Trends in Food Science & Technology 57 (2016) 146-155

Contents lists available at ScienceDirect



Review

Trends in Food Science & Technology

journal homepage: http://www.journals.elsevier.com/trends-in-food-scienceand-technology

Carbon dioxide absorbers for food packaging applications

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ARTICLE INFO

Article history: Received 2 June 2016 Received in revised form 25 September 2016 Accepted 26 September 2016 Available online 30 September 2016

Keywords: Fermented foods Fresh produce Chemical reaction Adsorption Modified atmosphere

ABSTRACT

Background: Although CO_2 gas is useful for the modified-atmosphere packaging of foods, excess CO_2 accumulation in a package may be detrimental to the quality of the product and/or the integrity of the package, particularly in the case of CO_2 -producing foods, such as fermented foods and fresh produce. In those cases, including CO_2 scavengers in food packages is beneficial for preserving the food quality and package integrity.

Scope and Approach: The common mechanisms that are exploited for CO₂ absorption in food packages are chemical reactions and physical adsorption. The CO₂ absorption capacity and absorption kinetics of chemical and physical absorbers were examined and reviewed with respect to their proper use in packages of CO₂-producing foods. The applications of CO₂ scavengers in food packages were examined in terms of the benefits achieved and their efficacy.

Key Findings and Conclusions: The CO₂ production characteristics and desired atmospheric conditions of foods must be established and tuned to the thermodynamic and kinetic properties of CO₂ absorbers sometimes in combination with the gas transfer behaviour of the package layer. The combined or synergistic use of CO₂ scavengers with other active packaging tools may be the direction for further research improving food quality preservation.

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1. Introduction: dual characteristics of carbon dioxide (CO₂) gas and the requirement for its absorption in food packages

Carbon dioxide (CO_2) is generally beneficial for food preservation and is thus often used as a flushing gas in modified atmosphere packaging (MAP). CO_2 at a properly high concentration inhibits microbial growth on foods and thus helps maintain their freshness and extend their shelf life (Cutter, 2002; Puligundla, Jung, & Ko, 2012). The antimicrobial effect of CO_2 is related to its high solubility in foods, although the mechanism by which it inhibits microbial growth has not been clearly elucidated. CO_2 gas is readily soluble in aqueous and fatty foods, with a higher level of solubility at a lower temperature (Chaix, Guillaume, & Guillard, 2014). Thus, the antimicrobial efficacy of CO_2 gas is more pronounced under chilled conditions, in which its solubility level is higher. Preservative MAP using a high CO_2 concentration is used mainly for chill-stored nonrespiring foods that are liable to microbial spoilage.

In addition to being used due to its antimicrobial effect, 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 antioxidative food packaging (Singh, Wani, Karim, & Langowski, 2011). Including CO₂ in the atmosphere of a package may reduce the pressure or volume of the package due to its high solubility in food matrices and may play a role in balancing the pressures between the inner headspace and the external environment of the package, which is occasionally beneficial for marketing MAP food products under conditions of low environmental temperature and pressure. However, the phenomenon of high CO₂ dissolution into foods is occasionally detrimental, causing package collapse and undesirable product quality in terms of flavour and texture at high CO₂ concentrations; thus, CO₂-based MAP must be used wisely, in harmony with food properties and the environmental conditions (Lopez-Rubio et al., 2004). The concentration of CO₂ must be properly limited and tuned to the properties of the food.

An optimum level of increased CO_2 concentration is helpful also for keeping the fresh produce by reducing the physiological activities such as respiration and ethylene production. Maintaining a proper CO_2 concentration and an optimal O_2 concentration in the package is necessary for the efficacy of a fresh-produce MAP system. The CO_2 produced via the respiration of the produce must be properly balanced with the CO_2 that passes out from the package. The same is true for the O_2 supply, which must be balanced with the O_2 consumption of the packaged fresh produce to maintain an



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optimal O₂ concentration that is in harmony with the CO₂ concentration. A CO₂ concentration above the tolerance limit causes physiological injury to the produce. Commodities that are sensitive to a relatively low CO₂ concentration (\leq 5%) include onion, lettuce, pear, artichoke, apple, apricot, carrot, cauliflower, cucumber, peach and potato (Watkins, 2000). The symptoms of CO₂ injury include discoloration, off-flavour development and internal tissue breakdown.

However, selecting packaging films for MAP of fresh produce to maintain both O_2 and CO_2 balances between respiration and permeation is often difficult. Various design tools for attaining a proper MA with the desired range of O_2 and CO_2 concentrations have been developed or proposed (Mangaraj, Goswami, & Mahajan, 2009; Rodriguez-Aguilera & Oliveira, 2009). Mathematical models to estimate the package atmosphere for a variety of variable combinations are useful to find useful available package conditions. For produce with a high respiration rate, micro-perforations have also been used to increase the rate of gas transfer from the package to avoid an unsuitable increase in the CO_2 concentration. Active packaging techniques such as those that employ a gas scavenger or emitter can be used to maintain the desired MA for an extended storage period.

Because CO₂ is the main product of the catabolic reactions that occur in biological systems, most non-pasteurized fermented foods produce significant amounts of CO2, depending on the storage temperature. Fermented dairy products, such as yogurt, and fermented vegetables, such as Korean kimchi, are typical examples of foods that produce CO_2 gas during their shelf life. Continuous CO_2 production is suppressed or allowed to occur to only a limited extent by short-term storage and distribution under coldtemperature conditions because it can cause changes in package volume or pressure upon temperature abuse or extended storage. Although the excessive accumulation of CO₂ is detrimental to product quality and/or package integrity, a suitable high degree of produced CO₂ is beneficial to give attractive flavour or preserving the best quality of some foods (Jansson, Edsman, Gedde, & Hedenqvist, 2001; Lee & Paik, 1997; Lee, An, & Lee, 2016). A slightly low CO₂ concentration promotes the growth of lactic acid bacteria and improves the quality of some fermented foods (Caplicec & Fitzgeralda, 1999).

For many of the packaged fresh produce or fermented foods mentioned above, a proper concentration of CO₂ is desirable and too high CO₂ concentration is often detrimental. Although there are special cases that benefit from very high CO₂ concentration requiring the use of CO₂ emitters in food packages, mostly moderate or low CO₂ concentration is often desired for the best quality preservation. As mentioned above, fresh produce package with the optimal CO₂ concentration along with beneficial O₂ concentration is frequently achieved by packaging films of high gas permeability properties balanced to the respiration activity of the product (Lee, Jo, Kwon, & An, 2014; Rodriguez-Aguilera & Oliveira, 2009). For the fermented food packages, package soundness and preferred food qualities can be attained with desired level of CO2 accumulation in the packages. Even though high CO₂ transfer property of the package layer is often helpful for keeping the desired CO₂ level and storage stability in the packages, it may not be sometimes enough or appropriate to handle with high undesirable production of CO₂ from the foods (Lee et al., 2014; Lim, Park, Cheigh, & Lee, 2001). Therefore in these cases, CO_2 absorbers can be the effective measures of controlling the CO₂ concentration in food packages in addition to their high gas transfer properties.

The type of CO_2 absorber used should be selected considering the characteristics of the food product, such as its CO_2 -production quantity, desired level of CO_2 and the package variables. The capacity and speed of the scavenger's CO_2 absorption should be taken account of for optimization. Whereas much attractive attention has been paid to active packaging technology and many reviews have focussed on innovative O2 scavengers over the last several decades (Lopez-Rubio et al., 2004; Ozdemir & Floros, 2004; Pereira de Abreu, Cruz, & Paseiro Losada, 2012; Rodriguez-Aguilera & Oliveira, 2009; Vermeiren, Devlieghere, van Beest, de Kruijf, & Debevere, 1999), to this author's knowledge, few attempts were tried to overview and evaluate the CO₂ absorbers applicable for food packaging. In contrast, whereas CO₂ absorption technologies for capturing CO₂ from the flue gases of manufacturing and power plants have been developed, these technologies are on a large-unit operational scale, and their hygienic status does meet the requirements for food applications. However, some of the scientific principles and data gathered in that area may be useful for food packaging applications. The aim of this review was to examine the CO₂ absorbers available for food packaging in terms of their mechanisms of action and their practical applications. Some desirable applications of these materials were also discussed.

2. Mechanistic principles of CO₂ absorbers used in food packaging

The absorption or removal of CO_2 from a gaseous phase can be theoretically achieved by a chemical reaction with an alkaline solution, physical adsorption, membrane separation and cryogenic condensation. Much research has been devoted to developing technologies for capturing CO₂ gas to protect the environment from global warming. Most of these technological developments targeted manufacturing plants and have limited direct application to food packaging. The cryogenic separation of CO₂ gas requires refrigeration equipment and its membrane separation requires high-pressurization equipment, which makes both technologies unsuitable for food packaging applications. Non-harmful chemical reactions and physical adsorption are appropriate for CO₂ scavenging in food packages. CO₂ scavenging materials can be enclosed in a sachet that is placed in the food package or fabricated as a sheet or coating. Chemical and physical absorbers can be combined in a formulation containing a synergistic additive or a catalyst.

2.1. Chemical absorbers

Although many alkaline solutions and salts can react with and remove CO_2 gas, calcium hydroxide $(Ca(OH)_2)$ is the CO_2 scavenger that is most commonly used in food packaging; this compound performs the following reaction (Rodriguez-Aguilera & Oliveira, 2009; Vermeiren et al., 1999):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

In solid form, this compound is safe for possible food contact. The reaction shown above is thermodynamically highly spontaneous and occurs with a desirable rate under the usual conditions of food-package storage and distribution. The reaction does not require any other reactants for scavenging CO₂ and produces CaCO₃ and water as its non-harmful reaction products. Based on the stoichiometry of Chemical Reaction (1), the mass-based CO₂-absorption capacity of Ca(OH)₂ is 1.35×10^{-2} mol g⁻¹ (Table 1).

Among the alkaline salts, sodium carbonate (Na_2CO_3) can react with CO_2 under moist conditions to produce sodium bicarbonate, in the following reaction:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$
⁽²⁾

The unique water requirement of this reaction means that Na₂CO₃ for CO₂ scavenging can be used under specifically defined conditions of a moisture supply, such as high-moisture food or

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