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Potential Use of Arrowtooth Flounder (*Atherestes stomias)* Protein as Edible Coating in Food Industry

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Abstract

Arrowtooth flounder is one of the largest and highly underutilized resources found in the Gulf of Alaska. It supplies enormous amounts of proteins only to be discarded due to a peculiar reason; the presence of endogenous proteolytic enzyme that turns the flesh mushy by breaking down the proteins in the tissue. Several researches have been done to minimize the effect of the enzyme only to achieve a limited success. Efforts have been attempted to incorporate the arrowtooth flounder in surimi manufacturing, although it has to be mixed with different fish like pollock to produce an acceptable surimi in the market. A new approach has been recently taken by some researchers to produce engineered fish protein powder from the underutilized arrowtooth flounder and use it as edible films and coatings on different food products. Different functional, nutritional and rheological properties of the arrowtooth flounder protein powders have been evaluated and products like fish protein mayonnaise have been successfully demonstrated. This review gives an in depth information of arrowtooth flounder protein's potential to the food industry as a component of surimi and edible films, coatings and the properties of proteins applicable to the food industry.

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Introduction

Arrowtooth flounder (*Atherestes stomias)* is one of the largest resources in Alaska and has not been profitably exploited by the seafood industry. Utilization of arrowtooth flounder resource was identified in 1990 by the National Fisheries Institute towards annual seafood consumption of twenty pounds per person. Processing difficulties, high bycatch and poor market conditions posed a roadblock to the development of this resource (Cullenberg 1995). Arrowtooth flounder is currently the most abundant groundfish species in the Gulf of Alaska. In 2003, the estimated biomass and available biological catch of arrowtooth flounder were reported to be 2,391,550 and 155,139 tons, respectively (NOAA 2004). The proximate composition of arrowtooth flounder fillets as reported by Sathivel et al. (2005) shows 5 % lipid, 77.4 % moisture, 17 % protein and 1.1 % ash on wet weight basis. Although a significant portion of this fish is harvested, it is not utilized for human consumption. Seafood processors producing fish fillets utilize 20-25 % of the harvest, while surimi companies use 10-15 % (M.A. Moir, Alaska Pacific Foods, pers. comm.). A billion pounds of protein are thrown into the ocean annually by Alaska's fishing and processing industries (Goldhor 1990).

Enzyme Significance

Underutilization of alternative species such as arrowtooth flounder is concurrent with problems of low recoveries in developed fisheries. However, arrowtooth flounder has not been developed commercially due to an endogenous proteolytic enzyme causing rapid softening of flesh during cooking (Greene and Babbitt 1990). Heat activated enzyme occurring in arrowtooth muscle degrades myosin affecting the textural properties of fillets and surimi (Wasson et al. 1992). Wilson and Choudhury (2003) used a technique of pH-stat to confirm with previous studies that the optimum temperature and pH of protease enzyme of arrowtooth flounder was 58^{o} C and 6.5, respectively. Protease inhibitors do not help in improving surimi yields of arrowtooth flounder (Reppond and Babbitt 1993). Choudhury and Gogoi (1996) reported destruction of enzymes using high energies and temperatures that are not feasible for the surimi industry. As a result over 90 % of arrowtooth flounder is discarded, ranging from 20,000-29,000 metric tons per year (Cullenberg 1995; Wasson et al. 1992). Wasson et al. (1992) isolated, purified and characterized the heat stable

protease in arrowtooth flounder for future utilization of this species in surimi production.

Emulsifying properties of proteins

An ability of a protein to aid the formation of an emulsion is related to its capacity to adsorb to and stabilize the oil-water interface. Emulsifying properties are important for many food applications or ingredient proteins. These are commonly discussed in terms of emulsifying capacity (EC), emulsifying stability (ES) and emulsifying activity (EA). The emulsifying capacity is the maximum amount of oil that is emulsified under specific conditions by a standard amount of protein.

Emulsions are not stable in thermodynamic strength. Emulsion stability can be affected by breakage of different emulsions by different processes depending upon temperature, gravitational field strength and concentration of oil in emulsion. Operationally, a stable emulsion is one that is slow to undergo various processes and eventually results in separation of oil and water phases. The ES is commonly measured in terms of the amount of oil and/or cream separated from an emulsion during a certain period of time at a stated temperature and gravitational field.

Extraction of proteins from fish

Various methods are used to isolate proteins and peptides from fish tissues. Protein powders are prepared by following a cooking method (Sathivel et al. 2005). After cooking, fat cells rupture releasing oil in the liquid phase. The oil is removed while soluble and insoluble proteins in heavy liquid and semisolid phases respectively are separated and freeze dried.

Similarly extraction of proteins from fish can be carried out by enzyme hydrolysis. Hydrolytic enzymes such as alcalase are used to cleave the peptide bonds in the protein. An important feature of enzyme catalyzed process is termination of reaction; hence the enzyme has to be inactivated by pasteurization. The emulsifying capacity of protein can be increased considerably by enzyme hydrolysis (Peterson 1981). Viscosity is another functional property, where high protein concentrations often desirable may be impossible to handle because of high viscosity. This problem can be overcome by hydrolysis. Proteins prepared by enzyme hydrolysis have marginal viscosity.

Use of salt solutions has been traditionally accepted as a means of isolating protein fraction from fish muscles. Separation of myoglobin

fractions using sodium chloride precipitation methods showed inconsistent and variable results (Dyer et al. 1950).

A protein can be isolated in its intact form by adjusting pH. Fish muscles are subjected to strong alkaline treatment and insoluble fraction of protein is separated after centrifugation. The remaining liquid is brought to an iso-electric pH and acid solubilized protein is separated. This protein has got limited solubility.

In cooking processes, proteins are partly or wholly denatured during heat treatment or extraction procedure and the protein becomes less hydrolysable (Sathivel et al. 2004). In acid solubilized protein, intact protein is separated which might affect the functional properties of protein. Proteins isolated by partial enzyme hydrolysis are cleaved and known to possess anti-oxidation properties against peroxidation of lipids and fatty acids (Kim et al. 2001).

Protein powder from arrowtooth enzyme extract

Although most of the past research focused on removal and inactivation of the arrowtooth protease, Tschersich and Choudhury (1998) proposed that protease be employed in the recovery of residual muscle tissues from fisheries by-products. Proteins recovered were dried to create quality proteinaceous functional ingredients. Soluble proteins are derived from substrate during digestion of mice and frames of pollock. The heat stable arrowtooth flounder protease enzyme broke down muscles and skin tissues and helped concentrate soluble proteins over a period of time. Protein balance showed a marked increase in grams of protein in the liquid fraction of the total protein in skin and frame samples.

Arrowtooth flounder surimi

Babbitt et al. (1993) evaluated processes for producing arrowtooth flounder surimi using a continuous wash decanter process. They concluded that arrowtooth surimi produced with a blend of 50% of pollock surimi worked well in various seafood products when tested under commercial conditions. The texture of arrowtooth surimi was observed to be softer, flavors different but not fishy and color was slightly yellowish, compared to Pollock surimi. The color of arrowtooth could be lightened by exploiting the water content of the surimi. Reppond and Babbitt (1997) reported lightening (L* values) of arrowtooth flounder surimi from 77.2 to 80.0 with increase in moisture by 1 %. No differences in sensory attributes were detected between pollock and arrowtooth surimi products.

The ability of surimi to form an elastic gel depends on myosin. Heat induced gelation of surimi is a complex process involving structural and functional changes in myofibrillar proteins. The physiochemical changes of arrowtooth flounder myosin during heating and gelation mechanisms were studied by Visessanguan et al. (2000). The report suggested that in the absence of endogenous proteinases, the thermal susceptibility of arrowtooth flounder myosin provided the base to form high quality protein gel.

Arrowtooth flounder fish protein powder

Seafood by-products are protein rich and have potential to be used as binders, emulsifiers and gelling agents in food industry (Phillips et al. 1994). Use of amino acids and peptides are already gaining momentum in energy drinks and other applications (O'Donnell and Dornblaser 2002). Sathivel et al. (2004) developed and evaluated fish protein powders from hereon referred to as FPP from arrowtooth flounder. The FPP were studied further for their functional properties such as nitrogen solubility, emulsion capacity, emulsion stability and fat adsorption.

Solubility is one of the important physiochemical and functional properties of protein concentrate. The high nitrogen solubility of FPP indicates potential applications in formulated food systems by providing attractive appearance and a smooth mouth feel to the product (Peterson 1981). The FPP prepared from enzyme hydrolysis has higher solubility due to smaller peptides with increased availability of polar residues to form hydrogen bond with water. The ability of a protein to form stable oil- in-water emulsions is due to its emulsifying capacity. Protein solubility, peptide lengths and hydrophobicity play an important role in emulsion properties (Gauthier et al. 1993). A positive correlation between surface activity and peptide length was reported by Lee et al. (1987) and that a peptide should have a minimum length of 20 residues to possess good emulsifying and interfacial properties. The FPP samples exhibited an excellent ability of fat adsorption. Fat adsorption capacity is an important functional characteristic of ingredients used in meat and confectionary industries.

A thermal analysis was applied to FPP of arrowtooth flounder during extraction and preparation to study their alteration in physical state. Knowledge of thermal decomposition of FPP can be used to improve their stability and functional properties. Arrowtooth flounder FPP showed higher emulsion stability, emulsion capacity and fat adsorption than soy protein concentrate (Sathivel et al. 2004).

The FPP soluble were measured for their functional properties which showed 95.7 % nitrogen solubility, 59.9 % emulsifying stability, 0.3 water activity, respectively (Sathivel et al. 2005). The arrowtooth flounder FPP samples were light yellowish in color (L* = 86.3, a* = 2.2, b* = 2.8). Sathivel et al. (2004) also reported the molecular weight for arrowtooth flounder FPP as 13 kDa. Use of arrowtooth flounder proteins as potential emulsifiers also depends on an important functional property known as the fat adsorption. Many meat and confectionery industries rely on the fat adsorption capacity of different ingredients. Sathivel et al. (2003) reported a greater ability of binding to soybean oil in soluble arrowtooth flounder FPP than the insoluble. Peterson (1981) reported smooth mouth feel and enhanced product appearance due to the high nitrogen solubility.

Application of arrowtooth flounder FPP in mayonnaise

Potential uses as food ingredients are impacted by functional properties of proteins such as water-holding capacity, gelation, foam stability and emulsion capacity. Egg yolk is commonly used as emulsifier in many foods (Parades et al. 1989) such as mayonnaise. However, the amount of cholesterol in single egg yolk exceeds the recommendation for cholesterol intake of 300 mg day^{-1} (Wardlaw and Insel 1995). One alternative is to convert proteins from arrowtooth flounder into a higher value food ingredient suitable for use as an emulsifier and food supplement. Mayonnaise is an oil-in-water emulsion containing basic ingredients (vegetable oil, egg yolk, vinegar, lemon juice) and additives. Emulsion stability is one of the most important qualities of mayonnaise. Other proteins have been reported to provide desirable emulsifying properties in mayonnaise and salad dressing systems (German et al. 1985; Song and Damodaran 1987). Sathivel et al. (2005) successfully proved that egg yolk can be substituted with arrowtooth flounder protein powder in an oil-in-water emulsion system such as mayonnaise. Soluble and insoluble proteins in arrowtooth flounder differ in their functional properties. Rheological studies showed that mayonnaise like products made from soluble protein of arrowtooth flounder has viscoelastic properties with G'> G". Sathivel et al. (2005) concluded that soluble protein powder from arrowtooth flounder can be used as a potential emulsifier and identified opportunities for development of value added products from underutilized arrowtooth flounder.

Edible films and coatings

Edible, protective coatings and film are applied to foods to prolong their storage life. Possible functions are to retard moisture migration, for

gas transport (O_2 and CO_2), oil and fat migration and soluble transport, improve mechanical handling properties of foods, impart added structural integrity to foods, retain volatile flavor compounds and carry food additives. For many food applications, important functional characteristics of an edible film or coating, is to resist migration of moisture. Labuza (1982) showed that increased water activity of about 0.40-0.45 results in loss of crispiness in dry cereal based snack foods. In addition to water vapor transmission suppressing transport of gases also influences storage stability of foods. In fact, the use of edible coatings to suppress aerobic respiration would have a significant economic advantage over equipment operation of controlled atmosphere packaging. Edible film or coating, if highly impermeable, may also retard absorption of oils in to the food, thus yielding improved nutritional and organoleptic qualities. Finally, edible coatings and films can reduce injury to frozen foods, lessen surface browning in foods susceptible to oxidation, and add structural integrity to structural and molded foods (Mellethin et al. 1982).

Applications of edible coatings in seafood

Frozen storage of fish is an effective means of preservation that prevents or minimizes undesirable chemical changes that a fresh fish undergoes. However, at long term storage, fish and fish products still deteriorate although at a reduced rate. The oxidation of unsaturated fatty acids or triglycerides in seafood involves the formation of free radicals and hydro peroxides. Compounds such as ketones aldehydes and epoxides are formed during oxidation of unsaturated fatty components. Lipid oxidation takes place in fresh and frozen seafood. Oxidized unsaturated lipids bind to proteins and form lipid-protein complexes (Khayat and Schwall 1983). Edible protective coatings can lessen the quality changes and prolong storage life in foods such as frozen fish by acting as barriers to control moisture, oxygen uptake, loss of volatile aromas and flavors and drip loss. Edible coatings can be made from proteins, polysaccharides and lipids or a combination of these materials either by layers or emulsions (Kester and Fennema 1986).

Many types of coating materials have been tested in attempts to maintain the quality of frozen seafood. Ice glazing has often been used to retard moisture loss and lipid oxidation (Khayat and Schwall 1983), but brittleness of ice and loss due to sublimation requires the fish to be reglazed periodically during frozen storage (Wheaton and Lawson 1985). Gelling polysaccharides as alginates have been applied as coatings to frozen foods, but were no more effective than ice glazing (Ijichi 1978).

Proteins have not been investigated as extensively as other biopolymers for edible coating and films (Krochta 1992).

Arrowtooth flounder as edible coating

Arrowtooth flounder protein can be used to prepare edible coatings. The recent study by Sathivel (2005) compared different coatings such as the egg albumin, chitosan, arrowtooth flounder protein, salmon protein and soy protein, respectively, on pink salmon fillets during 3 months of frozen storage. Results of the study showed that although chitosan (polysaccharide coatings) were superior, there were no differences in the relative moisture loss and lipid oxidation of the salmon fillets when compared with arrowtooth flounder protein coatings. The arrowtooth flounder coatings decreased the moisture loss, minimized lipid oxidation, and increased the yield significantly in comparison to non-coated fillets.

Use of arrowtooth flounder protein edible film

Edible films from the different soluble and insoluble proteins of arrowtooth flounder can be prepared. Edible films could be analyzed for moisture, ash, lipid and protein for the proximate composition. Color measurements can be obtained from the prepared edible films. The edible film solubility in water, HCl, NaOH and urea could be determined following the method of Rhim et al. 2000. Oxygen permeability and thermal decomposition rate of edible films prepared from arrowtooth flounder proteins can be measured.

Conclusions

In view of the growing concern for the environment, enormous post harvest losses and expensive pre-treatment standards, by-product management is a major problem in the entire seafood industry. While only a fraction of by-products is converted into fish meal and oil, the remainder is dumped into nearby marine waters. Different attempts to incorporate arrowtooth flounder in surimi production have not achieved a major breakthrough. Recovery of muscle proteins from fish processing by-products, by-catch and other underutilized fish such as the arrowtooth flounder, provides an avenue to augment utilization of harvested catch. This review tries to examine the potential of protein powders from arrowtooth flounder as an edible coating and edible films, evaluate its effective-

ness and compare their effects on rates of moisture loss and lipid oxidation on chilled and frozen salmon fillets. Arrowtooth flounder protein coatings have shown to retard the unfavorable chemical changes in fish fillets like lipid oxidation and moisture loss, during the frozen storage. The color and texture properties of the fish also seem to be better protected by the edible coatings than that of the non coated fillets. An increased coating yield, thaw yield, cooked yield and reduced drip losses in the fish fillets will certainly help the seafood industry in the U.S to consider the potential of arrowtooth flounder proteins as an invisible protective edible coating on seafoods.

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