MODIFIED ATMOSPHERIC PROCESSING AND PACKAGING OF FISH

Filtered Smokes, Carbon Monoxide, and Reduced Oxygen Packaging
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Demand for seafood around the world and within most countries is beginning to exceed the supply. Despite significant advances in aquaculture production, predicted trends indicate this deficit will grow through the next decade. Commercial response is seeking products from more distant and nontraditional sources, which include new varieties and alternative selections. More distant, international exchange is increasing. The most recent report addressing the status of world fisheries issued in 2005 by the Food Agricultural Organization (FAO; http://www.fao.org//DOCREP/007/y560De/y5600e.htm) indicates nearly 40% of the world fishery resources are involved in international exchange. Developing countries account for over 55% of the fishery exports, while developed nations (i.e., Japan, United States, and the EU) account for 82% of the total value of imports. Over 90% of this international exchange involves processed products. The growing dependence on more distant and time-consuming exchange of fishery products requires processing and packaging options that help preserve product quality and product shelf life. Continuing reliance on modified atmospheric processing and package is inevitable, but this technology involves concerns for operational issues, regulatory guidelines, and market expectations. This book offers the most recent assessments of this technology by a special selection of scientific, regulatory, and commercial expertise.
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I

USE OF CARBON MONOXIDE AND FILTERED SMOKES IN FISH PROCESSING
1

USE OF FILTERED SMOKES AND CARBON MONOXIDE IN FISH PROCESSING

W. Steven Otwell

1.1 Historical perspective

The use of smoke and carbon monoxide (CO) with seafood began shortly after the caveman invented fire and learned how to catch fish. As with many new discoveries, the results were preferred without a complete understanding of the causes or the consequences. The sensory benefits encouraged progressive refinements that are still occurring today. Although current users can reference significant experience since prehistoric time, the recent developments in fish processing with filtered smokes and carbon monoxide are driven more by benefits rather than understanding.

The current preference is for a more appealing color in red and pink tones in fish muscle exposed to smoke or gas blends containing carbon monoxide (CO). The red colors in the raw muscle are considered a sign of fresher or better quality fish than dark, yellowing, tan, or brown colors that denote aging, poorer quality, prior freezing, or actual product abuse. The color differences are largely due to the chemical state of certain pigments associated with the heme proteins in the fish muscle tissue (myoglobin) and blood (hemoglobin). Oxygen combines with the myoglobin to form the red pigment oxymyoglobin, which is essential for the function of the muscle, yet this pigment fades and progressively darkens to shades of brown as the muscle is oxidized during aging after death and during freezing. Applications of smoke or gases containing CO can maintain the red color in the muscle tissue.
Use of CO and Filtered Smokes

Exposure to CO actually “fixes” the red color such that the muscle tissue will resist oxidation or retain a portion of the red color during refrigeration or frozen storage. The CO reacts in a similar manner as oxygen but results in a more stable red pigment, carboxymyoglobin, that has a stronger bond with the heme proteins. The resulting shades and duration of the red colors depend on the amount and distribution of the heme proteins in the particular fish muscles and the amount of CO exposure.

The color changes in tuna and other fish muscle have been documented for many years (Brown et al. 1958; Sano et al. 1959; Sano & Hashimoto 1958; Heer & Karsti 1965), but commercial considerations to manipulate color with additions of CO did not emerge until the advent of processing with modified atmospheric packaging (MAP) in the 1970s. MAP became popular in efforts to extend the refrigerated shelf life of fresh fish by manipulating the gases used in MAP in order to retard the growth of spoilage bacteria. The effective MAP gas blends included varying concentrations of carbon dioxide (CO₂), nitrogen, and oxygen (Banks et al. 1980; Koski 1988; Martin 1981; Parkin & Brown 1982; Wilhelm 1982). Initial studies with meats suggested that small portions of CO could be incorporated in the MAP gas blends to help maintain red muscle color (Clark et al. 1976; El-Badawi et al. 1964; Gee & Brown 1978; Wolfe 1980). Concentrations as low as 1.0% CO were found to be effective in maintaining red color in MAP of fish (Brown et al. 1980). Interestingly, as of 2005, the obvious benefits of using CO in MAP of meats or seafood have not been incorporated in common processing operations. Possible deterrents may range from safety concerns in processing to consumer perception of the CO process and products, but recent patents and regulatory decisions recognizing the use of CO with meat and fish could renew commercial interests.

Patents for specific applications of CO to impart color in meats, poultry, and fish began to appear in the late 1980s. Woodruff and Silliker (1985) introduced a process to expose fish to about 0.10–1.5% CO in MAP with CO₂ levels higher than 10%. This patented process could not only be used for red color retention in fresh, nonfrozen fish, but it could also be applied to fish prior to frozen storage. Later, Yamaoka (1996) offered an alternative approach to apply CO to fish prior to packaging. The inventors considered the process was “extra-low temperature smoking” conducted by exposure to filtered smoke cooled between 0 and 5°C. One apparatus provided four basic steps: (1) Burning of wood to generate smoke; (2) filtering the smoke to remove tars; (3) cooling the filtered smoke below 5°C; (4) smoking the fish to impart taste and color retention. The patent claimed that the resulting
product would appear similar to raw fish, but the process could impart tastes depending on the processing temperatures, kind and quality of smoke, and selection of the filters. The actual claims indicated the process involved curing of the fish, including preimmersion in salt water prior to smoking.

In contrast, Kowalski (1999) patented a process to retain red color in fish muscle by applying filtered smoke that did not impart tastes and the finished product was to be frozen. Again, CO generated with smoke from burning of organic matter was the active agent necessary to stabilize the red color in the heme protein. The process was considered unique because of the burning temperature used to generate the smoke and the filtering process yielding a “super-purified smoke.” The burning temperature could range from 500 to 800°F (260–571°C). Super-purified was defined in terms of threshold levels for detection of odor and taste sensations in the filtered smoke and treated products. Product treated with the super-purified smoke would not exceed the threshold levels. The empirical evidence suggested these detection thresholds for the phenolic fraction in the gaseous vapor phase of the smoke would preferably range below 10.4 ppm. The preferred level for the total aromatic phenols in the fish was 9.4 ppm by weight per total weight of the treated product. It was not clear how these levels were derived or could be monitored, but the intent was production of stabilized color with no detectable smoke taste. The process would produce fish with “vitality” similar to fresh, nontreated fish. The patent definition for vitality was based on preserved freshness, color, texture, natural flavor, and moisture. The filtered smoke, with CO concentrations ranging about 30% by volume, was stored and aged in cylinders prior to direct application to cuts of fish held in plastic bags. The patent suggested this process would provide preservation through antimicrobial and antioxidant properties associated with common applications of smoke.

The Kowalski patent and concurrent reviews by the U.S. Food and Drug Administration (FDA) ignited commercial applications of filtered smokes and CO for color retention in seafoods (FDA 2000). Initial interest followed the intent of the patent for use with fish to be frozen. Freezing without detrimental discoloration of certain fish, primarily tunas, has opened significant markets in more distant locations that are not readily accessible with fresh, nonfrozen fish. In part, adoption of this technology explains the significant increase in imports into the United States from the Indo-Pacific regions beginning in 1996 (Table 1.1).

Although the original tasteless smoking process involving specific criteria for generation and filtering of smoke was protected with patents and royalty agreements, commercial innovations introduced
Table 1.1 Total annual imports of yellowfin tuna (Thunnus albacares) into the United States from a selection of Indo-Pacific nations.

<table>
<thead>
<tr>
<th></th>
<th>Indonesia</th>
<th>Philippines</th>
<th>Vietnam</th>
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<tr>
<td>1994</td>
<td>937</td>
<td>836</td>
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<tr>
<td>2002</td>
<td>3038</td>
<td>2798</td>
<td>2541</td>
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Note: Significant increases in imports since the 1996 introduction of processing seafood with filtered smokes and carbon monoxide.

new methods for filtering and applying smoke and some actual direct applications with CO gas. Modifications included batch-type operations in pressurized chambers, additional product treatments with ozone, and postharvest euthanasia of cultured fish. The option with least obligation and expense has been simple application with CO gas. This trend has created a debate between operations with filtered smokes vs. CO gas with allegations that direct applications with elevated concentrations of gas, higher than 30–40% CO, produce “unnatural colors” and more potential economic fraud through enhancement of inferior products. The controversy lacks for methods and standards to distinguish products and processes.

Despite the confusion, market demand for the treated product remains strong and commercial response is expanding with applications for more species and different product forms. Convenience, product appeal, availability of both frozen and thawed, and reduced costs are driving demand. Original frozen tuna steaks are now complemented with growing markets for a variety of fish from certain imports (i.e., groupers, snappers, mahimahi, swordfish, and shark) and aquaculture (i.e., Tilapia, catfish, and salmon). The selections still involve fishery resources from more distant locations, which require freezing to maintain product quality, but commercial inquiries are exploring applications for fresh fish.

Recent patents for the use of CO in stabilizing red color in fresh meats could encourage further applications with fresh fish. In 2002 Pactiv Corporation introduced a MAP system (ActiveTechTM) for case-ready...
meats and ground meats that provided color retention by packaging with gas blends of 0.4% CO, 30% CO₂, and 69.6% nitrogen (FDA 2002). Two years later, Precept Foods, LLC, followed with a MAP system with similar color controls in tray packs of beef and pork; this system was based on a gas blend of 0.4% CO, 20–100% CO₂, and 0–80% nitrogen (FDA 2004). Because of the market size and influence of these commodities, any success with CO packaging for color control in fresh meats could stimulate a similar response for fresh seafood.

1.2 Regulations

Intentional use of filtered smokes and CO to retain red colors in fish preceded any formal regulatory recognition. Letters seeking clarification for such commercial practice were exchanged between the FDA, the National Marine Fisheries Service (NMFS), Hawaii’s State Department of Health, and technical interests as early as 1996 (Brunetti 1998; Hoskins 1998; Young 1996). The concerns questioned food additive status for CO, product nomenclature for labeling, and potential economic adulteration (product enhancement). Mounting concern culminated in an FDA Import Bulletin issued in May 1999 in response to processing of tuna with “tasteless smoke” (TS) in Indonesia, the Philippines, and Taiwan (FDA 1999). The bulletin did not object to the new processes, but emphasized the requirement for mandatory labeling to distinguish fish treated with CO or TS. The recommended labeling information as part of the ingredient statement was “tasteless smoke (preservative to promote color retention).” According to the bulletin, treated products without appropriate labeling information would be considered misbranded. The bulletin also advised that abusive use of these preservatives, which could be distinguished as product with “artificial, unnaturally bright red color, should be subject to analysis for decomposition and histamine, since there is no official method to test for TS or CO.”

The initial FDA position was more formally restated in the following GRAS notification No. 000015 issued in response to a request by Kowalski’s company, Hawaii International Seafood, Inc. (FDA 2000). This response specifically addressed the use of TS with tuna products that were to be frozen after treatment in accordance with the original Kowalski patent. FDA considered that the TS was a preservative and that it required label declarations stating both the common and usual name of the ingredient and a separate description of its function. FDA cautioned that fish preserved with TS should not be represented as a
“smoked” product and it may also not be identified as a “fresh frozen” product. FDA regulations do not allow the use of the term “fresh” with products containing a preservative. Subsequent presentations by FDA (Brunetti 1998) offered additional examples for appropriate labeling which suggested a similar position for TS and CO treatments. The recommended labeling information for the ingredients statements included:

- Tuna, Carbon Monoxide (as a color preservative)
- Tuna, Tasteless Smoke (as a color preservative)

This position, recognizing use of CO, was further reinforced in an FDA letter to the NMFS Seafood Inspection Program, which identified “carbon monoxide” as the common and usual name for CO when used in foods (Wilson 2004).

Concurrently, the voluntary inspection program, based on fees-for-service conducted by the National Marine Fisheries Service, began working with various international firms to provide process verifications and operation audits for CO/TS products to be imported into the United States. In addition to their prerequisites for sanitation and product quality, NMFS has tried to develop a color scheme that relies on actual measurements for color shades and progressive fading in thawed product that distinguishes the proper commercial methods. Their program was to inspect and certify only tuna products treated with TS and only those products that originate from firms that NOAA has verified to employ acceptable process controls (McKeen 2002). The products were also to be in compliance with all other applicable legal and regulatory requirements. They provide a listing of the approved firms verified under contract with NMFS.

The controversial regulatory responses were influenced by the years of commerce and consumption of foods exposed to smoke that contains CO. Previous FDA regulations also recognized the food additive used for combustion product gas in food packaging that included a carbon monoxide content of 4.5% by volume (21 CFR 173.350). Likewise, the U.S. Department of Agriculture (USDA) has allowed the use of wood smoke containing CO as an ingredient in meat and poultry (9CFR 318.7, 381.147, and 424.21).

The more recent FDA decisions regarding the use of CO in MAP of meats have specially declared that CO is a “processing aid” that does not require product labeling declarations (FDA 2002, 2004). FDA was convinced that the small portion of gas (0.4% CO) as used in the MAP system for meats complied with the legal definition for a processing
aid because it did not have a lasting functional effect in the food and there would be no significant amount of CO present in the finished products. This position could influence considerations for the use of CO in MAP of fresh fish as originally observed by Brown et al. (1980).

Regulatory concern for product safety in consumption of foods exposed to CO has been addressed and there are no apparent concerns (FDA 2002, 2004; Kramer et al. 1978; Post 1979), yet investigations continue with specific focus on fish (Davenport 2000). Safety margins have been based on the limited amount of CO absorbed into treated foods and the significant reduction of CO during cooking.

The more imminent safety concerns for CO-treated fish involve potential color masking of inferior, partially or previously decomposed, or thermally abused fish that are more prone to development of elevated levels of histamine. Tuna is a species of concern for elevated histamine, which is associated with scombroid poisonings (FDA 2001). For this reason, FDA has conducted limited surveys of suspect TS-treated and CO-treated fish. In response to consumer complaints of scombroid poisoning in Las Vegas, 18 samples of tuna identified as TS-treated product were found to be decomposed (Cruz et al. 2002). Continuing assessments for 106 samples of treated tuna imported through California found over 26% of the products with histamine levels in excess of the FDA’s defect action level of 50 ppm histamine. No doubt the potential scombroid poisoning due to color masking of certain fishery products that would otherwise appear spoiled is concerning, but the safety benefits from use of TS and CO treatments deserve equal consideration. Because the majority of potential scombrotoxic fish such as tuna originates in locations distant from popular markets, freezing is the best method to control and reduce potential histamine (scombrotoxic hazards). Applications of filtered smokes or CO allow use of freezing, which would otherwise discolor the product and reduce the market value and acceptance. Attempts to market such fish from distant locations as fresh, never frozen products jeopardize both product quality and safety. Likewise, subsequent inventories and handling are safer for frozen products.

Despite the advantages of color retention in frozen products, potential food safety issues and product deception remain the primary reasons why most major nations are still opposed to the use or import of filtered smokes or CO-treated fish. Presently, similar CO/TS fish products are not approved for commerce in countries other than the United States. Japan issued a notice banning fish that have an initial CO content of $\geq 500 \mu g/kg$, which decreases significantly during 2 days of refrigerated storage (Japan, Food Sanitation Law—Article 6). Reasoning