Contents lists available at ScienceDirect

Trends in Food Science & Technology

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

Review

Carbon dioxide absorbers for food packaging applications

Dong Sun Lee

Department of Food Science and Biotechnology, Kyungnam University, 7 Kyungnamdaehak-ro, Changwon 51767, South Korea

ARTICLE INFO

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 CO_2 absorption in food packages are chemical reactions and physical adsorption. The CO_2 absorption capacity and absorption kinetics of chemical and physical absorbers were examined and reviewed with respect to their proper use in packages of CO_2-producing foods. The applications of CO_2 scavengers in food packages were examined in terms of the benefits achieved and their efficacy.

Key Findings and Conclusions: The CO_2 production characteristics and desired atmospheric conditions of foods must be established and tuned to the thermodynamic and kinetic properties of CO_2 absorbers sometimes in combination with the gas transfer behaviour of the package layer. The combined or synergistic use of CO_2 scavengers with other active packaging tools may be the direction for further research improving food quality preservation.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction: dual characteristics of carbon dioxide (CO_2) 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 non-respiring 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 CO_2 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 CO_2 dissolution into foods is occasionally detrimental, causing package collapse and undesirable product quality in terms of flavour and texture at high CO_2 concentrations; thus, CO_2-based MAP must be used wisely, in harmony with food properties and the environmental conditions (Lopez-Rubio et al., 2004). The concentration of CO_2 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

E-mail address: dongsun@kyungnam.ac.kr.

optimal O_2 concentration that is in harmony with the CO_2 concentration. A CO_2 concentration above the tolerance limit causes physiological injury to the produce. Commodities that are sensitive to a relatively low CO_2 concentration ($\leq 5\%$) include onion, lettuce, pear, artichoke, apple, apricot, carrot, cauliflower, cucumber, peach and potato (Watkins, 2000). The symptoms of CO_2 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 CO_2 is the main product of the catabolic reactions that occur in biological systems, most non-pasteurized fermented foods produce significant amounts of CO_2, 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 cold-temperature conditions because it can cause changes in package volume or pressure upon temperature abuse or extended storage. Although the excessive accumulation of CO_2 is detrimental to product quality and/or package integrity, a suitable high degree of produced CO_2 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 CO_2 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 CO_2 is desirable and too high CO_2 concentration is often detrimental. Although there are special cases that benefit from very high CO_2 concentration requiring the use of CO_2 emitters in food packages, mostly moderate or low CO_2 concentration is often desired for the best quality preservation. As mentioned above, fresh produce package with the optimal CO_2 concentration along with beneficial O_2 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 CO_2 accumulation in the packages. Even though high CO_2 transfer property of the package layer is often helpful for keeping the desired CO_2 level and storage stability in the packages, it may not be sometimes enough or appropriate to handle with high undesirable production of CO_2 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 CO_2 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 O_2 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 CO_2 absorbers applicable for food packaging. In contrast, whereas CO_2 absorption technologies for capturing CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 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 CO_2 scavenging in food packages. CO_2 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 CO_2 and produces $CaCO_3$ and water as its non-harmful reaction products. Based on the stoichiometry of Chemical Reaction (1), the mass-based CO_2-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:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \tag{2}$$

The unique water requirement of this reaction means that Na_2CO_3 for CO_2 scavenging can be used under specifically defined conditions of a moisture supply, such as high-moisture food or

Table 1
Thermodynamic properties of some CO_2-absorbing chemical reactions under standard state conditions at 25 °C.

Reaction	$\Delta H°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	Maximum capacity[a] (mol g^{-1})
$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$	−179.2	−131.4	−160.1	1.78×10^{-2}
$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$	−114.7	−74.4	−135.5	1.35×10^{-2}
$MgO(s) + CO_2(g) \rightarrow MgCO_3(s)$	−95.7	−48.4	−175.0	2.48×10^{-2}
$Mg(OH)_2 + CO_2(g) \rightarrow MgCO_3(s) + H_2O(l)$	−63.6	−21.4	−141.3	1.72×10^{-2}
$Na_2CO_3(s) + CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(s)$	−91.6	−26.1	−215.3	9.43×10^{-3}
$NaCl(aq) + NH_3(aq) + CO_2(g) + H_2O(l) \rightarrow NaHCO_3(s) + NH_4Cl(aq)$	−84.3	−10.4	−241.0	
$NaCOOCH_2NH_2(s) + CO_2(g) + H_2O(l) \rightarrow NaCOOCH_2NH_3{}^+ (aq) + HCO_3{}^- (aq)$[b]		−72.5		1.03×10^{-2}

[a] Adsorption capacity is based on the mass of the absorbent.
[b] The adsorption enthalpy of sodium glycinate is for 10% solution at 12 MPa and 40 °C, and its adsorption capacity value can be different with CO_2 dissolution in aqueous medium and the listed value here is based on the stoichiometric relationship of chemical reaction (Salazar et al., 2010).

humidified environment (Shin, Cheigh, & Lee, 2002). Although this characteristic limits the environmental conditions for its use, the unique moisture requirement of Na_2CO_3 for its CO_2 absorption can be exploited to control the rate of the scavenging reaction by regulating the supply of moisture to the scavenger system. The level of moisture permeability of the scavenger sachet film is a variable that can be used to achieve the desired rate of CO_2 absorption. Another disadvantage of Na_2CO_3 is its lower mass-based CO_2-absorption capacity of 9.43×10^{-3} mol g^{-1} compared with that of $Ca(OH)_2$ (Table 1). This lower capacity is due to relatively higher molecular mass of Na_2CO_3 in Chemical Reaction (2).

As mentioned above, CO_2 gas can react with and be removed with amino-acid salt solutions, the liquid phase of which is difficult to be used directly in food packaging applications. To construct them in a solid phase able to absorb CO_2, one of these compounds, sodium glycinate, which is widely used as a flavour enhancer in processed foods, was embedded in an agar film to allow the moisture absorption and the following reaction (Wang, An, Rhim, & Lee, 2015):

$$NaCOOCH_2NH_2 + CO_2 + H_2O \rightarrow NaCOOCH_2NH_3{}^+ + HCO_3{}^- \qquad (3)$$
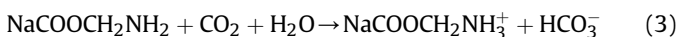
in which the mass-based CO_2 absorption capacity was calculated to be 1.03×10^{-2} mol g^{-1} (Table 1). This type of reaction can occur in a moisture-absorbing solid matrix with some degree of an aqueous phase. In the aqueous state, the absorption reaction of sodium glycinate is a combination of the above chemical reaction and CO_2 dissolution, the absorption capacity and rate of which depend on the sodium glycinate concentration and the CO_2 pressure level (Lee, Song, Maken, & Park, 2007; Salazar, Sánchez-Vicente, Pando, Renuncio, & Cabañas, 2010).

Calcium oxide, CaO, is often used for CO_2 absorption in large volumes in fresh produce transport vehicles but is not used in small food packages. MgO and $Mg(OH)_2$ have not been utilized for CO_2 absorption to a notable degree most likely due to their uncommon use as food additives and/or the low efficiency of their reactions. An iron-based O_2 scavenger has been reported to absorb CO_2 to some degree under the limited conditions of a carbonation reaction occurring on iron hydroxide, the mechanism of which has not been demonstrated clearly (Brody, Strupinsky, & Kline, 2001; Charles, Sanchez, & Gontard, 2006). Conversely, the O_2-absorption capability of iron-based scavengers is hampered by a CO_2-rich atmosphere (Rooney, 2005). The following equation represents a recently proposed mechanism of reaction by which a hydroxylated iron oxide surface with adsorbed moisture ($H_2O(a)$) absorbs CO_2 gas (Baltrusaitis & Grassian, 2005):

$$Fe-OH + H_2O(a) + CO_2(g) \rightarrow Fe-CO_3{}^- + H_3O^+(a) \qquad (4)$$
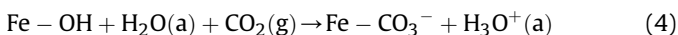
The reactions of chemical CO_2 absorbers and their thermodynamic properties are listed in Table 1, which shows the tendency of

the level of spontaneity and the change in the reaction enthalpy under standard conditions. Negative $\Delta G°$ values indicate the tendency toward the spontaneity of the reaction under commonly utilized conditions, and negative $\Delta H°$ values indicate the exothermic characteristics of these reactions.

2.2. Physical absorbers

CO_2 gas can be adsorbed onto physical adsorbents such as zeolite and activated carbon. Physical interactions are mostly responsible for the adsorption of CO_2 onto these adsorbents, although some degree of chemisorption may be involved. Physical adsorption is reversible in nature, with the equilibrium shifted forward or backward under varying environmental conditions. The microporous structure of physical adsorbents accounts for their gas adsorption. The pore volume, pore size distribution and surface area are important properties affecting gas adsorption. Those properties determine the bulk density, application area and further processing of physical adsorbents. Although many microporous materials have some degree of CO_2-adsorption capacity, only activated carbon and zeolite will be discussed here due to their practical potential in food packaging applications. For example, silica gel having CO_2 adsorption capacity much lower compared to activated carbon and zeolite, is used mostly as a desiccant in many types of food packages. The absorbers are in forms of powder, granules, beads, blocks or sheets usually packed in a porous sachet or pocket.

Activated carbon is characterised by its amorphous porous structure, which leads to its large surface area, broadly ranging from 500 to 2500 m^2 g^{-1}. The size of its pores are relatively large, generally ranging from 10 to 30 Å, and its bulk density ranges from 250 to 600 kg m^{-3}. The surface of activated carbon is more or less non-polar; thus, its gas adsorption is only slightly affected by the presence of moisture (Sjostrom & Krutka, 2010; Xu et al., 2013; Yang, 1987).

Zeolites are crystalline aluminosilicates with three-dimensional structures composed of tetrahedral primary units of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$. The assembly of these units results in frameworks containing open channels and cavities that differ in their shape, size and molecular architecture. These void cages absorb gas molecules. Depending on the manufacturing process utilized, the type and number of cations located in the cage sites can be modified to have different sizes of apertures. Table 2 shows the framework structures and general characteristics of zeolite types A and X, which are commonly used as gas adsorbents. The water capacity of these zeolites indicates the space in the cages that can accommodate H_2O molecules via adsorption. Their bulk density depends on whether they are in the form of powder, pellets or beads, among which powder has the lowest density.

The process of CO_2 gas adsorption onto physical absorbents is slightly exothermic (negative $\Delta H°$), with more adsorption occurring at a lower temperature (Table 3). The range of their CO_2

Table 2
Framework structure and general characteristics of zeolites as a gas adsorbent.

Attribute	Type 4A	Type 5A	Type 13X
Framework structure			
Major cation	Na	Ca or Mg	Na
Aperture size (Å)	4	5	10
Surface area ($m^2 g^{-1}$)	400—600	400—600	700
Bulk density ($kg m^{-3}$)	480—700	510—720	470—690
Water capacity (%, w/w)	20—23	20—23	23—30

Compiled from Yang (1987), Park, Kim, Cho, Kim, and Yang (1998), Mulloth and Finn (1998), Wang and LeVan (2009), Hauchhum and Mahanta (2014) and other sources.

adsorption enthalpy values is similar to or slightly greater than that of a solid food matrix ($\Delta H°$ of approximately -20 kJ mol^{-1}) (Chaix et al., 2014). Due to this negative $\Delta H°$ value, increasing the temperature moves the $\Delta G°$ value of physical absorbers in a positive direction, which means that there is less spontaneity and less or reversed adsorption at higher temperatures (desorption or release).

The amount of CO_2 adsorbed at a constant temperature increases with the increase in the CO_2 partial pressure, and this relationship is described by Henry's law in the simplest manner or by adsorption isotherm functions, such as the Langmuir, Freundlich, Toth and BET equations (Yang, 1987).

In addition to the porosity and surface area of physical absorbers, their hydrophobicity and the relative affinity of the adsorbent for the adsorbate gas molecules affect the selectivity of gas adsorption under a mixed-gas condition, which is common in food packages. In particular, CO_2 adsorption can be affected by the presence of moisture or may compete with moisture adsorption. The preference for CO_2 or moisture adsorption depends on the adsorbent and the adsorption conditions. Generally, physical CO_2 sorption on the adsorbent has been reported to be enhanced by the presence of a small amount of moisture but inhibited by a large amount of moisture (Marx, Joss, Hefti, Pini, & Mazzotti, 2013).

Water vapour is preferentially adsorbed over CO_2 gas onto zeolites, and the CO_2 gas present within the zeolite framework can be desorbed upon the later preferential adsorption of a large amount of water vapour (Fig. 1). The relative affinity or preference for water and CO_2 can result in time-dependent dynamics of adsorption/desorption under food-packaging conditions, which can be disadvantageous for stable CO_2 absorption or, conversely, can be exploited for the sophisticated control of CO_2 absorption. An overall understanding of the CO_2-adsorption isotherm as a function of water vapour and CO_2 pressures facilitates designing the desired CO_2 absorption profile. However, it must be mentioned that interactive adsorption differs according to adsorbent type used and the conditions of its use.

Compared to zeolites, activated carbon compounds containing hydrophobic groups are relatively more stable for CO_2 adsorption in the presence of moisture and moisture often has little effect on their CO_2 absorption (Sjostrom & Krutka, 2010; Xu et al., 2013). However, quantitative data regarding the effect of moisture on the CO_2 adsorption properties of activated carbon materials are scarce.

2.3. Kinetics of a CO_2-absorber system

Although the CO_2 absorption capacity of an absorber must be known to determine its total demand in the package design, its rate of CO_2 absorption must be determined to tailor the CO_2

Fig. 1. Adsorption of CO_2 onto zeolite 5A with different moisture loadings at 25 °C. Based on the data of Wang and LeVan (Wang & LeVan, 2010; 2009). ○: without H_2O adsorbed; ●: with H_2O adsorbed at 1.0 mmol g^{-1}; ■: with H_2O adsorbed at 3.4 mmol g^{-1}; ✕: with H_2O adsorbed at 9.4 mmol g^{-1}.

Table 3
Thermodynamic properties of physical CO_2 absorption under standard state conditions at 25 °C.

Adsorbent under dry state condition	$\Delta H°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	Adsorption capacity (mmol g^{-1})[a]	Reference
Activated carbon	−15.0	−7.65	24.4	2.83	Hauchhum and Mahanta (2014)
Activated carbon	−25.6			2.22	Park et al. (1998)
Activated carbon	−29.1			1.93 (40)	Lopes et al. (2009)
Activated carbon	−19.3			1.96	Saha, Jribi, Koyama, and El-Sharkawy (2011)
Zeolite 4A	−12.9	−7.30	18.5	3.26	Hauchhum and Mahanta (2014)
Zeolite 5A	−44.9			3.86	Mulloth and Finn (1998)
Zeolite 5A	−50.8			4.08	Park et al. (1998)
Zeolite 13X	−11.3	−7.93	17.6	4.22	Hauchhum and Mahanta (2014)
Zeolite exudates (commercial)	−36.0			3.70 (40)	Lopes et al. (2009)

[a] Adsorption capacity is experimental data or estimates from obtained from mathematical models at 25 °C and 1 bar, except when specific values are indicated in parentheses (in °C).

concentration profile in a given packaging system. The rate of a chemical CO_2 absorption reaction is described in the following first-order kinetics equation, with the reactant being CO_2 gas.

$$\frac{[CO_2]}{dt} = -k[CO_2] \tag{5}$$

where $[CO_2]$ is the CO_2 gas concentration (mol m^{-3}) in the package at time t (h) and k is the reaction rate constant (h^{-1}).

Solving Eq. (5) yields the integrated form that represents the CO_2 concentration profile in the package when there is no CO_2 production and no other absorption mechanisms are in effect, as follows:

$$[CO_2] = [CO_2]_o \exp(-kt) \tag{6}$$

where $[CO_2]_o$ is the initial CO_2 gas concentration (mol m^{-3}) in the package and the total amount of absorbed CO_2 during the time period t would be the product of the concentration change ($[CO_2]_o$-$[CO_2]$) and the free volume in the package.

The first-order rate constant for a commercial calcium hydroxide CO_2 scavenger was reported to be in the range of 0.006–0.233 h^{-1} by Charles et al. (2006) for temperatures of 5–35 °C. Although the rate constant is represented only in time of a dimensional unit, its magnitude is understood to be valid for the given conditions of the amount of absorber and the headspace volume during the non-restricted access of CO_2 gas to the absorber. Table 4 shows the chemical CO_2 absorption rate constants under various packaging conditions that have been reported in the literature. A higher temperature increases the gas absorption rate, with the activation energy ranging from 62.6 to 128.0 kJ mol^{-1} depending on the type of absorber (Charles et al., 2006).

The process of CO_2 adsorption on the surface of a porous physical absorber exposed directly to a CO_2-gas phase involves surface-film mass transfer, inter-pore diffusive gas transport and surface diffusion, all of which are affected by the porosity and surface area of the absorbent, the adsorption isotherm status, the gas flow conditions and the temperature among other factors (Yang, 1987). While the temperature and gas concentrations are the main external variables, the intrinsic variables of the adsorbent type and the surface conditions affect the CO_2 absorption process and its kinetics. Whereas a complex model can account for all of the related variables, a simplified first-order approach lumping all of the factors with relevant assumption is sufficient to describe the gas-adsorption kinetics in a stagnant gas phase in a food package, as follows:

$$\frac{dC_{CO2}}{dt} = q_m\left(C_{CO2}^* - C_{CO2}\right) \tag{7}$$

where C_{CO2} is the amount of adsorbed CO_2 (mol g^{-1}) at time t, C_{CO2^*} is the amount of adsorbed CO_2 at equilibrium (mol g^{-1}) and q_m is a lumped parameter of the mass transfer rate constant (h^{-1}) (Yang, 1987). Table 5 presents the first-order rate constants for activated carbon compounds and zeolites.

As another way to express apparently the mass transfer onto the absorber surface fabricated into sheet form, empirical simple form may be used to describe the rate of CO_2 absorption:

$$\frac{dn_{CO2}}{dt} = k_m S_a\left(p_{CO2} - p_{CO2,s}\right) \tag{8}$$

where n_{CO2} is the moles of CO_2 adsorbed onto the adsorbent, S_a is the surface area of the adsorbent (m^2), p_{CO2} and $p_{CO2,s}$ are CO_2 partial pressure (bar) in the gas phase and the hypothetical equilibrated CO_2 partial pressure (bar) on the adsorbent surface, respectively, and k_m is the mass transfer coefficient (mol h^{-1} m^{-2} bar^{-1}). In Table 4, the mass transfer coefficient values of k_m are also listed as indices of the kinetic parameters of a chemical absorber embedded in a bio-based polymer.

When the scavenger or absorber is located in a plastic sachet, the CO_2 permeability of the sachet film will determine the rate of CO_2 removal from the gas phase of the package, for which Eq. (9) being similar to Eq. (8) applies until its full capacity is reached (Chinnan & Yang, 1989, pp. 240–243), as follows.

$$\frac{dn_{CO2}}{dt} = \frac{\overline{P}_{CO2,s}S_s\left(p_{CO2} - p_{CO2,s}\right)}{L_s} \tag{9}$$

where $p_{CO2,s}$ and S_s are the CO_2 partial pressure (bar) inside and the surface area (m^2) of the sachet, respectively, and $\overline{P}_{CO2,s}$ and L_s are the CO_2 gas permeability (mol μm h^{-1} m^{-2} bar^{-1}) and thickness of the sachet film (μm), respectively.

In Eqs. (8) and (9), $p_{CO2,s}$ may be assumed simply as zero as long as the scavenger is in an active state for the removal or reaction with CO_2 gas until reaching its full capacity. In a simplified treatment for practical applications, $(\overline{P}_{CO2,s}/L_s)$ in Eq. (9) may be used interchangeably with k_m in Eq. (8) or be understood as a lumped parameter in a derivation from comparative connection.

3. Applications of CO_2 absorbers in food packaging

Any CO_2-absorbing material, whether chemical or physical, can be incorporated or fabricated in a variety of forms for use in food packages. Powder absorbents can be enclosed within a film bag or sachet to be placed in flexible or rigid packages. The absorber

Table 4
Kinetic parameters of CO_2 absorption by chemical absorbers that have been reported in the literature.

Absorber type	Package conditions (absorber and free volume)	Temperature (°C)	k (h^{-1})[a] or k_m (mol·h^{-1}·m^{-2}·bar^{-1})[b]	Reference or source
Ca(OH)$_2$	2.55 g in 1.2 L	20	0.064[a]	Charles et al. (2006)
Ca(OH)$_2$	5.65 g in 1.2 L	20	0.017[a]	Charles et al. (2006)
Ca(OH)$_2$	1.88 g in 0.865 L	15	0.016[a]	Calculated from Shin et al. (2002)
Na$_2$CO$_3$	2.69 g in 0.865 L	15	0.106[a]	Calculated from Shin et al. (2002)
Na$_2$CO$_3$ in dry agar film	5 × 6 cm film in 1-L jar with 10 mL water	10	0.44[b]	Wang et al. (2015)
Sodium glycinate in dry agar film	5 × 6 cm film in 1-L jar with 10 mL water	10	0.13[b]	Wang et al. (2015)

Table 5
First-order rate constants of some physical CO_2 absorbents that have been reported in the literature.

Absorbent type	Experimental conditions	Temperature (°C)	q_m (h^{-1})	C_{CO2^*} (mmol/g)	Reference or source
Active carbons	5-10 mg under purified CO_2 (99.98%) at a flow rate of 50 cm^3/min	25	2.3–2.5	1.04–1.26	Rashidi, Yusup, and Lam (2013)
Active carbons	Pellets of 3 mm in multi-layered column fed with multi-component gas flow	20–42	360		Park et al. (1998)
Zeolite 5A	Pellets of 3 mm in multi-layered column fed with multi-component gas flow	26–45	180		Park et al. (1998)
Amine-modified zeolite 13X	20 g in 80-L chamber under 1500 ppm CO_2	25	2.8–3.7	1.16–1.98	Lee, Hsieh, Chen, and Chen (2013)

Table 6
Applications of CO_2 absorbers in food packaging.

Food packaged	CO_2 absorber	Packaging conditions and other extra devices	Benefits of CO_2 absorber	Reference
Strawberry	Commercial product (EMCO®)	Fruits of 200 g in a film bag at 4 °C	Reduced mould decay incidence, delayed senescence, preserved sensory score and chemical quality attributes	Aday et al. (2011)
Pear	Commercial product (Ageless®)	One fruit in a film bag at 1 °C	Prevention of internal browning	Nugraha et al. (2015)
Eggplant	Commercial product (Lipman®)	3 fruits in a polyethylene film bag at 4 °C	Reduction in chilling injury observed as external and internal browning	Veasna et al. (2012)
Shiitake mushroom	Ca(OH)$_2$	8 perforated tray packages of 500 g each in perforated low-density polyethylene bag passed through the supply chain	Reduced yeast/mould growth and decay	An (2016)
Shiitake mushroom	Agar-based label incorporated with Na$_2$CO$_3$	200 g mushrooms in perforated bag at 10 °C	Less colour change, firmer texture, good flavour, low bacterial count, alleviation of humidity saturation inside the package	Wang et al. (2015)
Kimchi	Zeolite	Al-laminated pouch or jar of 500–600 g at 15 °C	Inhibition of volume expansion and pressure build-up	Lee et al. (2001)
Kimchi	Zeolite/Na$_2$CO$_3$ in polystyrene sheet or sachet	Al-laminated pouch or jar of 500–600 g at 15 °C	Inhibition of volume expansion and pressure build-up	Shin et al. (2002)
Kimchi	Ca(OH)$_2$	Al-laminated pouch of 80 g in vacuum at 10 °C	Prevention of pouch inflation	Lee et al. (2003)
Soy paste, red pepper paste	Ca(OH)$_2$	Glass jar packages of 180 and 150 g for soy sauce and red pepper paste at 13 °C	Alleviation of pressure build-up	Jang et al. (2000)
Carbonated beverage	Activated carbon	Activated carbon in a separate pressure compartment communicable in gas-phase with product space through membrane	Maintaining consistent CO_2 pressure inside the container and/or dissolution in the beverages	Rasmussen and Vesborg (2012)
Coffee	Granule formulation of Ca(OH)$_2$/silica gel/H$_2$O in capsule	Coffee-filled pod	Maintaining the aromas of freshly roasted coffee powders with maintaining constant package volume and structure	Crump et al. (2013)

materials can be processed with binder to form beads or pellets, which can also be placed in a bag or sachet. In rare cases, CO_2 scavengers in the form of granules or powders are exposed directly to an environmental atmosphere in which CO_2 accumulation must be controlled. An absorber material can be incorporated into plastic sheets or films. Table 6 lists some examples or cases of CO_2 absorbers that have been used in food and beverage packaging applications.

3.1. Fresh produce

The use of a CO_2 absorber in a fresh-produce package or container 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.

Passive CO_2 scrubbers consisting of lime enclosed in a membranous bag or placed in an air-flow box have been employed extensively to prevent the occurrence of an excessively high CO_2 concentration in fresh-produce containers during long-distance refrigerated transport (Brecht, Dohring, Brecht, & Benson, 2009). The level of CO_2 absorption is controlled by using a CO_2 sensor and a

predictive software device. The container system is generally equipped with other sophisticated automatic control instruments, such as those designed for O_2-concentration management and ethylene removal. Compared with their common use in produce transport, the use of CO_2 scavenger in individual consumer package of fresh produce is scarce, as shown in Table 6.

Including a CO_2 absorber consisting of sodium carbonate peroxyhydrate, sodium carbonate and sodium chloride in strawberry packages achieved the proper low level of CO_2 while maintaining the O_2 concentration at 5% and was thus effective in preserving the quality of the fruit in terms of its soluble solids, tissue structure, sensory score and soundness (Aday, Caner, & Rahvalı, 2011). 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 (Nugraha, Bintoro, & Murayama, 2015). Pears are sensitive to injury by CO_2 at concentration higher than 2% (Watkins, 2000). 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 (Veasna et al., 2012). 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% (An, 2016).

Systematic MAP design methodologies using CO_2 scavengers have been developed for shiitake mushrooms that are sensitive to a high CO_2 concentration. The optimal MA could be achieved by mathematical modelling to tune the CO_2-absorption kinetics of a CO_2-absorbing agar film (using Na_2CO_3 or sodium glycinate as the active compound) to the combination of the rates of produce respiration and gas transfer across the package layer (Wang et al., 2015). Materials with different CO_2 scavenging rates and capacities can be used in tailored package design to attain the desired CO_2 concentration for the required shelf life. This modelling approach can be used to design the appropriate CO_2 scavenging system for fresh-produce packaging with micro-perforations. A differential equation based on CO_2 mass balance has been set up with employment of Eq. (8), which describes the CO_2 absorption kinetics of the scavenging film whose surface is assumed to be in the state of completed CO_2 absorption reaction ($p_{CO2,s} = 0$), as follows:

$$\frac{dn_{CO2}}{dt} = \frac{ND_{CO2}A(0.00 - p_{CO2})}{L_d}\left(\frac{1}{RT}\right) + \frac{\overline{P}_{CO2}S(0.00 - p_{CO2})}{L}$$
$$+ WR_{CO2} + k_m S_a(0.00 - p_{CO2})$$
(10)

where n_{CO2} is the moles of CO_2 in the package, N is the number of perforations in the plastic package, D_{CO2} is CO_2 gas diffusivity in the air (m^2 h^{-1}), A is the area of a perforation (m^2), p_{CO2} is the CO_2 partial pressure of the package (bar), L is the thickness of the plastic packaging film (μm), L_d is the corrected length of perforation's gas diffusional resistance (m), $\overline{P}_{CO2}$ represents the CO_2-permeability of the plastic film (mol μm m^{-2} h^{-1} bar^{-1}), S is the surface area of the plastic package (m^2), W is the produce weight (kg), R_{CO2} is the respiration rate of CO_2 production (mol kg^{-1} h^{-1}), and S_a is the exposed surface area of the CO_2-absorbing film attached to the package (m^2), T is temperature (K) and R is a gas constant (8.314×10^{-5} m^3 bar K^{-1} mol^{-1}).

Combining Eq. (10) with differential equations for the O_2 and N_2 balances could be used to estimate the CO_2, O_2 and N_2 contents in a package with a CO_2 absorption film for screening or designing potentially applicable food packages (Wang et al., 2015). It should be noted that taking into account all the factors involved could lead to the optimal package conditions consisting of the packaging film and absorber.

A systematic package design method of fresh produce adopting the mass transfer of CO_2 scavenger sachet was developed and formulated as a software to give the required sachet dimension and CO_2 absorption demand leading to estimation of the scavenger amount (Lee et al., 2014). By matching the package variables to the product characteristics to obtain the optimal O_2 and CO_2 concentrations, the package conditions to achieve the target O_2 concentration was selected first and then the CO_2-absorber conditions to provide the desired CO_2 concentration was determined. Designing an MAP using a CO_2 scavenger sachet could start by replacing the last term in Eq. (10) by Eq. (9), as follows:

$$\frac{dn_{CO2}}{dt} = \frac{ND_{CO2}A(0.00 - p_{CO2})}{L_d}\left(\frac{1}{RT}\right) + \frac{\overline{P}_{CO2}S(0.00 - p_{CO2})}{L}$$
$$+ WR_{CO2} + \frac{\overline{P}_{CO2,s}S_s(0.00 - p_{CO2})}{L_s}$$
(11)

The CO_2 concentration to be achieved can be calculated by enforcing the steady state to Eq. (11). When there is a potential risk

for this equilibrated CO_2 concentration to surpass the CO_2 tolerance limit of the product in passive permeable plastic MAP, the CO_2 absorption demand ($n_{CO2,a}$) to reduce the CO_2 concentration to the optimal level ($p_{CO2,o}$) for a given shelf life of t_s (h) can be obtained from the mass balance relationship, as follows:

$$n_{CO2,a} = \left(WR_{CO2} - \frac{ND_{CO2}Ap_{CO2,o}}{L_d}\left(\frac{1}{RT}\right) - \frac{\overline{P}_{CO2}Sp_{CO2,o}}{L}\right)t_s$$
(12)

The surface area of the scavenger sachet (S_s, m^2) required to attain this amount of CO_2 removal can be obtained using Eq. (9) under the same assumption that the CO_2 partial pressure or concentration within the sachet is nil due to the complete reactive removal of CO_2, as follows:

$$S_s = \frac{n_{CO2,a}L_s}{\overline{P}_{CO2,s}p_{CO2,o}t_s}$$
(13)

In the case of a package composed of a CO_2-absorbing active film or sheet, Eq. (13) can also be used to determine its surface area by substituting k_m for ($\overline{P}_{CO2,s}/L_s$), as discussed above.

3.2. Fermented foods and coffee

Microbial activities continue during the storage and distribution of fermented foods that are packaged without pasteurisation or sterilisation, 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. Due to its characteristic high level of solubility in food, a certain extent of CO_2 accumulation in the package can be tolerated and is occasionally desirable under chilled storage conditions; the higher level of CO_2 solubility at lower temperatures favours chilled storage to allow an affordable level of CO_2 accumulation in the package headspace during the required shelf life of the product (Chaix et al., 2014). Employing strategies that promote high-gas transport through the packaging layer can prevent serious problems in volume expansion or pressure build-up (Lim et al., 2001; Piergiovnanni, Fava, & Moro, 1993). Yogurt and cheese products are generally packaged without the inclusion of CO_2 scavenger for chilled storage and a limited short shelf life, which limit their CO_2 production and allow a high level of CO_2 dissolution into the foods. However, the integrity or soundness of the package is threatened when the amount of dissolved CO_2 and/ or rate of gas transport are not sufficient to balance to CO_2 produced in great excess by the food. Foods that produce a large amount of CO_2 over an extended shelf life cannot be managed easily by low-temperature storage or a highly permeable packaging film.

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 (Lee, Cha, Hwang, & Park, 2003; Lee, Shin, Lee, Kim, & Cheigh, 2001; Shin et al., 2002). 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 (Jang, Hwang, & Lee, 2000). The typical rates of CO_2 production by kimchi (salt content of 2.3%, acidity $\leq$ 0.6%), soybean paste (salt content of 12.4%) and red pepper paste (salt content of 6.7%) were estimated or reported to be 7.6, 0.22 and 2.7 mmol kg^{-1} d^{-1} at 13 °C (Kim, Hwang, Lim, & Lee, 2000; Lee, Kwon, & Ha, 1997). Taleggio cheese in N_2-flushed packages at 6 °C was also reported to produce

CO_2 at a high rate of 2.5 mmol kg^{-1} d^{-1} (Piergionvanni et al., 1993). The rate of CO_2 production increased with increased temperature, the effect of which was shown by activation energy values ranging from 75 to 130 kJ mol^{-1}. CO_2 scavengers are useful or necessary for packaging these types of high CO_2-producing foods when they are stored or marketed at an ambient temperature or when their shelf life is relatively long.

The required absorption demand and rate of the packaged food system are the main concerns when selecting and designing a scavenger system. The design process starts with determining CO_2 production from the product during the shelf life period. And then mass balance is formulated, as shown in Fig. 2, which states that CO_2 gas produced ($n_{CO2,P}$) is kept as combination of components in the food as dissolved state ($n_{CO2,f}$), package headspace as gas phase ($n_{CO2,h}$), scavenger as absorption ($n_{CO2,s}$) and permeation (or transport) loss through the packaging layer ($n_{CO2,l}$), as follows:

$$n_{CO2,P} = n_{CO2,f} + n_{CO2,h} + n_{CO2,a} + n_{CO2,l} \tag{14}$$

The CO_2 produced intrinsically by the food through fermentation and/or biological reactions evaporates into the package headspace, where some of it is absorbed by the absorber and some is transported toward the exterior of the package by gas permeation or leaking; the remainder of this gas remains in the food matrix. By identifying each term of $n_{CO2,P}$, $n_{CO2,f}$, $n_{CO2,h}$ and $n_{CO2,l}$, the absorption demand on the scavenger ($n_{CO2,s}$) can be calculated. After determining the absorption demand on the scavenger, $n_{CO2,s}$, the required weight of scavenger can be estimated based on its capacity, as listed in Tables 1 and 3. When using an absorber in the form of sachet contents or as an active film structure, its surface area can be calculated using Eq. (13) for a given shelf life and under the given packaging conditions, as described above.

To describe transient or dynamic conditions, a differential form of Eq. (14), which is Eq. (15), can be formulated as follows:

$$\frac{dn_{CO2,P}}{dt} = \frac{dn_{CO2,f}}{dt} + \frac{dn_{CO2,h}}{dt} + \frac{dn_{CO2,a}}{dt} + \frac{dn_{CO2,l}}{dt} \tag{15}$$

Solving this differential equation using the proper initial and boundary conditions yields the time-dependent CO_2 balances and atmospheric compositions of the package, thus allowing the design of appropriate packaging conditions. A simplified assumption of the dominant or rate-limiting process can be applied to solve this equation. In some situations, the steady states of the CO_2 mass in the food and headspace ($dn_{CO2,f}/dt = 0$, $dn_{CO2,h}/dt = 0$) can be applied. An equilibration relationship between the food phase and headspace gas phase can be imposed using Henry's law to

determine the concentration of CO_2 in the food and the headspace (i.e. $n_{CO2,h}$ and $n_{CO2,f}$) (Jakobsen & Risbo, 2009). An equilibration between the physical absorbent and the package headspace caused by an adsorption isotherm may also exist (Fig. 2).

Whereas simple CO_2 absorption can be considered or accounted for in case that the one-way or complete absorption of CO_2 from the package occurs, more delicate case exists in which some level of CO_2 in the package is desired for taste preference and food quality preservation. For example, Taleggio cheese could be preserved with best sensory quality at CO_2 concentration of 10% (Piergionvanni et al., 1993). Kimchi and yogurt stored under high CO_2 conditions gave a better sensory performance (Jansson et al., 2001; Lee & Paik, 1997; Lee et al., 2016). Maintaining the proper CO_2 concentration in a package requires elaborately designed CO_2-scavenging system to have controlled CO_2 absorption properly balanced with items in Eqs. (14) and (15). To date, determination of the package variables to achieve this goal has not been tried. Future studies may investigate the dynamics of CO_2 absorption and dissolution in food and CO_2 permeation through packaging film, which will lead to optimal package design for providing a good quality of food preservation and package soundness.

A CO_2-adsorbing/releasing system has been developed for carbonated beverages such as beer to provide a consistent level of dissolved CO_2. A canister or plastic bag containing a physical adsorbent is placed within the beverage container to maintain a relatively constant level of CO_2 partial pressure that leads to the desired level of dissolved CO_2 in the beverage (Rasmussen & Vesborg, 2012).

A large amount of CO_2 is produced when coffee beans are roasted, which remains in roasted coffee beans and their powders. The CO_2 present in packaged coffee diffuses out to expand the volume of the package or increase the package pressure to an intolerable level during storage (Vermeiren et al., 1999). A CO_2 absorber placed in the coffee package helps maintain the integrity of the package structure (Crump et al., 2013). The amount and rate of CO_2 production from coffee products vary with roasting, grinding and tempering conditions (Anderson, Shimoni, Liardon, & Labuza, 2003), which needs to be considered in the absorber system. Using both O_2 and CO_2 scavengers is desired or has been proposed to preserve the freshness of coffee products (Brody et al., 2001). Currently, roasted coffee products are packaged in various flexible packages, rigid cans and small pods composed of plastic or aluminium. CO_2 scavengers can be utilized in these coffee packages in a variety of forms of sachet, granule, coating, film and sheet.

3.3. Research needs and prospect

Whereas there has been great interest and innovations in the field of oxygen-scavenger development (Lopez-Rubio et al., 2004; Ozdemir & Floros, 2004; Pereira de Abreu et al., 2012; Rooney, 2005; Vermeiren et al., 1999), relatively little attention has been paid to CO_2 scavengers. CO_2 scavengers have been used in limited cases in packages of high CO_2-producing foods. CO_2 scavengers have been applied using a trial-and-error approach rather than a systematic design process that accounts for CO_2 production by the food, CO_2 loss due to package permeation and the scavenger's absorption capacity. CO_2 production by food may not be a simple process but rather one that changes with time and other conditions. The food supply chain may have dynamic temperature conditions, and the behaviour and preference of the consumers may require more elaborate packaging atmosphere profiles, including the desired CO_2 concentration. Competitive absorption of CO_2, water vapour and other gases may occur in the packages, depending on the type of food and the package conditions, such as the MA and the presence of other absorbers. Thus, the CO_2 absorption by the
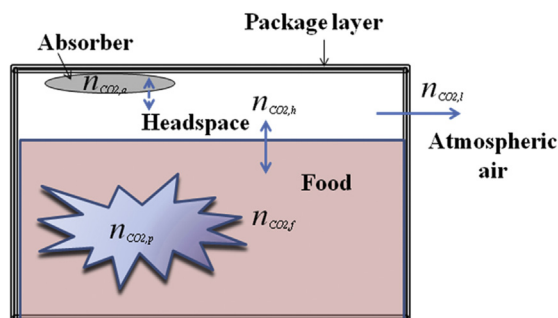
$$n_{CO2,p} = n_{CO2,f} + n_{CO2,h} + n_{CO2,a} + n_{CO2,l}$$

Fig. 2. CO_2 balance in a CO_2-producing food package containing an absorber. The thick arrows indicate the direction of CO_2 transfer or equilibrium among phases.

scavenger(s) must be balanced or tailored to the CO_2 production characteristics of food and the dynamics of the food supply chain. CO_2 permeation of the package layer may take part in the package design when needed or useful. In this context, optimization of CO_2-scavenging food packaging systems can be achieved by characterising the dynamics of the interactions among the food, the packaging material, the absorber device and the environment in terms of CO_2 production, dissolution, absorption and permeation. Innovations based on intelligent combinations of multi-disciplinary sciences and technologies are highly likely. Combining active and intelligent packaging tools such as O_2 scavengers and CO_2 sensors could have many advantageous results (Ghaani, Cozzolino, Castelli, & Farris, 2016; Puligundla et al., 2012). A CO_2 scavenger can be designed to play other roles in addition to CO_2 absorption (Ozdemir & Floros, 2004). For example, the chemical CO_2 absorbers, CaO and Na_2CO_3 can also simultaneously absorb some amount of moisture, and the absorbers can be combined with a hydro-gel for enhanced moisture absorption (Wang et al., 2015). Dual or multiple functions can be added to or combined with task of a CO_2 scavenger to optimize the preservation and improve the preference for packaged foods.

Although research and development of active packaging mostly focussed on individual consumer packages so far, the related innovative approaches may direct toward food logistics covering primary and secondary packages. The scavengers could be applied to the packaging logistic system optimizing or harmonizing the different levels or steps of unitized packaging holistically.

4. Conclusions

Chemical and physical CO_2 absorbers can be used to improve the level of preservation of packaged CO_2-producing foods during their storage and marketing. The properties of foods in terms of their CO_2 production and desired atmospheric conditions must be determined and be balanced with the thermodynamic and kinetic properties of the absorption reactions and capacities of CO_2 absorbers. Package's gas transport properties may also be considered as another interacting variable when necessary.

Acknowledgments

References

Aday, M. S., Caner, C., & Rahvalı, F. (2011). Effect of oxygen and carbon dioxide absorbers on strawberry quality. *Postharvest Biology and Technology, 62*, 179—187.

An, D. S. (2016). Effect of active master packaging system on preservation of fresh shiitake mushrooms in supply chain. *Journal of Korean Society of Food Science and Nutrition, 45*, 402—408.

Anderson, B. A., Shimoni, E., Liardon, R., & Labuza, T. P. (2003). The diffusion kinetics of carbon dioxide in fresh roasted and ground coffee. *Journal of Food Engineering, 59*, 71—78.

Baltrusaitis, J., & Grassian, V. H. (2005). Surface reactions of carbon dioxide at the adsorbed water−iron oxide interface. *Journal of Physical Chemistry B, 109*, 12227—12230.

Brecht, P. E., Dohring, S., Brecht, J. K., & Benson, W. (2009). Transportation technology and applications. In E. M. Yahia (Ed.), *Modified and controlled atmospheres for the storage, transportation, and packaging of horticultural commodities* (pp. 51—71). Boca Raton, FL, USA: CRC Press.

Brody, A. L., Strupinsky, E. R., & Kline, L. R. (2001). *Active packaging for food applications*. Lancaster: Technomic Publishing.

Caplicec, E., & Fitzgeralda, G. F. (1999). Food fermentations: Role of microorganisms in food production and preservation. *International Journal of Food Microbiology, 50*, 131—149.

Chaix, E., Guillaume, C., & Guillard, V. (2014). Oxygen and carbon dioxide solubility and diffusivity in solid food matrices: A review of past and current knowledge. *Comprehensive Reviews in Food Science and Food Safety, 13*, 261—286.

Charles, F., Sanchez, J., & Gontard, N. (2006). Absorption kinetics of oxygen and carbon dioxide scavengers as part of active modified atmosphere packaging. *Journal of Food Engineering, 72*, 1—7.

Chinnan, M. S., & Yang, C. C. (1989). Modeling the use of chemical adsorbents in controlling relative humidity and CO_2 for horticultural crops stored in polymeric films. In A. H. Ghee, N. Lodge, & O. K. Lian (Eds.), *Trends in food processing ii* (pp. 240—243). Singapore: Singapore Institute of Food Science and Technology.

Crump, J. W., Chau, C.-C., Mckedy, G. E., Payne, D. S., Powers, T. H., Solovyov, S., et al. (2013). Oxygen and carbon dioxide absorption in a single use container. European Patent Application EP2552803 A2.

Cutter, C. N. (2002). Microbial control by packaging: A review. *Critical Reviews in Food Science and Nutrition, 42*, 151—161.

Ghaani, M., Cozzolino, C. A., Castelli, G., & Farris, S. (2016). An overview of the intelligent packaging technologies in the food sector. *Trends in Food Science & Technology, 51*, 1—11.

Hauchhum, L., & Mahanta, P. (2014). Carbon dioxide adsorption on zeolites and activated carbon by pressure swing adsorption in a fixed bed. *International Journal of Energy and Environmental Engineering, 5*, 349—356.

Jakobsen, M., & Risbo, J. (2009). Carbon dioxide equilibrium between product and gas phase of modified atmosphere packaging systems: Exemplified by semihard cheese. *Journal of Food Engineering, 92*, 285—290.

Jang, J. D., Hwang, Y. I., & Lee, D. S. (2000). Effect of packaging conditions on the quality changes of fermented soy paste and red pepper paste. *Journal of Korean Society of Packaging Science and Technology, 6*, 31—40.

Jansson, S. E. A., Edsman, C. J., Gedde, U. W., & Hedenqvist, M. S. (2001). Packaging materials for fermented milk: Effects of material crystallinity and polarity on food quality. *Packaging Technology and Science, 14*, 119—127.

Kim, G. T., Hwang, Y. I., Lim, S. I., & Lee, D. S. (2000). Carbon dioxide production and quality changes in Korean fermented soybean paste and hot pepper-soybean paste. *Journal of Korean Society of Food Science and Nutrition, 29*, 807—813.

Lee, H. L., An, D. S., & Lee, D. S. (2016). Effect of initial gas flushing or vacuum packaging on the ripening dynamics and preference for kimchi, a Korean fermented vegetable. *Packaging Technology and Science, 29*, 479—485.

Lee, J. W., Cha, D. S., Hwang, K. T., & Park, H. J. (2003). Effects of CO_2 absorbent and high-pressure treatment on the shelf-life of packaged kimchi products. *International Journal of Food Science and Technology, 38*, 519—524.

Lee, S. C., Hsieh, C. C., Chen, C. H., & Chen, Y. S. (2013). CO_2 adsorption by Y-type zeolite impregnated with amines in indoor air. *Aerosol and Air Quality Research, 13*, 360—366.

Lee, D. S., Jo, Y. H., Kwon, M.-J., & An, D. S. (2014). Strategy and software application of fresh produce package design to attain optimal modified atmosphere. *Mathematical Problems in Engineering*. Article ID 363691.

Lee, D. S., Kwon, H. R., & Ha, J. U. (1997). Estimation of pressure and volume changes for packages of kimchi, a Korean fermented vegetable. *Packaging Technology and Science, 10*, 15—32.

Lee, D. S., & Paik, H. D. (1997). Use of pinhole to develop an active packaging system for kimchi, a Korean fermented vegetable. *Packaging Technology and Science, 10*, 33—43.

Lee, D. S., Shin, D. H., Lee, D. U., Kim, J. C., & Cheigh, H. S. (2001). The use of physical carbon dioxide absorbents to control pressure buildup and volume expansion of kimchi packages. *Journal of Food Engineering, 48*, 183—188.

Lee, S., Song, H.-J., Maken, S., & Park, J.-W. (2007). Kinetics of CO_2 absorption in aqueous sodium glycinate solutions. *Industrial & Engineering Chemistry Research, 46*, 1578—1583.

Lim, J. W., Park, E. S., Cheigh, H. S., & Lee, D. S. (2001). Effect of packaging unit and temperature on the volume expansion of flexible permeable package of kimchi. *Packaging Technology and Science, 14*, 41—48.

Lopes, F. V. S., Grande, C. A., Ribeiro, A. M., Loureiro, J. M., Evaggelos, O., Nikolakis, V., et al. (2009). Adsorption of H_2, CO_2, CH_4, CO, N_2 and H_2O in activated carbon and zeolite for hydrogen production. *Separation Science and Technology, 44*, 1045—1073.

Lopez-Rubio, A., Almenar, E., Hernandez-Muoz, P., Lagarn, J. M., Catal, R., & Gavara, R. (2004). Overview of active polymer-based packaging technologies for food applications. *Food Reviews International, 20*, 357—387.

Mangaraj, S., Goswami, T. K., & Mahajan, P. V. (2009). Applications of plastic films for modified atmosphere packaging of fruits and vegetables: A review. *Food Engineering Reviews, 1*, 133—158.

Marx, D., Joss, L., Hefti, M., Pini, R., & Mazzotti, M. (2013). The role of water in adsorption-based CO_2 capture systems. *Energy Procedia, 37*, 107—114.

Mulloth, L. M., & Finn, J. E. (1998). *Carbon dioxide adsorption on a 5A zeolite designed for CO_2 removal in spacecraft cabins*. Hanover, MD, USA: NASA Center for AeroSpace Information.

Nugraha, B., Bintoro, N., & Murayama, H. (2015). Influence of CO_2 and C_2H_4 adsorbents to the symptoms of internal browning on the packaged 'Silver Bell' pear (*Pyrus communis* L.). *Agriculture and Agricultural Science Procedia, 3*, 127—131.

Ozdemir, M., & Floros, J. D. (2004). Active food packaging technologies. *Critical Reviews in Food Science and Nutrition, 44*, 185—193.

Park, J.-H., Kim, J.-N., Cho, S.-H., Kim, J.-D., & Yang, R. T. (1998). Adsorber dynamics and optimal design of layered beds for multicomponent gas adsorption. *Chemical Engineering Science, 53*, 3951—3963.

Pereira de Abreu, D. A., Cruz, J. M., & Paseiro Losada, P. (2012). Active and intelligent packaging for the food industry. *Food Reviews International, 28*, 146—187.

Piergiovanni, L., Fava, P., & Moro, M. (1993). Shelf life extension of Taleggio cheese

by modified atmosphere packaging. *Italian Journal of Food Science, 5*, 115—127.

Puligundla, P., Jung, J., & Ko, S. (2012). Carbon dioxide sensors for intelligent food packaging applications. *Food Control, 25*, 328—333.

Rashidi, N. A., Yusup, S., & Lam, H. L. (2013). Kinetic studies on carbon dioxide capture using activated carbon. *Chemical Engineering Transactions, 35*, 361—366.

Rasmussen, J. N., & Vesborg, S. (2012). Method and a system for pressurising and dispensing fluid products stored in a bottle, can, container or similar device. US Patent Application US20120043352 A1.

Rodriguez-Aguilera, R., & Oliveira, J. C. (2009). Review of design engineering methods and applications of active and modified atmosphere packaging systems. *Food Engineering Reviews, 1*, 66—83.

Rooney, M. L. (2005). Oxygen-scavenging packaging. In J. H. Han (Ed.), *Innovations in food packaging* (pp. 123—137). Amsterdam: Elsevier Academic Press.

Saha, B. B., Jribi, S., Koyama, S., & El-Sharkawy, I. (2011). Carbon dioxide adsorption isotherms on activated carbons. *Journal of Chemical and Engineering Data, 56*, 1974—1981.

Salazar, V., Sánchez-Vicente, Y., Pando, C., Renuncio, J. A. R., & Cabañas, A. (2010). Enthalpies of absorption of carbon dioxide in aqueous sodium glycinate solutions at temperatures of (313.15 and 323.15) K. *Journal of Chemical and Engineering Data, 55*, 1215—1218.

Shin, D. H., Cheigh, H. S., & Lee, D. S. (2002). The use of Na_2CO_3-based CO_2 absorbent systems to alleviate pressure buildup and volume expansion of *kimchi* packages. *Journal of Food Engineering, 53*, 229—235.

Singh, P., Wani, A. A., Karim, A. A., & Langowski, H.-C. (2011). The use of carbon dioxide in the processing and packaging of milk and dairy products: A review. *International Journal of Dairy Technology, 65*, 161—176.

Sjostrom, S., & Krutka, H. (2010). Evaluation of solid sorbents as a retrofit technology for CO_2 capture. *Fuel, 89*, 1298—1306.

Veasna, H., Hwang, Y.-S., Choi, J.-M., Ahn, Y.-J., Lim, B.-S., & Chun, J.-P. (2012). 1-Methylcyclopropene and carbon dioxide absorber reduce chilling injury of eggplant (*Solanum melongena* L.) during MAP storage. *Journal of Bio-Environment Control, 21*, 50—56.

Vermeiren, L., Devlieghere, F., van Beest, M., de Kruijf, N., & Debevere, J. (1999). Developments in the active packaging of foods. *Trends in Food Science & Technology, 10*, 77—86.

Wang, H. J., An, D. S., Rhim, J.-W., & Lee, D. S. (2015). A multi-functional biofilm used as an active insert in modified atmosphere packaging for fresh produce. *Packaging Technology and Science, 28*, 999—1010.

Wang, Y., & LeVan, M. D. (2009). Adsorption equilibrium of carbon dioxide and water vapor on zeolites 5A and 13X and silica gel: Pure components. *Journal of Chemical and Engineering Data, 54*, 2839—2844.

Wang, Y., & LeVan, M. D. (2010). Adsorption equilibrium of binary mixtures of carbon dioxide and water vapor on zeolites 5A and 13X. *Journal of Chemical and Engineering Data, 55*, 3189—3195.

Watkins, C. B. (2000). Responses of horticultural commodities to high carbon dioxide as related to modified atmosphere packaging. *HortTechnology, 10*, 501—506.

Xu, D., Xiao, P., Zhang, J., Li, G., Xiao, G., Webley, P. A., et al. (2013). Effects of water vapour on CO_2 capture with vacuum swing adsorption using activated carbon. *Chemical Engineering Journal, 230*, 64—72.

Yang, R. T. (1987). *Gas separation by adsorption processes*. Boston, MA, USA: Butterworths.