What is *warmed-over flavor?*

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Warmed-over flavor (WOF) has long been recognized as one of the primary causes of quality deterioration in cooked, refrigerated and pre-cooked, frozen meat products (Tims & Watts, 1958). The term "meat flavor deterioration" has been proposed to include both the development undesirable flavors (WOF) with concurrent loss of of desirable meat flavor characteristics (Spanier et al., 1988; St. Angelo et al., 1990). WOF is usually associated with reheated meats which have been refrigerated for 48 hours or less; WOF can develop in pre-cooked frozen meats in a few days or weeks. WOF includes odors and flavors commonly described as *stale, cardboard-like, painty* or *rancid* (Vega and Brewer, 1994; Love, 1988).

American consumers spend less time preparing foods at home and more money on convenience products such as pre-cooked entrees than ever before (Dumagan & Hackett, 1995; Hollingsworth, 1996;Bell, 1993). WOF is unacceptable to consumers whether they are purchasing pre-cooked meats to be reheated at home, prime rib sandwiches made from yesterday's prime rib in a restaurant, or heating up left-over pot roast from Sunday dinner. As consumer demand for table-ready, reheatable entree items has increased, so have the WOF problem-solving efforts.

What causes WOF?

WOF starts with oxidation of meat fats (Willemot et al., 1985; Pearson et al., 1977). Polyunsaturated fatty acids (PUFA), which contain less hydrogen on the fatty acid carbon chain than they could, are more likely to oxidize than saturated fatty acids. PUFA, located primarily in the cell membrane as phospholipids, are prone to lose additional hydrogen atoms at points on the carbon adjacent to the points of unsaturation. Hydrogen abstraction from these points forms lipid (fat) *free radicals* which are extremely reactive and tend to take up oxygen (oxidize) very quickly. Once the fat molecule takes up oxygen, it usually breaks apart into smaller molecules, such as pentanal, hexanal, and 2,4-decadienal, which have the off-odors and flavors we recognize as *warmed over* (Vega and Brewer, 1994). These substances are extremely volatile and perceptible in very low concentrations (parts per billion) (Vega and Brewer, 1994). These small molecules are fat-soluble and may partition into the melted fat phase where they are retained until the fat is reheated (Mottram & Edwards, 1983). Meats containing more polyunsaturated fat are more likely to oxidize and develop WOF. Because of their relative PUFA content, fish > poultry > pork > beef > lamb as far as rate of off-flavor development due to oxidation and WOF is concerned (Cross et al., 1987).

A variety of things can trigger oxidation; most either add enough energy to push the oxidation reaction into occurring (heat, light, oxidizing enzymes), or they reduce the amount of energy necessary for the reaction to occur (metals, high-energy oxygen or enzymes). Heat (cooking) is one of the primary causes of the type of oxidation that occurs in WOF development. Heat causes proteins to coagulate so that they lose their functional capabilities: enzymes no longer assist with reactions, fibrous proteins can no longer hold onto water so they shrink, and the globin-bound heme fractions of hemoglobin and myoglobin can no longer hold onto iron. High temperature causes the release of oxygen and free iron as well as the production of free radicals (Kanner, 1994). The iron, which the globin-bound heme group usually holds onto and protects from coming into contact with oxidizable substances (Labuza 1971), now comes into contact with the PUFA. Free iron is unlikely to remain in its reduced (Fe^{2}+) state; it readily converts into its oxidized (Fe^{3}+) form. This conversion assists in generation of free radicals from meat fats (Love, 1987). There is still considerable debate as to the roles of heme-bound iron and free iron in the role of lipid oxidation (Gray and Pearson, 1994).

Oxidation is a chain reaction: once PUFA oxidation is initiated, it continues as PUFA free radicals catalyze additional free radical-generating reactions (Jadhav et al., 1996). The rate increases logarithmically. For this reason, heating meat encourages oxidation to proceed very rapidly. Salt, added for flavor and functional reasons to many processed products, has been shown to accelerate oxidation in pork patties (Buckley et al., 1989). Salt can enhance the activity of iron atoms thereby promoting iron-catalyzed oxidation and flavor deterioration (Kanner, 1994).

Metals, in addition to iron (copper, especially) supplied by water, processing equipment and spices, can also promote oxidation in meats. The most lipid pro-oxidative metals are transition metals able to undergo a single electron transfer during a change in oxidation states (Jadhav et al., 1996). Transition metals can react directly with lipids in oxidation reactions by reducing the amount of energy required for the formation of a free radical, and they catalyze the decomposition of the lipid hydroperoxide resulting in production of additional free radicals.

Light, especially certain wavelengths, can add enough energy to help the oxidation reaction get going. Light appears to *photoactivate* meat pigments and to elevate oxygen to a high-energy state increasing their abilities to participate oxidation (Jadhav et al., 1996). Some kinds of light, such as blue-purple fluorescent (and ultraviolet), are much worse than other types of light (red-orange tungsten halogen); the energy level of the former is ideal for promoting the oxidation reaction. The spectrum of light becomes important to the WOF problem because meat products, even pre-cooked, frozen items, may be displayed at retail for hours or days.

Oxygen is an integral part of the reaction that leads to WOF—unlimited availability increases the problem. The interior of whole muscle cuts contains very little oxygen, however mechanical manipulation may mix large amounts of air into the product. Grinding, chopping, mechanical deboning, chunking and forming, mixing and tumbling can all introduce air into the product ultimately promoting oxidation and WOF if the product is pre-cooked and stored (Sato & Hegarty, 1971; Pearson et al., 1977; Kanner, 1994).

Relationship of WOF to the meat industry.

When a consumer is dissatisfied with a product because of off-flavor, the reason for the flavor problem are immaterial, but the dissatisfaction may, and often does, result in future product rejection. The consumer will not be a repeat purchaser of that particular product (eg. pre-cooked breakfast sausage), and may discriminate against all products in that class (all pre-cooked sausage). The consumer maybe the family food buyer, the frozen pizza manufacturer, the wholesaler who supplies hospitals or the buyer for a fast-food restaurant chain. The economic damage to a manufacturer caused by unacceptable products goes beyond the product replacement cost; it includes, shipping and handling, time spent in handling the problem, and worst of all, the loss of reputation the company incurs when a product fails to meet the consumers expectations.

Prevention of WOF.

Prevention or delay of WOF development can be accomplished at several stages of the process. The raw materials are a critical part of prevention: fresh materials have had little time to undergo extensive enzymatic oxidation which can produce autocatalytic substances that will cause oxidation to continue even after the enzymes are inactivated by heat. Raw materials from animals whose diets have been supplemented with vitamin E (200 IU vitamin E/kg feed for pigs) are less susceptible to oxidation even when exposed to fluorescent light (Buckley et al., 1989; Ashghar et al., 1991). Vitamin E (alpha tocopherol) is a natural antioxidant which readily locates in the cell membrane where oxidation is most likely to be a problem because of the availability of relatively large amounts of PUFA.

Nitrite used in the curing of meat has long been know to have powerful antioxidative effects (Gray and Pearson, 1994) in concentrations as low as 50mg/kg of meat, completely inhibiting oxidation at 2000mg/kg (Sato and Hegarty, 1971). WOF in cooked pork can be reduced by a factor of five using the allowable nitrite level of 156ppm. The mechanisms by which this occurs are not completely understood but may include prevention of ferrous (Fe^2) iron release via complex formation with heme pigments, stabilization of PUFA in cell membranes, chelation of metal ions (Morrissey & Tichivangana, 1985; Freybler et al., 1989).

Antioxidants protect PUFA from oxidation by sacrificing themselves to the oxidation process; they delay the onset of oxidation by extending the induction period (Jadhav et al., 1996). Primary antioxidants are *free radical terminators* that bind the oxidative radical; antioxidants are consumed as they are converted to the oxidized state. Their protective effect is concentration-dependent, but it is also dependent on their fat-solubility and on the number of antioxidative sites on the molecule. Most antioxidants, including vitamin E, butylated hydroxyanisol (BHA), butylated hydroxytoluene (BHT), tertiary butylhydroquinone (TBHQ) and propyl gallate (PG) are phenolic substances, and may be naturally occurring or chemically synthesized; their fat solubilites differ affecting their applicability in muscle food systems. BHA, BHT,and TBHQ are effective at 100-200ppm, PG at 200-250ppm. The effectiveness of synthetic, phenolic antioxidants, compared to chelators, in the prevention of WOF is unclear; because they are lipid soluble, they are difficult to distribute in the product (Bailey, 1988). Shahidi et al. (1987a) found phenolic antioxidants to be effective in emulsion-type sausage products.

Oxidation, initiated or propagated by metal ions, can be effectively suppressed or delayed by chelating agents such as citric acid, ethylenediaminetetracetic acid (EDTA), and some phosphates which complex with metals (iron, copper) stabilizing them so they do not participate in the oxidation reaction. Combinations of sodium tripolyphosphate, pyrophosphate or hexametaphosphate (550ppm) with ascorbate (3,000ppm) effectively suppress lipid oxidation for 35 days in refrigerated, cooked pork (Shahidi et al., 1986).

Ascorbic acid and its mirror image molecule, erythorbic acid, function as oxygen scavengers in fat-containing foods. They are added to cured meat products to help prevent nitrosamine formation, but also serve to prevent lipid oxidation. In 1958, Tims and Watts demonstrated that ascorbic acid-phosphate mixtures retarded WOF development in cooked pork for up to 18 days (5-7°C). Ascorbic acid functions synergistically with other antioxidants and as a reducing agent (at low levels) alone. It can form a stable complex with prooxidant metals raising the energy required to initiate oxidation (Rajalakshmi & Narasimhan, 1996).

Herbs and spices contribute a variety of antioxidant substances. Common spices with antioxidative properties include rosemary, marjoram, sage, thyme, mace, allspice and clove (Bailey, 1988). Rosemary is particularly effective because of a number of phenolic compounds including carnosic acid (odorless), rosmanol (odorless), rosmariquinone and rosmaridiphenol which are effective antioxidants in steamed lard at 100ppm (Jadhav et al., 1996). Rosemary oleoresin (oil soluble) has been shown to be effective in turkey breakfast sausage (Barbut et al., 1985) and ground beef patties (St. Angelo et al., 1990). On the other hand, Lui et al. (1992) found that lipid stability in cooked, restructured pork steaks was with either water- or oil-soluble rosemary oleoresin+sodium tripolyphosphate was no greater than in those with phosphate alone during 8 months of frozen storage.

Maillard browning (reducing sugar-amino acid) reaction products, especially melanoidins, are strong antioxidants (Bailey, 1988). Products of the reaction of histidine with glucose have been shown to protect sausage from oxidation during frozen storage (Lingnert & Ericksson (1980). Bailey et al. (1987) reported that histidine-glucose reaction products (0.72%) greatly inhibited oxidation in pork.

Physical means of delaying the onset of WOF include oxygen exclusion by the use of technologies such as vacuum tumbling and vacuum stuffing prior to cooking, and vacuum packaging cooked products prior to storage. Because light can photosensitize meat pigments and oxygen, light exclusion may be a factor for some products. Pre-cooked products can be protected from oxidation by covering them with liquid or sauces prior to freezing. Covering pork with drippings or gravy made from the drippings can double the acceptable frozen storage life (-10 to -19°C) of cooked pork products (Korschgen & Baldwin, 1972; Dalhoff & Jul, 1965).

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