and 10. It was found out that majority of the poly-unsaturated fatty acids are omega-3 fatty acids for both fresh and dried cod heads leaving the ratio of n-6/n-3 to 0.02.

Fish oil has been found to be more liable to spoilage than other oils due to their greater number of unsaturated fatty acids. The greater the degree of unsaturation, the greater would be the tendency for fat oxidation (rancidity). It has been reported that there might be high risks of rancidity during prolonged storage conditions due to the fatty nature of fish (Sohn and Ohshima, 2011). The FFA for dried cod heads in this study were high, (30.4-36.4) gFFA/100g lipid and (30.1-36.8) gFFA/100g lipid for BA and BD respectively, since the dried cod heads are very rich in poly-unsaturated fatty acids. There was significant increase in the FFA of the dried cod heads of both bleeding methods during storage due to the storage conditions. Boran *et al.,* (2006) reported that FFA is a measure of hydrolytic rancidity, the extent of lipid hydrolysis by lipase action and that fish oil containing high levels of polyunsaturated fatty acids, is very susceptible to oxidative deterioration at varying velocities, strongly depending on the storage conditions and fatty acid profile.

The Peroxide value (PV) which is a primary indicator of oxidation of fat (rancidity) increased weekly up to week 3 and starts decreasing from week 4 to the end of the storage period in this study. The two bleeding methods followed similar trends but surprisingly the bled alive had a higher PV compare to the bled dead. By the week 5 of the storage period, the PV of both bleeding methods became similar without significant difference. This might be attributed to the processes involved in the production of the dried cod heads, the storage conditions after processing, homogenising and handling of the samples during analysis. The peroxide values corresponding to incipient spoilage are usually in the order of 20-40 milliequivalents of oxygen per Kg of sample (ml per Kg). However, Connell (1995) reported that when peroxide value is above 10-20, fish develop rancid taste and smell. By the 6th week storage period, the PV were 14.9 milliequivalents per Kg and 13.3 milliequivalents per Kg for bled alive and bled dead dried cod heads respectively. The peroxide value is a very sensitive analysis, care must be taken in PV measurement, the stage of peroxides degradation in the samples which might have been converted to other compounds.

The Total Volatile Basic Nitrogen (TVB-N) is synthesised by reaction from proteins. In this study, the TVB-N of the fresh cod heads from both bleeding methods fall within the acceptable limit of 20-30mgN/100g. Pearson, (1982) recommended that the limit of TVB-N acceptability of fish is 20-30 mg N per 100 g while Kirk and Sawyer, (1991) suggested a value of 30-40 mg N per 100 g as the upper limit. The just dried cod heads had very high TVB-N because of the drying process which took about 120 hours at temperature between (20-25) ^{o}C. During the storage period of the dried cod heads, there was significant reduction in the TVB-N for both bleeding methods throughout the storage period. TVB-N of the dried cod heads at the end of the storage period was 74.7 mg N per 100 g and 79.4 mg N per 100 g for bled alive and bled dead respectively, which are still higher than the recommended acceptable limit in food.

6 CONCLUSIONS

Dried cod heads from bled alive and bled dead cods were produced using geothermal energy at regulated temperature and relative humidity. The dried cod heads were stored at simulated storage conditions to simulate Nigerian storage conditions. The study found out that there was a significant effect of the bleeding methods on the colour of the dried cod heads, observed immediately after drying as well as during storage. That was the only observed effect of bleeding in this study. However, the study resulted as well that the water activity and moisture contents fluctuated as the storage conditions. The pH of the dried cod heads in this study was in the range at which spoilage bacteria will thrive and water rehydration was optimum at one hour of rehydration with tap water under ambient condition. The rehydration properties of the dried cod heads decreased as the storage period increased. The study indicated that dried cod head is a good source of protein, mineral and marine lipids which are excellent in polyunsaturated fatty acids especially omega-3 fatty acids. Additionally, the n-6/n-3 ratios of both the fresh and dried cod heads are within the recommended values by some researchers, thus constituting a healthy food. The storage for six weeks, under the designed conditions, had no significant effect on the nutritional properties but negative effect on freshness by inducing spoilage of the dried cod heads. Hence stable storage condition could improve the quality of the product.

RECOMMENDATIONS FOR FUTURE RESEARCH

The results from this study suggest that:

- Dried fish transport condition from Iceland to Nigeria need further investigation
- The study be carried out under stable storage conditions (Relative humidity and temperature) and longer period of storage.
- An equipment/method of homogenizing the cod heads to give a better homogenous sample be provided.
- The food safety aspects, microbiological analyses of fresh and dried cod heads be studied.
- The amino acids and mineral composition of fresh and dried cod heads be studied.
- The other species used in dried fish products be studied along with product development to strengthen the commercial ties between Nigeria and the Northern Atlantic raw material providers.

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APPENDIX

Appendix 1: Fatty acids profile and their percentage composition of fresh and dried cod heads.

Fatty acids composition	Fresh cod heads	Dried cod heads
	Mean ± SD	Mean ± SD
C14:0	1.7 ± 0.4	1.3 ± 0.1
C14:1	0.0 ± 0.0	0.0 ± 0.0
C15:0	0.3 ± 0.0	0.2 ± 0.2
C16:0	17.9 ± 0.8	19.1 ± 0.4
C16:1n9	1.8 ± 0.0	1.9 ± 0.1
C16:1	0.3 ± 0.1	0.2 ± 0.1
C17:0	1.1 ± 0.2	1.2 ± 0.2
C16:2n4	0.5 ± 0.1	0.7 ± 0.2
C17:1	0.1 ± 0.0	0.1 ± 0.0
C18:0	5.3 ± 0.2	6.1 ± 0.2
t C18:1n9	0.6 ± 0.3	0.5 ± 0.1
C18:1n11	12.8 ± 0.3	13.4 ± 0.2
C18:1n9	5.0 ± 0.8	5.9 ± 0.1
C18:1n5	0.4 ± 0.0	0.5 ± 0.0
t C18:2n6	0.2 ± 0.1	0.1 ± 0.0
C18:2n6	0.0 ± 0.0	0.1 ± 0.1
C18:3n3	0.8 ± 0.3	1.0 ± 0.3
C20:1n11	2.1 ± 0.7	1.8 ± 0.1
C20:1n9	0.6 ± 0.1	0.6 ± 0.0
C21:0	0.0 ± 0.0	0.2 ± 0.2
C22:0+C20:3n6	0.1 ± 0.0	0.1 ± 0.0
C20:3n3	3.7 ± 1.0	3.7 ± 0.3
C22:1n9	1.1 ± 0.9	0.5 ± 0.5
C20:4n6	0.5 ± 0.0	0.4 ± 0.0
C20:5n3	11.6± 0.6	10.4 ± 1.1
C24:0	0.1± 0.1	0.1 ± 0.1
C24:1	2.1 ± 0.4	2.3 ± 0.4
C22:5n3	1.8 ± 0.3	1.6 ± 0.1
C22:6n3	21.7 ± 2.0	19.8 ± 1.4
summ	94.2 ± 1.8	93.9 ± 1.0