Oxygen Scavengers Applications in the Dairy Industry

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Abstract

The oxygen can harm the quality of some foods leading to a decrease in their shelf-life. Oxygen presence in food packaging is mainly oxygen residues in food and content in the headspace of the package, the oxygen permeating through the packaging material as well as due to failures in the packaging process. Basically, oxygen can lead to food spoilage in several ways including: oxidative spoilage leading to quality loss in fats and fatty portions of foods, lipids oxidizing, degradation of proteins, pigments and vitamin, providing conditions that will enhance the growth of microorganisms, darkening and enzymatic browning.

Several approaches have been applied to remove the oxygen present in packed food; among them, oxygen scavengers have been widely used to preserve perishable food such as dairy products. In the present short review, we discuss the different practical applications of oxygen scavengers regarding dairy product packaging. Oxygen scavengers application was described in protection such dairy products as butter, cheese, chocolate, powdered milk, and yogurt, demonstrating their high usefulness.

Future trends in the development of various forms of oxygen scavengers have been signaled.

Keywords: Dairy product; Food packaging; Oxygen scavengers; Shelf life

Introduction

The shelf life of packaged foods is based on product structure as well as packaging characteristics and storage conditions [1]. The basic functions of food packaging are closely linked to their role in ensuring food quality and safety in the supply chain and during the storage of food products by consumers [2]. One of the factors causing the losses of food quality is oxygen. Deterioration processes involved are autoxidation along with light-induced oxidation and microbial growth [3]. The challenge for the food industry is to provide dairy products with viable quality to a consumer by adopting an appropriate selection of packaging material.

There are many ways to prevent negative effects of oxygen on the packaged products. One of them is the application of such additives as antimicrobial agents or antioxidants. However, these food additives are undesirable and have a negative image within consumers. The current inclinations in extending the shelf life, safety, and quality of foods depart from using additives to controlling the food packaging system. Since oxygen is a major factor of food spoilage emphasis is given to controlling the atmosphere inside the packaging, especially oxygen contents. Modified atmosphere packaging has been successfully used to extend the shelf life of fresh products. To reduce the access of oxygen, foods are packed with barrier materials and the headspace of packaging is flushed with inert gas. However, residual oxygen can remain in the headspace; it can also permeate into the packaging as well as be solved in food [4]. There is a two-way approach to reduce the oxygen contents in the packaging. One way is the reduction of oxygen permeability of plastic packaging through application multilayer composite materials. The second is to eliminate oxygen from packaged foods and headspace by application of oxygen scavengers. Oxygen scavengers are materials that remove oxygen from the packaging through a chemical reaction. Oxygen scavengers extend shelf life of products by eliminating oxygen without being a part of the food itself, i.e., they are not food additives and they work from the outside. A multitude of oxygen scavengers was developed and tested [5,6]. Most of them can be subsumed under two broad categories: organic and inorganic systems. Inorganic systems are based on iron powder or different iron compounds mixed with activators. They are applied in the form of sachets or blended with polymer carriers. The iron based system is one of the most important commercial systems. Usually, iron powder exhibits particle diameter in the range of 10 to 30 micrometers which is much higher than the thickness of the packaging film. Another limitation is the inertness of metallic iron in dry conditions and needs humidity to work as an oxygen scavenger that eliminates their application for the packaging of dried or water sensitive products. All these drawbacks can be eliminated by the application of nano iron [4].

Oxygen Scavengers in Some Dairy Products Protection

During the storage and packaging of different dairy products like cheese, milk, dry powdered milk, butter, and yogurt, it is very important to ensure that they do not have any contact with oxygen as it will result in oxidative dilapidation and spoilage dairy products. It is to solve these issues that oxygen scavengers are so important for the food processing industry, especially the dairy branch. Examples of the use of oxygen scavengers in this area are mentioned in many review works, both the older ones, such as Brody AL [7], Miltz J et al., [8], Harima Y [9], Tian F, et al., [10], Realini CE, et al., [11], Cichello SA [12] as well as the latest ones published by Apicella A, et al., [5],...
Dey A, et al. [6], Rinkal P, et al., [13], Ščetar M, et al., [14]. Many studies showed the effectiveness of oxygen scavengers for different foods. Examples of the use of absorbers for selected dairy products will be listed in alphabetical order.

**Butter**

Butter is a dairy product that is highly susceptible to lipid oxidation, this phenomenon leads to the development of undesirable odors, resulting in an alteration of the organoleptic properties and the nutritional value, and therefore decreasing its shelf-life [15]. In several reviews, including already mentioned, butter is mentioned as one of the products that can be protected against rancidity by using oxygen scavengers. Recently, the evaluation of oxygen absorber system effectiveness in butter containers has been investigated by Spanish scientists [16]. They found that the applications of oxygen scavengers systems have demonstrated effectiveness and utility in reducing oxygen levels from the butter containers and could be a good option to protect butter samples from oxidation.

**Cheese**

As is well known, microorganisms play a key role in cheese production. Starter cultures for cheese manufacturing are typically mesophilic derived from traditional dairy-propagated starters. The relationship exists between the redox state in milk and acidification kinetics of the predominant subspecies in DL-starter cultures and oxygen dissolved in milk [17]. However, some microorganisms are useful in cheese production, others are not and can cause cheese deterioration. Generally, hard cheeses that do not have high water content are prone to mold attack, while moist cheeses can be affected by bacteria. Also, the fats contained in some cheeses are prone to oxygen oxidation in the air, which can lead to rancidity of cheese. The control of oxygen levels in packs of oxygen-sensitive food products such as cheese is necessary to maintain product quality over-determined shelf life. Oxygen is directly or indirectly associated with major spoilage associated with hard cheese. Modified Atmosphere (MAP) packaging is used for prevention. By using oxygen-deficient gas mixtures, you can extend the shelf life of hard cheese, protecting against oxidation and the spread of unwanted perishable microorganisms. Hard and semi-hard cheeses are usually packed with 100% carbon dioxide, while for soft cheeses the proportion is usually between 20 and 40 percent, with the remainder nitrogen [18,19]. The results of microbiological analyses and sensory evaluations of stored cheese samples indicate that active packaging is nearly as effective in extending the shelf-life of ripened cheese as vacuum packaging and modified atmosphere packaging [20]. However, if the packaging, packaging, storage, or distribution conditions are not met, then the benefits of atmosphere modification will be ineffective and oxygen will affect the quality of the cheese. Application of oxygen scavengers preserves the freshness of cheeses products without the use of fungicides, bactericides, or other stabilizers [21] and is a more simple solution than MAP from a logistic point of view. Many oxygen scavengers bidder mention cheeses as a potential area of application for their products. However, we must bear in mind that some cheeses must breathe. Absorbers should rather not be used for bloomed and blue cheese, because it can lead to botulism that occurs under anaerobic conditions. Recently, edible coatings and films have been pointed out which, in addition to their edibility, can be used to reduce weight loss and prevent microbial spoilage by controlling the rate of oxygen and carbon dioxide exchange and as a carrier of antimicrobial compounds [22]. However, the rind is the biggest source of surface mold growth. An interesting solution seems to be coating the cheese paper with a “2 in 1” type coating, containing an oxygen absorber, and at the same time exhibiting antimicrobial properties [23]. It significantly extends the shelf life of perishable cheeses.

**Chocolate**

Chocolate packaged with an oxygen absorber in a barrier packaging material will maintain its aroma, taste and nutritional quality substantially longer than other packaging methods; the shelf life was at least 12 months irrespective of packaging material [24].

**Powdered milk and baby food based on powdered milk**

Lipid oxidation is a reaction which is a factor limiting the storage time of milk powder [25]. This problem has been known for a long time. Already in 1922, the negative impact of oxygen on powdered milk was noticed [26]. In later works, attempts to prevent this phenomenon by appropriate treatment or packaging in inert gas or vacuum have been reported [27]. The effect of oxygen on powdered milk and its changes are exhaustively presented in the review of Tehrany E et al., [28] and the literature references cited therein.

Lipid peroxidation is responsible for changes in the taste and smell of milk powder, which are formed as a result of the resulting secondary reaction products (alkanes, alkenes, aldehydes and ketones). These compounds give foreign smells and cause the loss of nutrients of milk powder, thus limiting its durability. Autooxidation due to the binding of oxygen to unsaturated fatty acids is a serious problem for dried dairy products, especially full-fat ones.

In general, milk powder packaging systems must protect the powder from exposure to moisture, O2 and light, and to likely external logistic factors.

It is important that already in the early stages of product creation, to reduce the amount of oxygen in the space between the product and packaging to below 2%. Lowering the content to 0.5-1% delays the development of aftertaste, but it does not completely prevent changes. This can only be achieved by using oxygen scavengers [4]. A positive effect on quality at the time of purchase of dried dairy products packaged commercially with oxygen scavengers was described by Lloyd et al., [29].

Whole milk powder has a maximum storage time of 6 months at room temperature; however, the shelf life can be extended to 12 months if the product is packaged in cans under reduced pressure or an inert gas such as nitrogen. The use of an oxygen absorber allows extending this period to 3 years [30].

An DS, et al., described the effects of modified atmosphere packaging conditions on quality preservation of powdered infant formula [31].

There has also been a publication on the use of oxygen scavengers to prevent the bad taste of UHT milk during storage [32].

**Yogurt**

The poor survival of probiotic bacteria in commercial yogurts below the recommended 106 cfu/g can limit their ability to exert positive health benefits in humans. Probiotic bacteria, added to
yogurt to impart health benefits, require a low-oxygen environment for maximum viability [33,34]. Anaerobic and microaerophilic probiotic organisms require the lowest possible level of oxygen in the commercial packaging to ensure the viability of the required number of cells in the finished product with the desired functionality and avoid the toxicity and death of microorganisms Bifidobacterium bifidum and Lactobacillus acidophilus [35] are particularly exposed to the harmful effects of oxygen during storage. Yogurt industry’s material of choice for packing this product is generally high - impact polystyrene which exhibits low barrier to oxygen permeation [36,37]. This way of packing yogurt frequently leads to the loss of their probiotic viability [35]. Miller CW et al., [35,38] reported that oxygen scavengers incorporated into PS containers created best conditions for favorable growth of anaerobic probiotic cultures. Talwalkar K et al., [33] investigated the effect of oxygen scavengers integrated packaging materials in comparison with traditional packaging on the survival of bacteria in yogurt and show great advantage of packaging with incorporated oxygen scavengers. Further examples of such applications can be found e.g. in the monograph on food quality assurance by Mohan CO, et al., [39].

Oxygen - barrier packaging combined with an oxygen - scavenging material was found to be the most effective system to prolong shelf - life of yogurt [38].

General Remarks

The use of oxygen-absorbing materials in packaging is a current trend in active packaging, especially in food packaging. Oxygen scavengers are a technology that extends the shelf life and maintains the quality and freshness of food products. Commercial oxygen absorbers currently take many forms, mainly sachets, films (as part of the packaging) and labels. Very recently (June 2020) MSN announced the list of 10 Best Oxygen Absorbers Based on more 6,500 reviews [40]. There is no perfect solution, each has its own advantages and disadvantages, and each time you need to choose the right oxygen absorber for a specific solution.

Manufacturers of traditional iron-based oxygen scavengers declare that they can be safely placed in food packaging. They will not harm the food with which they come in contact, because they are packed in tightly sealed sachets. Oxygen scavenger’s, like those with silica gel designed to absorb moisture, are labeled “Do not eat” because of the possible toxicity if the contents of the sachet would be eaten. Brody AL, et al., [41] discussed the issue of safety in the case of classical iron based oxygen scavengers. LD50 for iron is 16g / kg body weight, which means you would have to eat about 160 absorbers to get deadly poison. However, small children and dogs cannot read.

Oxygen scavengers must be FDA approved for food contact. Japan and Australia also have their regulations in this area. In Europe, certificates are issued by EFSA - European Food Safety Authority.

Recently, however, oxygen scavengers incorporated directly into packaging materials have better consumer acceptance than using sachets. For this reason, the oxygen scavengers industry has become increasingly interested in the development and application of their novel forms. One of these forms is different types of oxygen absorbing films. An excellent review article by Gaikwad KK et al., is worth recommending in this subject [42]. He presented the strengths and weaknesses of individual varieties of these films. So far most commercial oxygen scavenging films from packaging of oxygen-sensitive food are based on different forms of iron. Very often, opponents of this solution stated potential metal contamination as disadvantages of iron-based scavenging films. Even if it were, it is still smaller than the migration of organic antioxidants from the film to the product. This migration can occur when the iron particles used are larger than the thickness of the foil. However, the use of nano-iron has been found to eliminate this problem [43]. In addition, iron is a health supplement [44] for treatment of anemia [45].

Much has been promised after oxygen-based oxygen scavengers. The main problem with this technology is that by-products such as organic acids, aldehydes, or ketones can form during the reaction between polynsaturated molecules and oxygen, which can affect food quality, including color and rancid development as well as bad smell.

In recent years naturally derived oxygen scavenging systems are becoming increasingly important [46]. However, as with organic oxygen scavengers, their reactive capacities per unit weight are so far limited.

The only solution that effectively competes with films based on nanoiron is multilayer PET films containing as one of the layers active substance absorbing oxygen. They are not only the subject of laboratory tests [5,47,48] but, importantly, PET haze due to oxygen scavengers was reduced [49] and PET bottles with oxygen scavengers are market available. Mohan CO et al., [39] Conto F et al., [50] indicate the possibility of their use for milk distribution as a cheaper alternative to paperboard cartons packaging.

Conclusion

The presented different practical applications of oxygen scavengers concerning dairy product packaging show their usefulness in their protection against the harmful effects of ambient oxygen. There are subsequent reports about their use to protect packaged food [43] with particular emphasis on recent advances in dairy product packaging [51-53]. Oxygen scavenger applications not only protect packed dairy products against the negative effects of oxygen and prolong their shelf life but also can avoid food wasting which is the current worldwide problem. There is no perfect solution, each has its pros and cons, and each time you need to choose the right oxygen absorber for a specific solution. They protect the product from outside and eliminate the need for unhealthy preservatives such as Sorbates, Benzoxates, BHA, BHT, Sulphur Dioxide. Oxygen scavenger producers should be more involved in implementing marketing strategies for their use in food protection, especially in developing countries.

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Conflicts of Interest

The authors declare no conflicts of interest.
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