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Review Influence of salt on lipid oxidation in meat and seafood products: A review

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ABSTRACT

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Sodium chloride, commonly known as salt, is a widely used additive in food industry due to its preservation and antimicrobial properties provided by its ability to reduce water activity. Moreover, the addition of salt to meat and seafood aims at improving water retention capacity and enhancing flavor due to its influence on the activity of some enzymes responsible for flavor development. On the other hand, salt added in meat and seafood can favor lipid oxidation, which is one of the main responsibles for quality losses in the food industry. In this review, the main mechanisms of fatty acids and cholesterol oxidation are described as well as the influence of salt on lipid oxidation in meat and seafood. Besides, the possible mechanisms of the pro-oxidant action of sodium chloride are presented and potential solutions to inhibit the salt action in lipid oxidation and decrease the salt content in food are discussed.

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1. Introduction

Lipids, naturally present in food or added to processed food, have an important role in nutrition and flavor development. Moreover, lipid oxidation is the major cause of quality loss in food and a huge challenge to food industry and food scientists. Lipids present in food are susceptible to oxidative reactions resulting in the development of off-flavors, and

* Corresponding author. *E-mail address:* neurabragagnolo@gmail.com (N. Bragagnolo). loss of liposoluble vitamins and other bioactive compounds (Erickson, 2008; Chaiyasit, Elias, McClements, & Decker, 2007; Kolakawska & Bartosz, 2014; Souza & Bragagnolo, 2014). In fact, secondary products of lipid oxidation can also react with proteins, peptides and amino acids, contributing to protein oxidation which can result in loss of essential amino acids and changes in the protein or peptide structure leading to loss of functionality or biological function (Estévez, 2015; Estévez & Luna, 2016).

Lipid oxidation in meat and seafood starts immediately after slaughtering and continues during the post-mortem aging, while



muscle is converted into meat, and even during storage and processing. Several factors influence the rate and intensity of lipid oxidation in meat, among them there are some pre-slaughter events such as stress and physical injuries, and post-slaughter events such as pH, carcass temperature, cold shortening and tenderization techniques, for instance electrical stimulation. In addition, processing parameters also influence the oxidative stability of meat products, such as the composition and quality of raw meat, cooking or heating conditions, comminuting (grinding or mincing), the use of additives like salt, nitrite, spices and antioxidants, type of packing, as well as the temperature of distribution and storage, among other factors (Erickson, 2008).

The development of lipid oxidation can be followed by the primary products of fatty acid oxidation, such as hydroperoxides and conjugated dienes, or secondary oxidation products, such as pentanal, hexanal and malonaldehyde. Malonaldehyde is usually determined colorimetrically as tiobarbituric reactive substances (TBARS) (Mariutti & Bragagnolo, 2015). Other compounds that can be used for oxidation measure are the products of cholesterol oxidation, especially 7-ketocholesterol, and some aldehydes derived from fatty acid oxidation, such as 4-hydroxynonenal (HNE), and the fatty acids themselves, mostly the unsaturated fatty acids.

Sodium chloride (NaCl) is one of the most used additives in meat industry due to its low cost and diverse functionalities. Salt has preservative and antimicrobial properties as a direct consequence of its ability to reduce water activity of foods. Addition of salt to meat products improves the water retention capacity and also enhances meat flavor by influencing some enzyme activities. However, salt is widely known to accelerate lipid oxidation and consequently generate undesirable changes in color and flavor of meat and meat products decreasing their shelf life. In some cases, lipid oxidation is desirable, such as in the development of the typical aroma of some meat products like ham and dry cured loin and sausages (Jin et al., 2012).

2. Mechanisms of unsaturated fatty acid oxidation

The oxidation of unsaturated fatty acids is a complex phenomenon that occurs in the presence of oxygen, enzymatically or non-enzymatically, and is induced or catalyzed by light, heat, photosensitizers, metals and oxygen and nitrogen reactive species.

Non-enzymatic oxidation can occur by two mechanisms: autoxidation and photo-oxidation. The two mechanisms depend on the presence of oxygen; autoxidation occurs in the presence of molecular or triplet oxygen (${}^{3}O_{2}$), while photo-oxidation occurs in the presence of singlet oxygen (${}^{1}O_{2}$). Enzymatic oxidation occurs by the action of lipoxygenase and differs from the non-enzymatic oxidative processes. The role of enzymatic oxidation is not preponderant in meat and meat products; therefore, its mechanism will not be discussed in this review.

2.1. Autoxidation

The main mechanism of lipid oxidation in muscle food is autoxidation. Autoxidation consists in the reaction of triplet oxygen with organic compounds at moderate conditions. Triplet oxygen is a diradical species, i.e. one pair of its even number of electrons has parallel spins, and therefore, it can react promptly with radical species. The direct reaction of triplet oxygen with unsaturated fatty acids is not possible because their double bonds are in singlet spin state (electrons with opposite spin). Thus, an initiator to remove an electron from the unsaturated lipid generating a radical is necessary in order to the reaction between the triplet oxygen and an unsaturated fatty acid occurs. Therefore, lipid autoxidation is a chain reaction process induced by free radical generally described by means of three steps: initiation, propagation and termination. These steps are already well known and described by several researchers (Min & Boff, 2002; Frankel, 2005; Chaiyasit et al., 2007; Kim & Min, 2008; Schaich, Shahidi, Zhong, & Eskin, 2013).

Briefly, the initiation step occurs in the presence of initiators, such as light, heat, sensitizers, metals and/or oxygen and nitrogen reactive species. Then, the unsaturated fatty acids loose a hydrogen radical (H•) generating a fatty acid alkyl radical (R•) in the carbon atom that requires less energy. The bond energy necessary for abstraction of one alkyl hydrogen is 100 kcal/mol, while to remove allylic and bisallylic hydrogens, respectively, 75 and 50 kcal/mol are required (Min & Boff, 2002). In fact, the number of double bonds in the fatty acid molecule is related with the oxidation rate, for instance, in a proportion of 1:12:25 for oleic, linoleic and linolenic acid, respectively (Min & Boff, 2002; Kim & Min, 2008). During the propagation step, the free radicals react with triplet oxygen forming peroxyl radicals and these react with another fatty acids forming hydroperoxides. Several hydroperoxides are formed and due to their high instability, they decompose generating new radicals. The vast majority of the formed hydroperoxides are conjugated hydroperoxides (Belitz, Grosh, & Schieberle, 2009) Fig. 1 shows the main hydroperoxides derived from the autoxidation of linoleic acid, i.e. 13hydroperoxyoctadeca-9,11-dienoic acid and 9-hydroperoxyoctadeca-10,12-dienoic acid, that are conjugated hydroperoxides.

The decomposition of hydroperoxides is accelerated in the presence of transition metals, and in the case of meat and meat products, iron is the principal responsible (Erickson, 2008). The main characteristics of the propagation step are high oxygen consumption, increase of peroxide and hydroperoxide contents and alteration of the sensory characteristics of the food. In the termination step, the last step of autoxidation, a large amount of peroxyl radicals is accumulated and these radicals will react among each other generating non-radical compounds. Under atmospheric pressure, the combination between peroxyl radicals will occur forming unstable intermediate compounds that will decompose into stable non-radical compounds. Under low oxygen pressure, for instance in frying oils, the termination reactions will occur between alkyl radicals forming high molecular weight compounds such as dimmers or polymers of fatty acids. During this step, oxygen consumption and hydroperoxide content tend to decrease, the sensory changes increase and physical alterations start.

2.2. Photo-oxidation

The molecular oxygen in the ground state is in the triplet state $({}^{3}O_{2})$, being a diradical, and it can be activated by electronic excitation to a singlet state $({}^{1}O_{2})$. There are several ways of singlet oxygen generation, being the combination of ultraviolet light and photosensitizers, such as chlorophyll, myoglobin and riboflavin, the main one occurring in food (Frankel, 2005; Min & Boff, 2002; Kim & Min, 2008).

Singlet oxygen is more electrophilic than triplet oxygen, therefore, highly reactive. For instance, the reaction rate between linoleic acid and singlet oxygen is 1450 times higher than with triplet oxygen (Min & Boff, 2002).

Singlet oxygen reacts directly with unsaturated fatty acids through a cycloaddition mechanism forming fatty acid hydroperoxides. The singlet oxygen interacts with the carbon atoms located between the double bond, causing change of position and configuration of the double bond. Thus, mono-, di- and triunsaturated fatty acids, like oleic, linoleic and linolenic acid, will generate mixtures of two (9- and 10-hydroperoxides), four (9-, 10-, 12- and 13-hydroperoxides) and six hydroperoxides (9-, 10-, 12-, 13-, 15- and 16-hydroperoxides), respectively. Linoleic acid can form two conjugated and two non-conjugated hydroperoxides, while linolenic acid can form four conjugated and two non-conjugated hydroperoxides. Fig. 2 shows the two hydroperoxyoctadec-8-enoic acid and 9-hydroperoxyoctadec-10-enoic acid).

2.3. Decomposition of hydroperoxides

The hydroperoxides formed from unsaturated fatty acids by autoxidation, photo-oxidation or enzymatic oxidation will decompose in low Download English Version:

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