Journal of Aquatic Food Product Technology

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/wafp20

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To cite this article: Jannicke Fugledal Remme, Guro Møen Tveit, Morten Bondø, Rasa Slizyte, Aðalheiður Ólafsdóttir, Rósa Jónsdóttir, Margrét Geirsdóttir & Ana Karina Carvajal (2022) Valorisation of Frozen Cod (*Gadus morhua*) Heads, Captured by Trawl and Longline by the Oceanic Fleet, by Enzymatic Hydrolysis, Journal of Aquatic Food Product Technology, 31:5, 483-495, DOI: 10.1080/10498850.2022.2060055

To link to this article: https://doi.org/10.1080/10498850.2022.2060055

Published online: 17 Apr 2022.

JOURNAL OF AQUATIC FOOD PRODUCT TECHNOLOGY
2022, VOL. 31, NO. 5, 483–495
https://doi.org/10.1080/10498850.2022.2060055

Valorisation of Frozen Cod (*Gadus morhua*) Heads, Captured by Trawl and Longline by the Oceanic Fleet, by Enzymatic Hydrolysis

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ABSTRACT

In the Norwegian oceanic fleet, whitefish onboard processing creates a great amount of rest raw materials. Cod heads are nutritious and a good source for production of high-quality marine peptides. Frozen cod heads, captured by trawl or longline, were evaluated based on the lightness and redness in the neck cut to compare the quality in heads from the different fishing gears. The heads were subjected to enzymatic hydrolysis. The hydrolysates have been chemically and sensory characterized. There was no significant difference in quality or chemical and sensory characteristics based on type of fishing gear. The resulting hydrolysates were of high quality, although moderately bitter. The study demonstrates that frozen cod heads from the oceanic fleet can be an excellent source of high-quality proteins for human consumption.

KEYWORDS

Fishing gear; Quality; Enzymatic hydrolysis; Protein hydrolysate; Cod heads

Introduction

Atlantic cod (*Gadus morhua*) is one of the most important gadoid fish species in commercial fisheries in Norway (Rotabakk et al. 2011). Present consumer attention, increasing preference for natural products (Berton-Carabin and Schroën 2019; Ozturk and McClements 2016), and increased demand for proteins due to population growth make it more important to use fishery resources more sustainably. It is estimated that as much as 43% by weight of all whitefish is regarded as rest raw materials (Hjellnes et al. 2020; Slizyte et al. 2005; Tveit et al. 2020). The rest raw material, after production of fillets or headed/gutted whitefish, from the oceanic fishing fleet have a high potential for increased value creation.

Cod heads represent about 20% of whole fish weight. They contain high levels of protein (14–15%), low lipid contents (4%), and about 6% ash (Remme et al. 2022; Tveit et al. 2020). Their chemical composition makes them a highly suitable raw material for the manufacture of high-quality protein products. Since the seafood industry is key to wealth creation and employment in Norwegian coastal areas (Johansen et al. 2019), there is heightened interest in new technologies for the utilization and value creation of cod heads. Enzymatic hydrolysis is one of a number of methods that could be used to transform cod heads into more profitable and marketable products, as hydrolysis is increasingly being used to recover valuable components from marine rest raw materials (Bougatef et al. 2012; Dale et al. 2019; Dauksas et al. 2005; Eko Irianto and Nuri Fawzya 2018; Gildberg et al. 2002; Marti-Quijal et al. 2020; Sae-Leaw et al. 2016; Slizyte et al. 2005; Šližytė et al. 2009; Ucak et al. 2021; Wald et al. 2016) The residual materials are rich in essential amino acids (Liaset and Espe 2008), and the inclusion of hydrolysates in food or feed will increase nutritional value. WHO recommends 0.83 g protein/kg body weight a day (WHO 2007). The trend for average dietary protein intake is increasing (Shan et al. 2019), due to a healthier diet and population growth and illustrates the need for new protein sources.

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The intrinsic quality of whitefish is affected by fish size, season of catch, sexual maturation, fishing ground (Bøknæs et al. 2001; MacCallum et al. 1968), and catching methods (Botta et al. 1987; Rotabakk et al. 2011). Fishing gear has multiple impacts on fish (Digre et al. 2017; Esaiassen et al. 2004; Larsen and Rindahl 2008; Huse et al.), and the choice of fishing gear is determined by several complex parameters, e.g. historical aspects, fuel prices, politically decided fishing quotas, and prices of frozen vs. fresh raw material. In Norway, approximately 30% of the cod has been caught by bottom trawl and 15% by longline (www.fisheries.no). Longline fish is inflicted with gaffing damage (Larsen and Rindahl 2008; Rotabakk et al. 2011), as gaffing is a necessity for rescuing drop offs (Rotabakk et al. 2011). During gaffing, it is crucial for the fishermen to hit the fish in the head to avoid damage in the more valuable filet. This, however, may lead to hemorrhages and reduced quality for the heads. Trawl caught fish is inflicted with bruises during hauling (Digre et al. 2017). Cod caught by trawl have significantly higher average of bruises and poorly bled fish compared to cod caught by longline (Rotabakk et al. 2011). Proper bleeding of white fleshed fish results in more attractive products. It is likely that the time from the fish being brought onboard until bleeding is on average longer on a trawler than a longliner, as longlining brings only one fish at a time on board, while trawling brings the whole catch at once (Rotabakk et al. 2011). Injuries are observed to increase with increasing catch size (Digre et al. 2010). Generally, on board fishing vessels, bleeding and gutting fish are difficult tasks with large hauls. It is not unusual for large hauls of fish taken by bottom trawl to be kept in storage bins for hours before bleeding and gutting. The last fish in the storage bin are often dead before bleeding, and this leads to muscle discoloration due to insufficient exsanguination and pressure on the fish (Olsen et al. 2013).

Fish protein hydrolysates may be utilized as protein enrichment in food products and as functional ingredients. A major challenge in the production of protein hydrolysates for human consumption is the formation of bitter and unpalatable flavor (Aspevik et al. 2016; Fu et al. 2018b; Idowu and Benjakul 2019; Liu et al. 2016; Steinsholm et al. 2020). Bitter taste development is related to the formation of small hydrophobic peptides generated in the hydrolysis process (Asao et al. 1987; Aspevik et al. 2016; Fu et al. 2018b; Kim and Li-Chan 2006). Hydrolysates contain peptides, free amino acids, minerals, salt, vitamins, and other water-soluble molecules that contribute to the sensory profile (Liaset and Espe 2008; Shumilina et al. 2015; Sundekilde et al. 2018). An objective evaluation of sensory properties is imperative for quality assessment of food-grade hydrolysates and is preferably performed by a trained taste panel (Kemp et al. 2018). Several scientific studies have addressed flavor development in protein hydrolysates based on marine and poultry substrates (Aspevik et al. 2016; Fu et al. 2018b; Šližytė et al. 2017).

The aim of this study was to produce high-quality protein hydrolysates from frozen cod heads captured by trawl and longline and to study whether fishing gear affects quality and sensory characteristics of the protein hydrolysates produced.

Materials and methods

Chemicals and enzymes

Papain (Performase ®GSM80) and Bromelain (2400 GDU/g) were procured from Enzybel International S.A. (Villers-le-Bouillet, Belgium). All enzymes comply with the recommended purity specifications for food-grade enzymes given by the joint FAO/WHO Expert Committee on Food Additives (JECFA) and the Food Chemicals Codex (FCC). Methanol, chloroform, hexane, formaldehyde used for chemical analysis were all obtained from Merck (Darmstad, Germany). Cytochrome C, aprotinin, insulin A, leucine enkephaline, Val-Tyr-Val, and Gly-Tyr (all from Sigma Chemical Co, St. Louis, MO, USA) were used as standards for molecular weight distribution. All chemicals were of reagent grade.

Raw material

Atlantic cod (*G. morhua*) were caught by trawl or longline at similar time of year (January 2020) to ensure comparative raw materials and adequacy of the results. After catch, the fish were gutted and beheaded on board the fishing vessel. Heads were sorted from three trawl catches (T1, T2, T3) and two longline catches (L1, L2), shown in Table 1, directly frozen pre-rigor in blocks (20 kg) in plate freezers, transported to the lab, and stored (- 20°C) until thawing in May 2020.

Thawing

On the day of hydrolysis, the heads were thawed. Thawing of the frozen cod heads was done in 600 liter bins with running tap water (5–8°C) for 3.5 hours. Temperature was measured in the water and in three cod heads pr. catch.

Color

After thawing, heads were evaluated according to the redness of the flesh along the neck cut. The heads were photographed using a 36.3-megapixel FX-format Nikon D800E, with a Nikon 35 mm f/1.8 G FX AF-S lens and a Nikon Speedlight SB900 full-spectrum flash. The lens and flash each had mounted linear polarizing filters, crossed at 90 degrees relative to each other. The purpose of the polarizing filters was to remove specular reflections and to provide more accurate color imaging of the skin. Images were acquired with full manual settings on the camera (1/250 sec exposure, ISO 100, F/5.6) and exported in NEF RAW format for post-processing. An X-rite ColourChecker was photographed by the same equipment/settings, and a custom color correction profile was created and applied to the RAW-photos during post-processing using Adobe Lightroom software. Images were then cropped, resampled, and exported in JPEG-format for final processing and analysis in LabVIEW software (NI, Austin, TX, USA).

For final image analysis, two LabVIEW programs were developed. The first program was a user interface where a rectangular area on the cut surface of the neck/heads is selected manually. The selection is done as equally as possible and with groups randomized. The selection is focused on keeping an area of the meat and avoiding bone and surface blood. The area selected is then exported as an RGB-thumbnail, as well as a copy of the original image with a green square illustrating the selected area. The second program performs a conversion of the thumbnails from RGB into CIE L*a*b* color values. For comparison reasons, both mean L*a*b*- and mean RGB-values from each thumbnail are extracted and exported to a spreadsheet file for multivariate statistical analysis. The mean L*a*b*- and RGB-values of each thumbnail were exported to a spreadsheet file for further statistical analysis.

Enzymatic hydrolysis

Before hydrolysis, the heads were cut into smaller pieces by hand and minced using a Hobart mincer (model AE200) with 10 mm diameter holes. The hydrolysis was performed in 4-liter closed glass reactors with an electrical impeller. Minced cod heads (2 kg) were mixed with 1 kg tap water. When the temperature of the mixture reached 50°C, the enzymatic hydrolysis was begun by adding 0.1%

Table 1. An overview over the raw material used in this study.

Sample name	Fishing gear	Catch size (kg)	Number of heads evaluated (20 kg)
T1	Trawl	17300	11
T2	Trawl	12600	12
T3	Trawl	15000	12
L1	Longline	17094	8
L2	Longline	17480	8

papain and bromelain (by wet weight of raw material). After 60 min, enzymes were inactivated by rapid heating (2–5 min) to 90°C and held there for 10 min. Mixtures were cooled on ice to a temperature below 60°C before centrifugation in 1 liter batches at 2250 × g for 15 min (at room temperature). The fractions, water-soluble proteins, and insoluble matter were separated by pouring out the water-soluble fraction, which was frozen and freeze-dried prior to further analysis. Hydrolysis was performed in duplicate.

Chemical characterization

Moisture in the powders was determined gravimetrically after drying at 105°C for 24 h. Ash content was estimated according to AOAC. Total N was determined by CHN-S/N elemental analyzer 1106 (Carlo Erba Instruments S.Pa., Milan, Italy), and crude protein was estimated by multiplying total N by a factor of 6.25 (Mariotti et al. 2008). Extraction of lipids from the samples was performed according to the method of Bligh and Dyer (1959). The degree of hydrolysis was evaluated as the proportion (%) of cleaved peptide bonds in the protein hydrolysate, by the formol titration method described by Taylor (1957). All measurements were performed in triplicate.

Molecular weight distribution

Dry powders were dissolved in water to a concentration of about 1 mg/ml. All samples were analyzed in triplicate. The samples were analyzed on a Hitachi HPLC with a UV detector at 220 nm, using a Superdex peptide 10/300 column. The run was isocratic with 30% acetonitrile, 0.1% TFA in water, at 0.4 ml/min. The sample volume was 30 µl. The tests were conducted at room temperature. The standards used were cytochrome C (12327 Da), aprotinin (6512 Da), insulin A (2531 Da), leucine enkephalin (555.6 Da), Val-Tyr-Val (379.5 Da), and Gly-Tyr (238.2 Da). The regression line for the standards were $r^2 = 0.994$. The molecular weight was divided in intervals: below 200 Da, 200–500 Da, 500–1 000 Da, 1 000–2 000 Da, 2 000–4 000 Da, 4 000–6 000 Da, 6 000–8 000 Da, 8 000–10 000 Da, 10 000–15 000 Da, 15 000–20000 Da, and above 20 000 Da.

Sensory evaluation

Sensory evaluation of cod head protein hydrolysates was carried out focusing on sensory characteristics of different groups of fish proteins. Five sample groups of cod head hydrolysates were analyzed and compared: three from trawl caught cod (groups: T1, T2, and T3) and two from longline caught cod (groups L1 and L2). A profiling method (Generic Descriptive Analysis, GDA) was used to evaluate all samples (Lawless and Heymann 2010). Seven panelists, all trained and experienced in evaluation of fish protein hydrolysates, evaluated all samples (ISO 8586:2012 2014).

Two panel training sessions were carried out prior to the evaluation to develop the GDA scale and synchronize the panelists' use of the scale. The scale for hydrolyzed proteins consisted of nine attributes (Table 2). During evaluation, the intensity of each attribute for a given sample was described using a 15 cm line scale, which in analysis was transformed to numbers from 0 to 100. All protein hydrolysates were dissolved in cold tap water in 2% concentration. Each sample was ~10 ml of protein solution. The samples were presented at room temperature to the panelists in clear 30 ml plastic beakers. All samples were coded with three-digit numbers, and a duplicate was evaluated for each sample group. The sensory evaluation program FIZZ (2.50B, Biosystémes) was used to collect sensory data. The program Panelcheck (V1.4.0, Nofima, Tromsø, Norway) was used to evaluate the performance of the panel and individual panelists.

Table 2. Sensory attributes and attribute definitions for hydrolyzed proteins. Scale: None (0) to much (100).

Sensory attribute	Definition
ODOR	
dried fish	dried fish
fish skin	fish skin, fish processing facility
sour	sour odor
FLAVOU	
dried fish	dried fish
fish skin	fish skin, metallic
sour	sour flavor
salty	salty flavor
bitter	bitter flavor
astringent	astringent

Statistical analysis

All experiments and measures were performed three or more times, except for the hydrolysis trials that were conducted in duplicate. Statistical analysis was performed using Microsoft Excel 2010 (Redmond, WA, USA). Significance was calculated using a t-test ($p < .05$). Results are reported as mean ± standard deviation. For evaluation of sensory attributes, the statistical program NCSS 2000 (NCSS, UT, USA) was used to calculate analysis of variance (ANOVA, general linear model) to compare results from the sample groups. The program Panelcheck (V1.4.0) was used to evaluate the performance of the panel and individual panelists. A correction was made for different uses of scale by the panelists. Duncan's test was used to calculate multiple comparisons between sample groups. The significance level was set at 5%.

Results and discussion

Thawing

The temperature logs from the thawing procedure are shown in Figure 1. The heads were thawed in running cold water (Roiha et al. 2018), and starting temperature of the heads differed from −3.4°C to −9.5°C. The initially warmest heads needed 1 h to reach 0°C, whereas the coldest heads needed 45 minutes more to reach the same temperature. Tveit et al. (2020) showed that freezing of whole heads to a temperature of −15°C required 5–6 hours. In the same study, thawing from −15°C required 4 hours. The difference may be explained by the temperature logs, which were placed in the heads before freezing (Tveit et al. 2020). In this study, temperature logs were placed in the heads by drilling into the frozen material. This, however, was challenging and time-consuming, which lead to heads that had already started thawing when the logs were in place.

Color

The quality was evaluated according to redness and lightness of the flesh in the neck cut of the heads. Evaluation of redness and lightness to compare damages and quality have previously only been done on fish fillets. Fishing gears have multiple impacts on fish quality and can result in quality degradation (Digre et al. 2010; Esaiassen et al. 2004). Previous studies on fillets show that trawl caught fish are often higher in redness and darker than longlined fish, due to poor bleeding (Rotabakk et al. 2011). The trawl caught heads were sampled from three catches: T1, T2, and T3. Heads in catch T1 and T2 were less red than heads in catch T3 (Figure 2). Digre et al. (2010) observed that injuries increase with catch size. In this study, there was no correlation between catch size and redness in the neck cut. The largest haul was catch T1, whereas catch T3, which was redder, had a lower size.

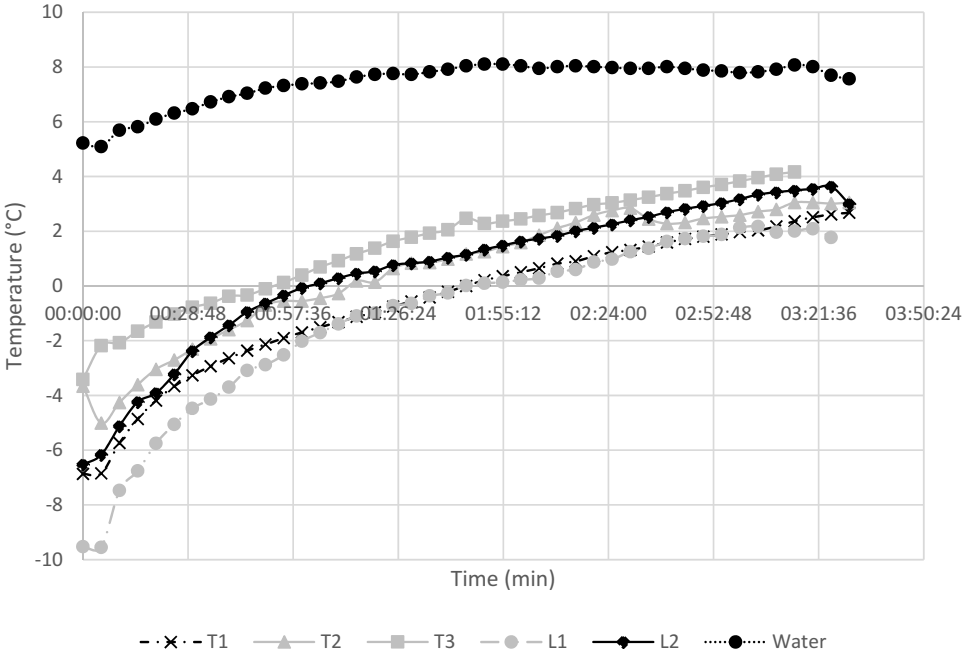

Figure 1. The temperature curve for thawing of whole cod heads in running water at 6°C.

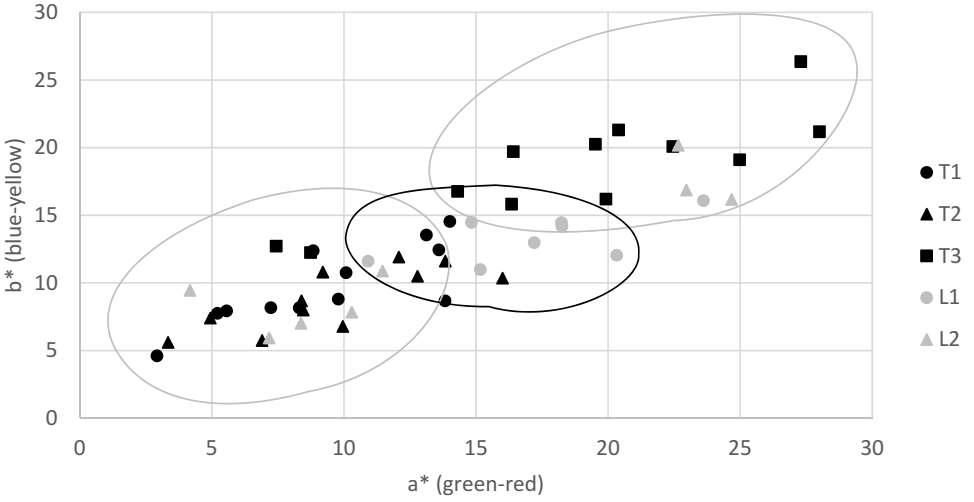

Figure 2. The redness in the neck cut. The upper grey ring shows the high redness in T3, whereas the lower grey ring shows less redness in T1 and T2. The black ring in the middle shows that the heads in catch L1 are more equally red, compared to the heads in L2.

The heads from longlining were redder than trawl catch T1 and T2 and less red compared to T3. The expectation was for whiter neck cuts, based on results reported in fillets (Rotabakk et al. 2011); it is, however, possible that gaffing can lead to some of the redness. When gaffing fish, it is crucial to aim for the head, and this leads to bleeding in the heads. Comparing trawl and longline, there was no significant difference in the color nor in lightness between the two types of fishing gear (Figure 3).

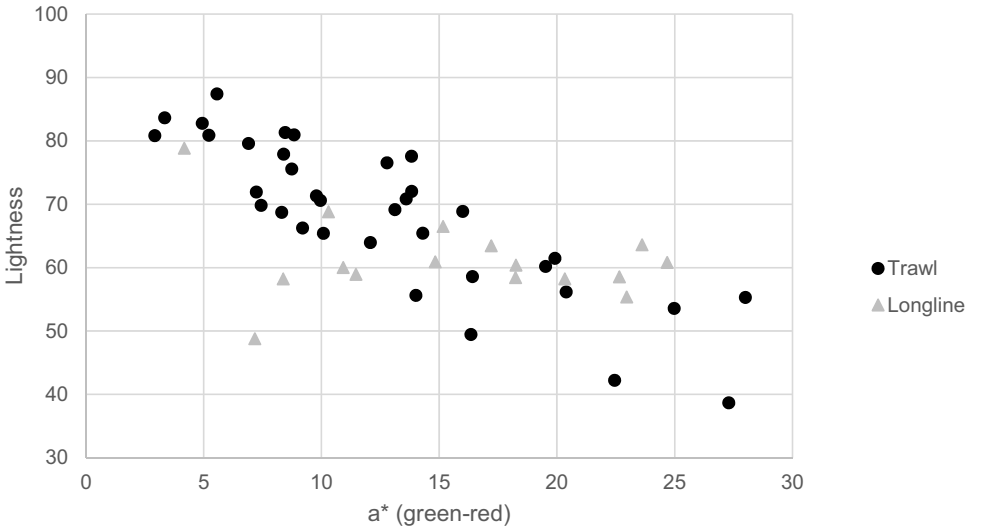

Figure 3. The lightness in trawl and line caught cod heads are evenly distributed between catches and fishing gear.

Color is one of the major attributes affecting the consumer perception of quality (Francis 1995; Olsen et al. 2013; Soldatov 2006). It is generally accepted that whiteness is positive, and redness is negative when evaluating color of cod loins. The neck cuts differ in redness and lightness and reflects increased residual blood in some heads compared to others. The neck cut can therefore be used to evaluate quality. This study shows that there were differences in redness between catches, but also within catches. There were, however, no significant differences in redness and lightness between heads captured from different fishing gear.

Hydrolysate yield

After centrifugation, all hydrolysis trials produced two fractions: (1) fish protein hydrolysates (FPH) and (2) sediments. No oil or emulsion phases were detected. The amount of lipids in the cod heads were insufficient to form a separate fraction after hydrolysis, indicating that any lipids present were distributed between the FPH and sediment fractions. In trials using a raw material consisting of a mixture of cod viscera and backbones, a minimum of 6 g of lipid per 100 g of wet weight raw material was required in order to produce a separate oil fraction (Slizyte et al. 2004). The chemical composition of cod heads is 78% water, 7% ash, 1–4% lipids, and 11–15% protein (Remme et al. 2022; Tveit et al. 2020). The cod heads in the study by Remme et al. (2022) had a lipid content insufficient to form a separate lipid fraction. The enzyme combination of papain and bromelain 1:1 gave a high dry matter content when used on cod heads (Remme et al. 2022). In the same study, several enzymes were tested, giving a dry matter range of 4–8%. The FPHs produced in this study consisted of 92–93% water and 7.1–7.4% dry matter (Table 3). Both longline and trawl caught cod head protein hydrolysates had a mean dry matter content of 7.3%.

Table 3. Mass balance in hydrolysis trials with cod heads from three trawl and two longline catches, and dry matter (%) in the hydrolysate.

	Hydrolysate (g)	Sediment (g)	Dry matter in hydrolysate (%)
H1	1948.1	926.8	7.4
H2	1893.0	965.6	7.4
H3	1926.2	957.6	7.1
L1	1851.3	1010.1	7.2
L2	1876.6	986.6	7.3

Freeze-dried FPH

The proximate chemical composition of FPHs is shown in Table 4. High-quality FPHs should have a high content of protein and low content of ash and lipids. Lipid oxidation is of great concern to the food industry and consumers because it results in unpalatable flavors, unpleasant odors, dark coloring, and potentially toxic reaction products (Kristinsson and Rasco 2000; Lin and Liang 2002; Spinelli et al. 1972). The Food and Agriculture Organization of the United Nations has issued a standard stipulating that the lipid content in FPHs used for human consumption must not exceed 0.5% (w/w) (He et al. 2013). Lipid content in freeze-dried FPHs from trawl and longlined cod heads were on average 0.6%. The correct commercial enzyme effectively produces hydrolysate with a low lipid content, whereas hydrolysis with only endogenous enzymes failed to have the same positive effect on lipid concentrations (Remme et al. 2022).

Ash contents were relatively high in hydrolysates from cod heads: about 7.7% for both trawl and longline caught heads. It is believed that the amount of bone affects the ash content. Ash contents also vary with type of enzyme, as the combinations of papain and bromelain produced hydrolysates with significantly lower ash contents ($P < .05$) compared with trials using endogenous enzymes and Protamex (Remme et al. 2022). The protein content in FPHs from trawl and longline caught cod heads was 91.2 ± 1.1% and 92.1 ± 0.9%, respectively. Heads from longlining have two different neck cuts, one when the fish is used for fillets (j-cut) and another for headed/gutted fish (n-cut).

Amino acid composition

The amino acid composition for trawl and longline caught cod heads is shown in Table 5 and shows no significant difference between the two different fishing gears. The dominant amino acids in these CHPH are glutamic acid/glutamine and glycine, which represents 10.2 ± 0.2% and 11.5 ± 0.2% of all the amino acids, respectively. Several studies have reported the same predominance of glutamic and aspartic acid in fish hydrolysates of several fish species (Vázquez et al. 2019). In addition, aspartic acid (5.5%), serine (5.3 ± 0.3%), proline (5.9 ± 0.1%), alanine (5.8 ± 0.1%), lysine (5.1 ± 0.1%), and arginine also make up a large part of the amino acids in the CHPH. Essential amino acids (Ile, Leu, Val, Lys, Met, Phe, Thr, His, Arg) are also significantly present in the CHPH and make up around 29% of the amino acids.

Degree of hydrolysis (DH)

The degree of hydrolysis represents the proportion of cleaved peptide bonds present in a protein hydrolysate. The DH of the FPHs was found to vary from 16.0% to 17.0% (Table 4). An optimum DH value has yet to be established, so it is currently not known how to both optimize solubility and minimize bitterness based on DH. The DH of the hydrolysate and the size of produced peptides highly influence the surface activity of FPHs (Jeon et al. 1999; Kristinsson and Rasco 2000). Several reports have suggested that there is an optimum molecular size or chain length for peptides that ensures good foaming and emulsifying properties, and that extensive hydrolysis that produces small peptide molecules reduces these properties (Adler-Nissen and Olsen 1979; Jeon et al. 1999; Kristinsson and Rasco 2000; Lee et al. 2014; Quaglia and Orban 1990; Šližytė et al. 2009). Another important factor that

Table 4. Proximate chemical composition and degree of hydrolysis (%) of freeze-dried FPHs from three trawl and two longline catches. Values are given as a mean ± std.

Sample	Protein (%)	Ash (%)	Water (%)	Lipid (%)	DH (%)
T1	90.2 ± 1.0	7.9 ± 0.3	1.1 ± 0.2	0.6 ± 0.1	17.0 ± 0.6
T2	91.6 ± 1.2	7.5 ± 0.3	0.6 ± 0.1	0.8 ± 0.1	16.5 ± 0.2
T3	91.5 ± 0.7	7.8 ± 0.7	1.3 ± 0.3	0.5 ± 0.1	16.4 ± 0.2
L1	91.5 ± 0.6	8.2 ± 0.6	1.6 ± 0.2	0.7 ± 0.2	16.6 ± 0.6
L2	92.9 ± 0.6	7.5 ± 0.1	1.0 ± 0.6	0.6 ± 0.6	16.0 ± 0.3

Table 5. Amino acid composition (g/100 g) for the combined trawl and longline cod head protein hydrolysates.

Amino acid	Trawl	Line	Mean	Std
Taurine	1.1	1.1	1.1	0.0
Hydroxyproline	2.0	2.0	2.0	0.0
Aspartic acid + Asparagine[e]	5.5	5.5	5.5	0.0
Threonine[e]	2.9	3.0	3.0	0.1
Serine	5.1	5.5	5.3	0.3
Glutamic acid + Glutamine	10.0	10.3	10.2	0.2
Proline	5.8	6.0	5.9	0.1
Glycine	11.3	11.6	11.5	0.2
Alanine	5.7	5.8	5.8	0.1
Cystine (Cys-Cys)	0.0	0.1	0.1	0.1
Valine[e]	3.2	3.3	3.3	0.1
Methionine[e]	1.8	1.9	1.9	0.1
Isoleucine[e]	2.2	2.2	2.2	0.0
Leucine[e]	4.3	4.4	4.4	0.1
Tyrosine	1.4	1.5	1.5	0.1
Phenylalanine[e]	2.4	2.4	2.4	0.0
Histidine[e]	1.4	1.4	1.4	0.0
Hydroxylysine	0.3	0.3	0.3	0.0
Lysine[e]	5.0	5.1	5.1	0.1
Ammonia	1.1	1.1	1.1	0.0
Arginine	5.3	5.4	5.4	0.1
SUM amino acids	77.8	79.9	79.4	
SUM essential amino acids (%)	28.7	29.2	29.2	

[e] *essential amino acids*

impacts the usefulness of FPH as a food ingredient is solubility. The solubility of FPHs increases with increasing DH (Gbogouri et al. 2004; Jamdar et al. 2010). A downside of high DH, however, is the production of bitter and astringent peptides (Adler-Nissen 1986; Saha and Hayashi 2001). The extent of changes in sensory properties is attributed to the degree of hydrolysis and, in particular, to the release of low molecular weight peptides constituted of hydrophobic amino acids (Raksakulthai and Haard 2003; Saha and Hayashi 2001).

Molecular weight distribution

In this study, fish protein hydrolysates were separated using gel chromatography in order to analyze peptide size composition (also known as molecular weight distribution). Since enzymes have specific cleavage positions on polypeptide chains, the resulting FPH products will consist of peptide molecules of different lengths (Barkia et al. 2010). The chain length of peptides, which depends on the DH, is of special interest in relation to FPH sensory characteristics, such as bitterness, as well as functional properties, such as emulsion capacity and solubility (Gbogouri et al. 2004). An analysis of peptide size distribution (Table 6) shows that the molecular weight distribution is similar in trawl and longline caught CHPH. Seventy percent (70%) of the peptides is below 5 kDa in size, and 94% is below 15 kDa. Most peptides, about 33%, are between 1 and 2 kDa, while 56% is under 2 kDa. In a previous study, with fresh heads from the coastal fleet that were hydrolyzed under the same

Table 6. Proximate molecular weight distribution for cod head hydrolysates from line and trawl caught fish.

Sample	> 20 kDa	20–15 kDa	15–10 kDa	10–5 kDa	5–2 kDa	2–1 kDa	1–0.5 kDa	0.5–0.2 kDa	< 0.2 kDa
T1	0.03 ± 0.00	0.21 ± 0.06	14.10 ± 2.60	12.43 ± 0.99	17.20 ± 0.34	32.88 ± 2.03	10.22 ± 1.42	2.94 ± 0.44	10.00 ± 0.10
T2	0.05 ± 0.00	0.17 ± 0.07	12.51 ± 1.94	11.89 ± 0.43	17.00 ± 0.10	34.14 ± 1.47	11.30 ± 0.81	3.22 ± 0.19	9.73 ± 0.14
T3	0.05 ± 0.01	0.12 ± 0.00	13.32 ± 0.12	12.67 ± 0.01	17.54 ± 0.11	32.94 ± 0.08	10.16 ± 0.07	3.01 ± 0.01	10.20 ± 0.59
L1	0.07 ± 0.00	0.14 ± 0.02	12.66 ± 2.26	12.34 ± 0.73	17.38 ± 0.14	33.74 ± 1.58	10.61 ± 0.95	3.06 ± 0.29	10.00 ± 0.30
L2	0.06 ± 0.0	0.12 ± 0.02	12.91 ± 1.74	12.77 ± 0.63	17.73 ± 0.14	33.18 ± 1.41	9.98 ± 0.83	2.89 ± 0.25	10.35 ± 0.44

Table 7. Generic Descriptive Analysis (GDA) mean values of sensory attributes (scale 0–100) for five sample groups of hydrolyzed fish proteins.

Sensory attribute	T1	T2	T3	L1	L2	p-value
ODOR						
Dried fish	19	29	23	23	23	0.163
Fish skin	21	24	23	26	27	0.452
Sour	3	5	5	3	4	0.363
FLAVOR						
Dried fish	27	30	25	26	28	0.712
Fish skin	23	28	28	33	31	0.191
Sour	5	5	4	4	6	0.829
Salty	7	6	6	6	7	0.410
Bitter	13	14	14	15	19	0.594
Astringent	20	17	16	20	22	0.098

conditions, there were major differences in MW-distribution. In this study, 39% of the peptides were between 2 and 5 kDa in size. Eighty percent (80%) of the peptides were smaller than 5 kDa in size, and 40% were smaller than 2 kDa.

The MW of bitter-tasting peptides is somewhat disputed (Fu et al. 2018b; Idowu and Benjakul 2019), but more recent studies indicate an association between the bitter attribute and peptides with MW 0.5 to 1 kDa (Aspevik et al. 2016; Fu et al. 2018b).

Sensory analysis

No differences were seen between sample groups for hydrolyzed fish proteins (Table 7). Average value for fish skin flavor was highest in samples L1 and L2 but lowest in sample group T1. All samples had a mild odor and flavor of dried fish and fish skin but no sour odor and very mild or hardly detectable salty taste. All samples had a trace of bitter taste. A mild astringency was detected in all samples, with the strongest in L1 and L2 and weakest in T2 and T3.

Bitterness in FPHs is associated with hydrophobicity, degree of hydrolysis, molecular weight, proline residues, type of enzymes, and amino acid sequences (Idowu and Benjakul 2019). Bitterness limits the use of FPHs in food. Hydrophobic groups of amino acids responsible for bitterness are tryptophan, phenylalanine, isoleucine, trypsin, valine, and leucine (Idowu and Benjakul 2019). The more hydrolysis, the higher the extent of degradation of native protein structure and the more exposure of hidden hydrophobic peptides causing bitterness are attained (Fu et al. 2018a; Idowu and Benjakul 2019). Several methods have been described to reduce bitterness, such as extraction with alcohol (Wasswa et al. 2007), treatment with activated carbon (Saha and Hayashi 2001), chromatographic separation (Liu et al. 2014), and the use of butanol (Dauksas et al. 2004). However, all mentioned methods will result in a significant loss in yield. A reduction in yield can make commercial production irrelevant. Before debittering methods are used, hydrolysis should be adapted and optimized based on the raw material.

Conclusions

Fishing gear affects the quality of cod heads. Cod heads from both trawl and longline differ in redness in the neck cut, and this is related to poor bleeding. In this study, however, there were no significant differences in cod heads from three trawl catches and two longline catches. Cod heads from both fishing gears resulted in white protein hydrolysates, with no significant differences detected. The hydrolyzed proteins had a mild fish odor and fish flavor, a trace of bitter flavor, and were mildly astringent. The lipid content was low (0.65 ± 0.11), and the protein content was high (above 90%), indicating that cod heads are an excellent source for production of protein hydrolysates that can be used for human consumption.

Acknowledgments

This research study was funded by the Norwegian Seafood Fond (FHF, grant no 901308) and the research council of Norway (RCN, grant 313945 (SMART) and 294539 (SUPREME)), for which we are most grateful. We are also grateful to the company Leinebris and Lerøy/Havfisk for supplying cod heads from longline and trawl, respectfully. We also extend our thanks to Marte Schei, Merethe Selnes, Revilija Mozuraityte and Bendik Toldnes at SINTEF Ocean for their assistance during experimental and analytical work.

Author agreement statement

The authors hereby declare that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This research study was funded by the Norwegian Seafood Research Fund [grant no. 901308] and the Research Council of Norway [grant nos. 294539 and 313945] for which we are most grateful.

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