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Current Scenario of Gas Scavenging Systems Used in Active Packaging - A Review

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Abstract Due to the rise of customer's alertness about fresh foods to health, in the past few years, the consumption of fresh food has increased sturdily. The use of gas scavengers is the most appropriate packaging technologies for fresh, fresh-cut produces and in ready to eat products. The gas absorber/scavenger has ability to protect or stabilize the wanted properties and shelf life of food. The success of gas absorbers in food depends on many parameters such as types of foods, storage temperature, relative humidity, initial gas concentration, and the characteristics of package materials. In this review article, we focus on the most recent research trends in gas scavenging systems used in food packaging, future trends. Intense research from industry and engineers remains important to the development of gas scavenging package that fulfill consumer requirements, enhance product quality, and offer environmentally friendly design and cost-effective application.

Keywords Food packaging, Active function, Gas scavenger

Introduction

In recent years, consumers have become increasingly conscious about their health and are hence are willing to pay a higher price for healthy, fresh food. Consequently, the consumer food industries have begun to apply advanced technologies to preserve the freshness and nutrients of food. The preservations techniques like use of synthetic preservatives, salting, blanching, use of high temperature, and drying of foods used in the past that persevere till today[1-3]. Nevertheless, some foods are served fresh without the use of synthetic food preservatives. Earlier in the 20th century, a number of chemicals were incorporated into food products to absorb different gases like, oxygen, and carbon dioxide gases[4].

The use of polymer packaging materials varying in gas permeability started to be widely used by the 1970[5]. Concerns regarding the oxidation by oxygen and also the oxygen which transmits through the packaging material lead to the development of chemical means of oxygen removal by using packets or sachets within the package, which saw the beginnings of new category of packaging called active packaging, including oxygen absorbers[6].

Carbon dioxide is generally beneficial for food protection and is thus often used as a flushing gas in modified atmosphere packaging (MAP). High concentration of CO_2 prevents microbial growth in food products and hence it benefits to maintain their freshness and extend their shelf life[7]. CO_2 is used to protect foods from oxidation. Nitrogen (N_2) is commonly used to inhibit oxidation, but CO_2 is often combined with N_2 for antioxidant food packaging. An ideal level of improved CO_2 concentration is helpful also for maintaining the fresh produce by decreasing the physiological activities such as respiration, ethylene production and so on [8]. The global market increasing year by years as presented in Table 1. This is because of the high demand for fresh and safe food.

The ripening of fruit and vegetables is a bio-chemical process that is caused by ethylene gas, a natural plant hormone. It initiates and accelerates the ripening of fruit and vegetables, and then causes them to deteriorate[9-11]. By lowering the level of ethylene gas surrounding fruits and vegetables, their shelf life can be greatly increased, slowing the maturation of fruit and greatly reducing decay as shown in Fig. 1. When produce is shipped, trucked, and flown from farm to market, the producers and commercial industries utilize devices to absorb the ethylene gas that fruits and vegetables emit as they ripen[12]. The use of these devices essentially stops the ripening process so that produce can be shipped to market looking freshly picked, and not wilted or fuzzy. These ethylene gas absorbing or neutralizing devices (with an organic carrier medium of volcanic ash) have been utilized safely by both producers and industries for over 20 years[13]. The different types of gas scavenging systems used in food packaging are as presented in

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Table 1. Global market value (million US $) of gas absorbing packaging

Type of scavenger	2001	2005	2010	Market share (%)
Oxygen scavengers	371	660	985	37
Carbon dioxide scavengers	81	108	156	6
Ethylene scavengers	30	57	100	3
Odor absorbers	28	47	70	3

Table 2. Selected examples of gas scavenging systems in active packaging

Active systems	Active materials	Food applications
Oxygen scavengers	Iron based, Metal/acid Nylon MXD6, Metal (e.g. platinum) catalyst Ascorbate/metallic salts Enzyme based	Bread, cakes, cooked rice, biscuits, pizza, pasta, cheese, cured meats and fish, coffee, snack foods, dried foods and beverages
Carbon dioxide scavengers	Iron oxide/calcium hydroxide Ferrous carbonate/metal halide Calcium oxide/activated charcoal Ascorbate/sodium bicarbonate	Coffee, fresh meats and fish, nuts and other snack food products and sponge cakes
Ethylene scavengers	Potassium permanganate Activated carbon Activated clays/zeolites	Fruit, vegetables and other horticultural products

Fig. 1. Process to extend shelf life of food using gas scavenger.

Table 2.

The aim of this review is to provide an overview of research studies on different type of gas scavenging material used in food packaging applications and look at future trends and challenges. We first discuss the major types of gas scavenging materials, their activation reactions, food applications. Then we provide an overview of issues such as safety when we use these gas absorbers.

Functional gas scavenging systems

1. Definition

Functional gas scavenging systems refer to the incorporation of gas scavenging system into the packaging material or the use of material in the form of sachets and put it into the package for maintaining and extending food shelf life[14]. Packaging may be termed active when it performs some desired role in food preservation other than providing an inert barrier to external conditions

2. Mechanism of gas scavenging

The most common oxygen scavenger is based on ferrous iron oxide (Iron II Oxide; FeO)[15]. As shown in Scheme 1. it activate with water from the environment and automatically commences absorbing the residual oxygen within the headspace of package becomes hydrated with atmospheric moisture to oxidize to a ferric state; hydrated iron (III) oxide (ferric oxide). Under ideal conditions, approximately 2.2 g of ferrous carbonate is used to absorb 100 cc of oxygen[16].

$$Fe \rightarrow Fe^{2}+ + 2e-$$
$$1/2\ O_2 + H_2O + 2\ e^- \rightarrow 2\ OH^-$$
$$Fe^{2}+ + 2\ OH^- \rightarrow Fe(OH)_2$$
$$Fe(OH)_2 + 1/4\ O_2 + 1/2\ H_2O \rightarrow Fe(OH)_3$$

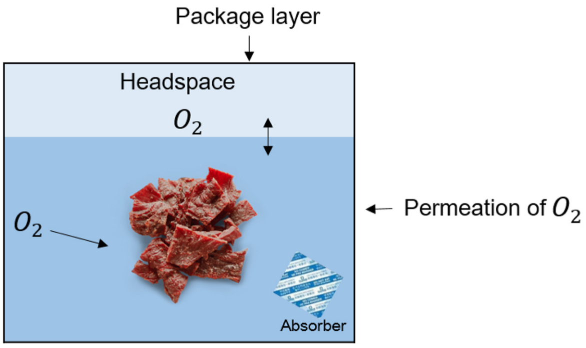

Fig. 2. Oxygen balance in food package containing an oxygen scavenger.

The essential absorption capacity and rate of the packaged food system are the main worries while selecting and designing a gas scavenger system. The design process starts with determining O_2 concentration in the package also permeation of oxygen from the packaging wall during the storage period and then mass balance is formulated which states that O_2 in as combination of components in the food as dissolved state, package headspace as gas phase, scavenger as absorption and permeation of oxygen loss through the packaging layer as shown in Fig. 2.

Typical gas scavengers

1. Oxygen scavenger

The various effects of oxygen on preserved foods and beverages includes rancidity of unsaturated fats (i.e. 'off-flavors' and toxic end-products), darkening of fresh meat pigments by promoting the growth of aerobic bacteria and fungi, stale odor of soft bakery foods and phenolic browning of fruit/vegetables[3]. Moreover, the deterioration of flavor of beer, loss of vitamin C (ascorbic acid) and acceleration of respiration in fruit and vegetable based foods, with the loss of aroma of beverages (coffee and tea) through oxidation of aroma oils and discoloration of processed foods such as fresh meat, fruit and vegetables has a strong influence on consumer purchasing in the retail food industry[17]. Economic loss due to spoiled food is enormous and often a hidden cost of production, estimated at 1.3 billion tons per year in a study conducted for the FAO[18].

Oxygen scavenging or absorbing materials offers several benefits, such as inhibiting the formation of microbial growth, maintaining the quality of lipid-containing foods (preventing rancidity), avoiding discoloration, and avoiding oxidation. Currently, commercial oxygen scavengers take the form of sachets, films (directly in the package), labels, etc. Incorporating scavengers directly into the packaging materials has better consumer acceptance than using sachets[19]. Oxygen scavenging packaging was the largest segment of active packaging in 2005, accounting for 37% of the global market by value[20]. The existing commercial oxygen scavengers for food packaging applications are presented in Table 3. Chemical reaction of ferrous based oxygen absorber rusting process as follow

$$4Fe + 3O_2 + 6H_2O \ 4Fe(OH)_3$$

2. Carbon dioxide scavenger

High levels of carbon dioxide usually play a beneficial role in retarding microbial growth on meat and poultry surfaces and in delaying the respiration rate of fruits and vegetables. Since carbon dioxide is more permeable than oxygen through many plastic films used for the food packaging, most of the carbon dioxide inside the package usually permeates through

Table 3. Commercial oxygen scavengers used in food packaging

Manufacturer	Commercial name	Base material
Ciba specialty chemicals	Self plus	PET Co-polyester
Chevron Chemicals	-	Benzyl acrylate
Visy Industries	$ZERO_2$	Photosensitive dye
CMB Technologies	OXBAR	Cobalt catalyst
Toyo Seikan Kasiha Ltd.	Oxyguard	Iron based
CSP Technologies	Active-Films®	UV-radiation
Cryovac Sealed air	OS1000	Light activated scavenger
Mitsubishi gas chemical	AGELESS OMAC	Iron based
Sorbed India	Activ-Films™	Iron based
Crowne, cork and seal	Oxbar	Iron based
AMOCO	Amosorb 3000	Iron/Co-polyester
Continental PET	CPTX 312	-
Bioka Ltd	-	Enzyme based

the film. For instances where the package has a high permeability to carbon dioxide, a carbon dioxide emitting system may be necessary to reduce the rate of respiration and suppress microbial growth. The use of a dual function system consisting of an oxygen scavenger and a carbon dioxide emitter is the usual practice for extending the shelf life of highly perishable foods[7]. Table 4 shows the list of carbon dioxide scavengers available in market for food packaging applications

On the contrary, dissolved carbon dioxide formed after the roasting of coffee may cause the package to burst, if the roasted coffee is packed in a can or aluminum foil pouch. This released carbon dioxide from freshly roasted coffee can be scavenged through the use of a carbon dioxide scavenger. Multiform Desiccants Incorporated has developed a CO_2 absorbing sachet that is composed of a porous envelope containing calcium oxide and a hydrating agent, such as silica gel, on which water is adsorbed. In this system, water reacts with calcium oxide and produces calcium hydroxide, which then reacts with CO_2 to form calcium carbonate[21].

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

3. Ethylene scavenger

Ethylene gas is an odorless, colorless gas that exists in nature and is also created by man-made sources. As fruits, vegetables and floral products mature, ethylene gas is released into their packaged environment. In many cases, perishable products (such as fruits, vegetables and flowers) are sensitive to ethylene gas and can ripen or mature quicker when exposed to ethylene gas[22]. In addition, certain fruits and vegetables are high producers of ethylene gas thereby creating the need to separate, ship, or store produce based on their ethylene profile. Ethylene also accelerates the rate of chlorophyll degradation in leafy vegetables and fruits. Hence, the removal of ethylene gas from the package headspace slows senescence and prolongs shelf life[23].

As presented in Table 5, the most well-known, inexpensive, and extensively used ethylene scavenging system consists of potassium permanganate imbedded in silica. The silica absorbs ethylene, and potassium permanganate oxidizes it to ethylene glycol. Silica is kept in a sachet highly permeable to ethylene, or it can be incorporated into a packaging film[22]. Potassium permanganate is not integrated into food contact surfaces of packaging films due to its toxicity. The substrate surface area and the amount of potassium permanganate affect the performance of these systems. Another system available to absorb ethylene is based on impregnating zeolite with potassium permanganate, and then coating the impregnated zeolite with a quaternary ammonium cation[24]. This system is not only capable of absorbing ethylene from the medium, but also other organic compounds, such as benzene, toluene, and xylene.

Food applications

1. Oxygen sensitive food

As presented in Table 6, commercially the oxygen scavengers used in various food products to maintain their freshness and extending shelf life Oxygen scavenger have been

Table 4. Commercial carbon dioxide scavengers for food packaging applications

Manufacturer	Commercial name	Form
Mitsubishi gas chemical Co. Inc.	Freshock, Ageless E	Sachets
Evert-fresh Corp	Evert-fresh green bags	Sachets
Ever-fresh type G	Evert-fresh USA	Sachets
Oxyfresh	Emco Fresh Technologies Ltd.	Sachets
Lipmen	Lipmen	Sachets

Table 5. Commercial ethylene scavengers used in food packaging

Manufacturer	Trade name	Form	Base material
Purafil	Purafil	Sachets	Potassium paramagnet
Delta trak	Air repair	Sachets	Potassium paramagnet
Dennis green Ltd	Mrs Green extra life	cartridge	Potassium paramagnet
Nippon container Co.	Fain	Films	-
Grofit Plastics	Biofresh	Zipper bag	-
Sekisui Jushi	Neupalon	Sachets	Active carbon
Odja Shoji Co.	BO films	Film	Ceramic
Evert fresh Co	Green bags	Bags	Minerals
Dessicare	Ethylene eliminator pack	Sachets	Zeolite

successfully implemented in roasted and ground soybeans to prevent lipid oxidation. The use of oxygen absorbers with almond kernels (*Prunus dulcis*) provides a 12 month shelf life irrespective of container oxygen barrier[25]. An oxygen absorber decreased the formation of hexanal content, degradation of color; however the an increase in the concentration of saturated fatty acids and decrease in monounsaturated fatty acids was observed over the 12 month period at storage of 20°C. It appears that oxygen absorbers are crucial for packaging of nuts and seeds to protect against degradation of fatty acid composition, an important nutritional characteristic and determinant of market value. Mexis et al.[26] analyzed the effect of active packaging and packaging material oxygen permeability on the quality retention of dark chocolate with hazelnuts. They developed and tested two packaging materials: one with PET/LDPE and the other with PET coated with SiO_x/LDPE (PET-SiO_x/LDPE). Matche et al.[27] developed a modified linear LDPE film by incorporating an oxygen scavenger such as zinc, iron, or ascorbic acid. The bread packed in the oxygen scavenging films grew a very minute quantity of microbial growth, which is under the prescribed limit. The sensory analysis showed good taste and texture of both buns and bread until the fifth day.

2. Fresh produce

The use of a CO_2 absorber in a fresh-produce package is based on the principles of MAP to maintain the proper O_2 and CO_2 concentrations or avoid an injurious level of CO_2, for which one must consider the rate of produce respiration and gas transfer through a permeable package, as mentioned above. A CO_2 scavenger was beneficial in inhibiting or delaying the internal browning of pears in the film bags with a 6-8% O_2 concentration[35]. Pears are sensitive to injury by CO_2 at concentration higher than 2%. Chilling injuries in eggplants can be prevented or delayed by using a CO_2 scavenger, which maintained a CO_2 concentration of 0.4% inside the package for up to 5 days at 4°C. Shiitake mushrooms, which are susceptible to high CO_2 concentration damage, benefited from the reduced level of decay provided by a CO_2 absorber-containing MAP system that maintained the O_2 concentration at approximately 9% and the CO_2 concentration at 1-4%[7].

3. Fermented products

Microbial activities continue during the storage and distribution of fermented foods that are packaged without pasteurization or sterilization, which result in CO_2 gas production likely to cause increases in package volume or pressure. Examples of foods in these categories include kimchi, yogurt, cheese and soy paste. The amount of CO_2 produced differs with the food type, compositional ingredients and the temperature[36].

The use of scavengers, such as $Ca(OH)_2$, zeolite or Na_2CO_3, could alleviate the volume expansion or pressure build-up of a flexible or rigid package of kimchi producing large amounts of CO_2[37]. A combination of zeolite and Na_2CO_3 in a sachet or sheet has been employed to exploit their different CO_2 absorption responses to moisture. Including $Ca(OH)_2$ in a sachet also reduced the level of pressure increase in packaged soybean paste and red pepper paste, both of which produce a large amount of CO_2. Taleggio cheese could be preserved with best sensory quality at CO_2 concentration of 10%. Kimchi and yogurt stored under high CO_2 conditions gave a better sensory performance. The applications of CO_2 scavengers in various kinds of food and their benefits are presented in Table 7.

4. Ethylene absorbers

Nitrous oxide (N_2O) has been demonstrated to inhibit ethylene production in the controlled atmosphere storage of postharvest climacteric fruits to extend their shelf life. As shown in Table 8, the N_2O was used alone or in combination with reduced oxygen levels on the postharvest ripening of mature green banana fruit and the results showed that it slowed down

Table 6. Applications of oxygen scavengers used in food packaging

Food	Oxygen scavenger	Benefits
Pork patties	Commercial product (Freshcare®)	Effective method to prevent lipid oxidation in pork patties[28]
Ham	Palladium based	Prevents discoloration of ham[29]
Chinese Steamed Bread	Commercial product	The microbiological safety of steamed bread is significantly preserved in terms of inhibiting the growth of spoilage organisms[30]
Fresh cut apple	Commercial product	Shelf life extension of fresh cut apple[31]
Strawberries	Commercial product (ATCO-100)	Shelf life extension of fresh strawberries[32]
Ground meat	Commercial product (Ageless®)	Shelf life extension of ground meat (5–6 days) [33]
Processed Meatball Product	Commercial scavenger +LLDPE	Shelf life extension of meat a ball[34]
Bun and bread	zinc, iron, or ascorbic acid	Effective in extending shelf life of food products like bread and bun[27]

Table 7. Applications of CO_2 scavengers used in food packaging[7)]

Food	CO_2 scavenging material	Benefits
Strawberry	Commercial product (EMCO®)	Reduced mold decay incidence, delayed senescence, preserved sensory score and chemical quality attributes[32)]
Pear	Commercial product (Ageless®)	Prevention of internal browning[35)]
Eggplant	Commercial product (Lipman®)	Reduction in chilling injury observed as external and internal browning[38)]
Shiitake mushroom	$Ca(OH)_2$	Reduced yeast/mold growth and decay[39)]
Shiitake mushroom	Agar-based label incorporated with Na_2CO_3	Less color change, firmer texture, good flavor, low bacterial count, alleviation of humidity saturation inside the package[40)]
Kimchi	Zeolite	Inhibition of volume expansion and pressure build-up[41)]
Kimchi	Zeolite/Na_2CO_3 in polystyrene sheet	Inhibition of volume expansion and pressure build-up[42)]
Kimchi	$Ca(OH)_2$	Prevention of pouch inflation[42)]
Soy paste, red pepper paste	$Ca(OH)_2$	Alleviation of pressure build-up[43)]
Carbonated beverage	Activated carbon	Maintaining consistent CO_2 pressure inside the container and/or dissolution in the beverages[44)]
Coffee	Granule formulation of $Ca(OH)_2$/ silica gel/H_2O in capsule	Maintaining the aromas of freshly roasted coffee powders with maintaining constant package volume and structure[45)]

Table 8. Applications of ethylene scavenger in food packaging

Food	Ethylene scavenger	Benefits
Banana	Potassium permanganate	Shelf Life increased[49)]
Fresh apple	Commercial product	Extend Shelf-Life[50)]
Tomato	Palladium based	Shelf Life increased[51)]
Avocado	1methylcyclopropene & palladium	Avocado fruit-ripening process extended[52)]
Broccoli	Commercial product	Broccoli shelf life extended for 5 days[53)]

the fruit ripening, and extended the storage life, with no adverse effect on physicochemical qualities. This gas was also used in other fresh food packaging and storage, such as fresh-cut pineapple, onion bulbs[46)], fresh-cut kiwifruit[47)], pears[48)].

5. Safety and regulatory aspects

The use of gas scavengers in the package is rising and hopeful technologies that will progressively be applied in the years to come to extend shelf-life and improve the quality, safety and integrity of packaged foods. In recent years, many gas controlling systems have been developed and it is expected that new concepts such as organic and natural based absorbing materials will become commercially available in the near future. However, for innovative food packaging technologies to be successful, they must comply with regulations.

The food-contact application of systems may have an effect on various European regulations for packaged food, such as regulations for food-contact materials, food additives, biocides, modified-atmosphere packaging, and hygiene of foodstuff, labelling and packaging waste. As all active and intelligent systems can be considered to be food-contact materials, the EU framework directive (Directive 89/109/EEC) appears to be of primary importance. It is, therefore, worthwhile to investigate the possibilities to adapt this directive to regulate intelligent packaging in Europe.

The increasing development of gas absorbing packaging systems challenges the current regulatory framework, which must now address new technical considerations to ensure the safety, quality, and stability of food products that use such packaging. Although the legislation applied to traditional packaging can be adapted to active packaging[8)], specific laws and guidelines should be introduced to clarify the legal uses of novel technologies in food packaging. In the United States, current FDA regulatory programs include the food additive petition (FAP) program, generally recognized as safe (GRAS) notification program, and food contact substance (FCS) notification program, which provide an authorization process for direct food additives, GRAS substances, and indirect additives, respectively. Migratory active packaging should follow the FAP program or GRAS notification because this technology releases antioxidants into food as an intended technical effect. Non-migratory antioxidant packaging needs to follow the FCS notification program because the active agent is unlikely to migrate to the food. Japan is also leading the way in the development and use of gas absorbing packaging systems for food, and active packaging concepts have penetrated markets in Australia. The development of active packaging in the EU market is limited, and most of the products already on the market in the United States, Japan, and Australia cannot yet be introduced in Europe because of inadequate and more-stringent EU legislation. The regulation of active packaging in the EU is still evolving, and certain inherent constraints in the law (such as the overall migration limit) result in a set of hurdles for the regulation to keep up with rapidly developing technological innovations. The new active and intelligent packaging directive introduced in 2009 across Europe (EC Regulation 450/2009) is expected to bring much-needed clarity to this sector and pave the way for the launch of new products in the European market.

6. Future trend

Research in the field of gas scavenging packaging materials is very dynamic and developed in relation with the search for environment friendly packaging solutions. Nanotechnologies are projected to play a vital role, taking into account all additional food safety considerations and filling the presently existing gap in knowledge. They will be involved in the development of triggered/controlled release of active agents and for targeted material. New non-migratory materials for innovative functions such as in-package food processing are also a promising field of development.

The use of gas scavengers in the form of sachets, films, and closures is well established in the commercial market, but the use of gas scavengers in plastics continues to attract researchers. New research depends on the focus of the food and packaging industries. A major motivator should be the curiosity of food scientists to seek ever better results when they introduce new products to the market. Another important motivator is the need to maintain current quality levels as newer packaging materials become available. This is already visible with the introduction of rigid jars, bottles, and glass. The potential effect on canned food has not yet been determined but is expected to be large.

Conclusion

Gas scavenging technologies offer different opportunities in the food preservation. Gas scavenging is widely studying area of food packaging that can confer many preservation benefits on a wide range of food products. Gas scavenging packaging is a technology developing a conviction because of recent research and developments in packaging, material science and continuously increasing demands of healthy and fresh food by consumer. The development and implementation of this type of gas scavenging packaging will depend on the acceptance and cost-effectiveness for industry and consumers.

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