Development of perforation-mediated modified atmosphere packaging to preserve fresh fruit and vegetable quality after harvest

Envasado em atmósfera modificada y películas perforadas para preservar la calidad de frutas y verduras frescas después de su cosecha

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The use of perforations as a means of obtaining large size containers suitable for modified atmosphere packaging (MAP) would greatly enhance the applicability of this technology for storage and distribution of fresh and minimally processed products. General concepts of MAP, and advantages and drawbacks of using perforations to achieve it are discussed. Products for which perforated packages can be used are listed. The variables that affect this type of package are presented and the methodology for designing an adequate package is described and illustrated with the case study of shredded cabbage.

Keywords: perforation, modified atmosphere packaging, shredded cabbage, minimally processed foods

El uso de perforaciones para obtener recipientes de gran tamaño adecuados para el envasado con atmósferas modificadas (MDP) podría incrementar de gran manera la aplicación de esta tecnología para el almacenamiento y distribución de productos frescos y mínimamente procesados. En este trabajo se revisan los conceptos generales del MDP y las ventajas e inconvenientes del uso de las perforaciones en esta tecnología. Se enumeran los productos envasados con envases perforados. Se evalúan las variables que afectan a este tipo de envasado y la metodología para el diseño de un envase adecuado. A modo de ejemplo se aplica esta tecnología al envasado de la col troceada.

Palabras clave: atmósfera modificada, películas perforadas, col troceada, alimentos mínimamente procesados

INTRODUCTION

Postharvested fruits and vegetables are highly perishable products. Over-ripening and ageing, mechanical injuries, trimming, water loss, decay, biological factors such as diseases and pests, and physiological disorders are the principal causes of postharvest losses (Salunkhe and Desai, 1984 a,b) . One estimate predicts that nearly 30–40% of the crops harvested in the developing countries never reaches the consumer due to the spoilage and mishandling that occur during distribution (Miller, 1976; Lioutas, 1988). As an example, Sparks (1976) stated that the total percent losses at the wholesale, retail and consumer levels can reach 40% for strawberries and almost 30% for peaches. The postharvest preservation of these commodities is thus an efficient technique to reduce the tremendous fresh produce losses, maintain the produce quality and extend its shelf life throughout the postharvest chain, consequently increasing its commercial value. The use of perforated modified atmosphere packaging is a potential technique for postharvest preservation of fresh horticultural commodities, and is of particular interest for large bulk quantities. However, it needs more fundamental research and experimental validation before its eventual commercial use.

In this work general aspects of modified atmosphere packaging and concepts, advantages and limitations of perforations as a means of atmosphere modification are discussed. Perforated modified atmosphere packaging design is outlined, stressing important factors and processes that influence the overall dynamic modified atmosphere packaging system. Products that can potentially be used in perforation packaging systems are listed. Respiration rate models are discussed and a preliminary study on the respiration rate of shredded cabbage is presented. The gas exchange through a perforation is analyzed. The applicability of this system is tested by simulation using a simplified model that allows the design of a perforated package for shredded cabbage.

Factors optimizing preservation

Postharvest deterioration can be controlled by primary and secondary factors. The primary factors to optimize preservation of horticultural commodities are selection of varieties of crop plants with improved storage characteristics, application of proper plant protection systems, harvesting at optimum maturity stage, minimizing mechanical injuries due to handling, using proper sanitation procedures to reduce microbial infection, and providing the optimum temperature and relative humidity during all postharvesting steps (Kader *et al.*, 1989). Temperature control (precooling and cold storage) has been identified as the crucial factor to extend the shelf life of produce. Biological reactions generally increase two- or three-fold for every 10 °C rise in temperature (Zagory and Kader, 1988). Secondary factors include modification of oxygen (O_2) and carbon dioxide (CO_2) concentrations in the atmosphere surrounding the commodity to levels different from those in normal air. Typically, fresh fruits and vegetables are stored in high CO_2 concentrations and low O_2 concentrations (Kader, 1989; Saltveit, 1989).

Although the contribution of secondary factors is not as significant as the initial product quality and the temperature control, their additive effect (making use of the hurdle concept) is important to preserve the overall produce quality. On chilling sensitive produce, for example, the use of CA/MA may overcome the impact of low temperature injury. With the use of these postharvest techniques for preservation, many commodities may be available out of season, increasing the flexibility in meeting market demands, and may be shipped to distant consumer markets with a high standard of quality.

CA/MA TECHNOLOGY

The technique of modification of the atmosphere surrounding perishable products is referred to as controlled atmosphere (CA) or modified atmosphere (MA). In CA the atmosphere is created artificially and the gases are continually monitored and adjusted to maintain the optimal gas concentrations. In MA the gaseous environment is modified naturally by the interplay among the physiology of the commodities and the physical environment. Thus, the control of the atmosphere in MA is less precise than in CA. Several articles have been published on the benefits of CA/MA technology and the extension of products' shelf life (Wolfe, 1980; Anzueto and Rizvi, 1985; Nakhasi *et al.*, 1991; Zagory and Kader, 1988; Brody, 1989).

Beneficial effects

As living organisms, fresh fruits and vegetables continue their life processes after harvest. Therefore, high levels of respiration and other metabolic processes associated with maturation, ripening and senescence continue after picking. Despite several research works on atmosphere modification, our knowledge of the physiology of MA effects remains sketchy and empirically based. Several authors reported that the use of CA/MA has a direct effect on retarding senescence, reducing respiration rate, decreasing ethylene (C_2H_4) production, reducing sensitivity to C_2H_4 action, decreasing lignification, reducing the incidence and severity of certain physiological disorders such as those induced by C_2H_4 (scald of apples and pears) and by chilling injury of some commodities, reducing susceptibility to decay, and controlling insect pests in some commodities (Brecht, 1980; Kader *et al.*, 1989). It is important to emphasize that these beneficial effects occur as long as the levels of O_2 and CO_2 are within the range tolerated by the commodity.

In reviewing the effects of CA/MA on pathogens of fruits and vegetables it was concluded that the technique reduces susceptibility to pathogen growth (Brecht, 1980; El-Goorani and Sommer, 1981) because produce senescence is delayed. El-Goorani and Sommer (1981) also noted that oxygen levels below 1% and/or CO_2 levels above 10% are needed to suppress fungal growth significantly. Another reason why CA/MA technology increases the produce shelf life is the respiration control of microbial pathogens.

Detrimental effects

Exposure of fresh fruits and vegetables to O_2 levels below their tolerance limits or to CO_2 levels above their tolerance limits may hazard the produce and decrease its storage life (Kader *et al.*, 1989). Low levels of oxygen may increase anaerobic respiration, with the consequent accumulation of ethanol and acetaldehyde causing off-flavors. Products may also experience irregular ripening and increased susceptibility to decay. Physiological disorders, such as brown stain (a form of CO_2 injury) on lettuce, internal browning and surface pitting of pome fruits, and blackheart in potatoes (Brecht, 1980; Kader *et al.*, 1989) may be induced. Carlin *et al.* (1990) observed high potassium ion leakage and high lactic acid bacteria growth in one kind of package of fresh grated carrots, when exposed to anaerobic conditions. A very important issue to take into consideration is the growth of pathogens. Some anaerobic strains can grow very well in vegetable tissues under low oxygen atmospheres and this obviously constitutes the major health hazard of CA/MA products.

Current applications

Current applications of CA and MA technologies are controlled atmosphere storage (CA storage), waxes and other surface coatings and modified atmosphere packaging (MAP). With CA storage there is an active sustained control of the composition of the gases in the storage facility (room or shipping container), regardless of the product respiration or leaks in the storage facility. CA storage is expensive and requires a certain amount of energy to maintain storage conditions. Therefore CA storage is more appropriate to long-term storage commodities and to large quantities of produce (Mannapperuma *et al.*, 1989), such as apple, cabbage, kiwifruit and pear (Kader *et al.*, 1989).

MODIFIED ATMOSPHERE PACKAGING

MAP is an atmosphere control that relies on the natural process of respiration of the product and the gas permeability of the package holding the product. Due to respiration there is a build up of CO_2 and a depletion of O_2 that must be regulated by the packaging, which has selective permeabilities for O_2 and CO_2. In steady state the O_2 flow entering the package equals the O_2 consumed by respiration and the CO_2 flow leaving the package equals the CO_2 produced by respiration. Because of the limitations of CA storage, the MAP technique was developed to provide the optimal atmosphere, not for the entire storage facility but for just the product, thus maintaining the desired atmosphere during almost all postharvest steps, even at the retail display. As well as the benefits of modifying the O_2 and CO_2 levels, MAP has the additional benefits of water loss prevention, produce protection and brand identification. MAP has a special interest in high value and highly perishable produce such as minimally processed fruits and vegetables, cut or sliced, for example, lettuce, celery, cabbage and broccoli (Kader *et al.*, 1989).

MAP can be applied to shipping containers and retail packages (Kader *et al.*, 1989). Retail packs can be presented in two types of containers: (i) ellipsoid-cylindrical polymeric bags with sealed ends; and (ii) parallelepipedic square trays sealed across the top with polymeric films (Exama *et al.*, 1993), and also in individual film wrapping (Barmore, 1987). The first two retail packs may contain several intact commodity units or minimally processed produce, while the last one is used only for individual units of commodity.

To achieve the desired atmosphere more rapidly the modification of the atmosphere in the package can be helped/accelerated by the use of absorbers or by pulling a vacuum and replacing the atmosphere with the desired one; these procedures are known as active modification, by contrast, to passive modification without these adjuvants.

Polymeric films

Permeable polymeric films are the most popular of the available barriers to create modified atmospheres (Talasila *et al.*, 1992a). Polyvinylchloride (PVC) used primarily for overwrapping, and polyethylene used for bags have been the most commercially used films (Barmore, 1987; Robertson, 1993) but the advances in co-extrusion technology allowed the development of new materials with a wider range of permeabilities. In polymeric films the permeability to CO_2 is much higher than the permeability to O_2, therefore the level of CO_2 that may be obtained inside the package is limited by the O_2 concentration. An attempt to have a high CO_2 concentration inside the package would potentially expose the product to anaerobic conditions due to a lack of O_2 supply. This limitation restricts the use of polymers to products that require CO_2 concentrations lower than 8% (Emond, 1992). Cameron (1989) concluded that the desirable concentrations for preservation of cherries cannot be accomplished with polymeric films alone. Exama *et al.* (1993) analyzed the suitability of commercially available plastic films for MAP, concluding that most films did not provide the adequate permeability and ratio of CO_2 to O_2 permeabilities required to achieve the optimal concentrations inside typical packages for MA. In addition, polymeric films have several disadvantages: they are not strong enough for packages much larger than the small consumer ones; their permeability characteristics change unpredictably when they are stretched or punctured; they are a barrier to water vapor causing condensation inside packages and creating conditions favorable for microbial growth and decay of produce; and any accidental puncture can change the desired modified atmosphere composition because pressure inside the package may be lower than the atmospheric pressure (Marcellin, 1974; Talasila *et al.*, 1992a; Talasila *et al.*, 1995). Despite great advances in polymer technology, the uniformity and constancy of polymeric films are not yet totally satisfactory and neither is the effectiveness of the seal. In their review on MAP, Kader *et al.* (1989) referred to the problem that a given film is often reported to have a broad range of permeabilities, reflecting high variability in the measurements and variations in fabrication among manufacturers and even among batches from the same manufacturer. Cameron *et al.* (1995) verified large variations between different batches of polyethylene films on oxygen and carbon dioxide permeability coefficients. Beit-Halachmy and Mannheim (1992) measured a large range of O_2 and CO_2 permeability values of two types of polyvinylchloride films posing a difficulty in predicting gas concentrations in MAP at equilibrium.

PERFORATED MODIFIED ATMOSPHERE PACKAGING

The limitations of polymeric films presented above and the growing interest towards MAP of large packages and pallet loads of product (Barmore, 1987; Kader, 1992) resulted in the development of the so-called modified atmosphere bulk packages. The modified atmosphere bulk packages can be an impermeable covering with a diffusion window to allow gas exchange. The diffusion window may be a very permeable silicone membrane (Marcellin, 1974) or a perforation (Emond and Chau, 1990a; Emond *et al.*, 1992), or a set of perforations alone or in conjunction with windows of polymeric films (Emond *et al.*, 1991). The covering can be a gas-tight material such as waxed fiberboard, Plexiglas, polyethylene or other polymer cover, or even a gas-tight metal container. Therefore, a single perforation or several perforations in a container, depending on its physical characteristics, may act like a polymeric film in the regulation of gas exchange to provide the optimum conditions inside the packages. The number and position, as well as the area and length, of perforations will control the atmosphere inside the container. Very little research has been done on perforated modified atmosphere packages. Perforations have already been described in the literature as macroscopic and microscopic holes in polymeric films. For some authors they have been a means of reducing the cooling time (Kader *et al.*, 1989) and of preventing condensation inside the package, for others a means of achieving the desired atmosphere that would otherwise be impossible: the ratio of permeabilities does not allow it or film permeability is not sufficient for high respiring products (Cameron, 1989; Exama *et al.*, 1993; López-Briones *et al.*, 1993). Marcellin (1974) used a perforation in bulk packages to equilibrate the pressure inside the package. Perforated modified atmosphere of bulk packages with impermeable covering has been studied by Emond (1992).

Advantages

There are some advantages of perforations over polymeric films (Emond and Chau, 1990b).

(a) Commodities requiring high CO_2 concentrations with relatively high O_2 concentrations can be packaged with this system. Because their CO_2/O_2 ratio is lower than one (Silva, 1995; Fonseca *et al.*, 1996), perforation systems can obtain a high CO_2 concentration without reducing the O_2 concentration inside the package below critical levels tolerated by the product.
(b) Perforations have higher permeability than polymeric films. Permeability of oxygen in air is about 8.5 million times that in low density polyethylene film and this ratio is 1.5 million for carbon dioxide (Mannapperuma *et al.*, 1989). Thus, the size and the number of perforations required to obtain the optimal conditions are small whereas polymeric films require relatively large surfaces.
(c) A flexible system is obtained due to the ability to change the gas transfer coefficients by changing the size and shape of the perforations.
(d) Perforations can be easily changed when the package is exposed to different temperatures, allowing the package atmosphere to be adjusted when respiration rates change.
(e) The material of the package can be any gas impermeable material. Thus, MAP using perforations can

be adapted easily to various packages, including large bulk packages.

(f) Water vapor condensation will be prevented.

(g) The package is reusable.

Disadvantages

This kind of packaging technology cannot be applied for all commodities. Potential commodities are limited by the permeability ratio of the perforation to products with determined tolerance range of O_2 and CO_2 concentrations. Another problem with these larger containers is the non-uniformity of concentrations inside the package due to gas stratification. A poor distribution of gases in the package may shorten the storage life of the product. For larger packages, more than one perforation may be used to reduce gas stratification inside the package. However, it is also foreseen that multiple perforations will induce a draft through the package, thus making the prediction of gas concentration inside the package rather difficult. Two perforations of the same size may not necessarily give twice the effect of a single perforation unlike polymeric films, where increasing the film surface area results in a proportional increase in permeability (Emond and Chau, 1990b).

PERFORATED MODIFIED ATMOSPHERE PACKAGING DESIGN

More fundamental research has to be developed to reach full understanding of this technology. The development of a mathematical model to predict the gas concentrations inside a package, instead of a trial and error (pack and pray) approach, is the efficient way to properly design a package. Creating the atmosphere best suited for the extended storage of the produce while minimizing the period of time required to achieve the desired atmosphere is the objective of modified atmosphere packaging design. A MAP system incorrectly designed may be ineffective or even shorten the storage life of a product. If the desired atmosphere is not established rapidly the package has no benefit, and if O_2 and/or CO_2 levels are not within the recommended ranges of O_2 and CO_2 concentrations the product may experience serious alterations, already mentioned, and its storage life will be shortened. MAP should therefore only be done if it is done well. Cameron *et al.* (1995) found, in MA packages of precut mixed salad, extremely low levels of O_2, accumulation of ethanol and the presence of 'fermented' odors and flavors, indicating that the package design was not capable of maintaining aerobic conditions.

Designing a MAP system for a particular commodity requires analyzing the commodity, the packaging and the environmental factors, and developing a predictive model of the gas concentrations inside the package as a function of these factors. The commodity factors include specification of the commodity, its weight and optimum atmosphere for preservation, as well as the respiration rate as function of temperature and gas concentrations. In terms of packaging factors, the first decision to take is to choose the kind of packaging. If the packaging system is a polymeric flexible film the crucial design aspect is the selection of a film with correct permeability properties, surface area and thickness. If the packaging system is an impermeable covering with perforations the crucial parameters are: dimensions and shape of the covering; area and length of perforations; and their number and position required to minimize concentration gradients inside the package.

Knowledge of the surrounding conditions that the package will be exposed to (relative humidity, temperature, and O_2 and CO_2 concentrations) is essential, as these are the environmental factors to be analyzed. In the postharvest chain the temperature varies along the different steps of the chain: usually low during storage, eventually higher during shipment and definitely higher at retail display. The package design with temperature variation is more difficult because changes in temperature may affect respiration rate and gas exchange through the package barrier and consequently gas concentrations inside the package.

The differential equations of mass balance for O_2 and CO_2 in a perforated package, assuming no gas stratification and considering also that there are no interactive effects between the perforations and that the consumption of O_2 and production of CO_2 are only due to the respiration process of the produce, reduce to:

$$V \frac{dy_{O_2}}{dt} = NK_{O_2}(y^*_{O_2} - y_{O_2}) - R_{O_2} W \tag{1}$$

$$V \frac{dy_{CO_2}}{dt} = NK_{CO_2}(y^*_{CO_2} - y_{CO_2}) + R_{CO_2} W \tag{2}$$

Optimal O_2 and CO_2 concentrations for preservation of a selected produce

Much research has been done on the optimum atmosphere conditions for many commodities. Exact optimum conditions vary with the product, cultivar, maturity stage at harvest, temperature and duration of storage (Kader, 1980). A summary of CA/MA requirements and the optimum atmospheric conditions for selected vegetables was presented by Saltveit (1989), and for fruits other than pome fruits by Kader (1989). A classification of fresh fruits and vegetables according to their tolerance to reduced O_2 and elevated CO_2 was presented by Kader *et al.* (1989). López-Briones *et al.* (1993) indicated the optimal concentrations for mushrooms. Mannapperuma *et al.* (1989) supplied a plot of recommended modified atmospheres for the storage of a number of fresh vegetables, with oxygen concentration as the abscissa and carbon dioxide concentration as the ordinate. Optimal concentrations for minimally processed products are not so well documented. The tolerance of minimally processed products to CO_2 levels is expected to be higher than that of intact products, because the barrier to diffusion is smaller (Kader *et al.*, 1989). Kaji *et al.* (1993) reported the optimal concentrations for shredded cabbage.

It is important to know which potential products can be used in this type of package. A simple analysis to determine the suitability of perforation packaging systems to any produce is given by Emond and Chau (1990b). At steady state the equations describing the gas exchange across a package can be written as:

$$NK_{O_2}(y^{x}{}_{O_2} - y^{eq}{}_{O_2}) = R_{O_2}W \tag{3}$$

$$NK_{CO_2}(y^{eq}{}_{CO_2} - y^{x}{}_{CO_2}) = R_{CO_2}W \tag{4}$$

The ratio of these two equations leads to:

$$\frac{K_{CO_2}(y^{eq}{}_{CO_2} - y^{x}{}_{CO_2})}{K_{O_2}(y^{x}{}_{O_2} - y^{eq}{}_{O_2})} = \frac{R_{CO_2}}{R_{O_2}} \tag{5}$$

The relationship between the concentrations of O_2 and CO_2 at equilibrium in the package depend on: (i) the concentrations outside the package; (ii) the ratio of CO_2 to O_2 mass transfer coefficients, known as the β ratio; and (iii) the ratio of the production rate of CO_2 to the consumption rate of O_2, namely the respiratory quotient (RQ).

Thus, knowing the respiratory quotient of the product, the β ratio of the perforation and the concentrations outside the package, the calculation of the relationship between O_2 and CO_2 concentration is straightforward. In a study on the gas exchange through perforations we concluded that the β ratio for any perforation was not influenced by any factor and that the average value was 0.82 ± 0.04. Perforation packaging systems cannot therefore be applied to all produce. This β value is adequate for the following list of products: blackberry, strawberry, raspberry, blueberry; sweet cherry, cantaloupes, fig, lemon, parsley, grapefruit, lime, shredded cabbage and spinach.

Respiration rate of selected produce

The control of respiration is the most important effect of modification of atmosphere (Zagory and Kader, 1988). The respiration process takes in oxygen and generates carbon dioxide, and therefore respiration is slowed down by decreasing available O_2. Elevated CO_2 concentrations can also have a direct action in reducing respiration rate by virtue of Le Chatelier equilibrium principles (Wolfe, 1980). Respiration is a metabolic process that provides the energy to the biochemical processes of the plant and consists of the oxidative breakdown of organic reserves to simpler molecules including CO_2 and water with a release of energy. The organic substrates broken down in this process may include carbohydrates, lipids and organic acids. The ratio of CO_2 produced to O_2 consumed, known as the respiratory quotient, is normally assumed to be equal to one if the metabolic substrates are carbohydrates. If the substrate is a lipid RQ is assumed to be 0.7, and if it is an acid 1.3. Therefore, RQ can range from 0.7 to 1.3. It is much greater than one when anaerobic respiration takes place, even if the substrate is a carbohydrate (Mannapperuma *et al.*, 1989). Carlin *et al.* (1990) obtained a RQ of six with grated carrots in a packaging film, indicating anaerobic respiration. Beit-Halachmy and Mannheim (1992) found an RQ of approximately one for mushrooms at 20°C above 1.5–2% of O_2; below this O_2 level the RQ increased rapidly to a value higher than six.

The respiration rate of a fresh produce can be expressed as the oxygen consumption rate and/or the carbon dioxide production rate. The respiration rate depends on the type and maturity of the commodity as well as on the surrounding gas concentrations and temperature (Kader *et al.*, 1989). Thus, the development of an adequate model for predicting the concentrations of O_2 and CO_2 in a perforated modified atmosphere bulk package requires the development of empirical equations relating respiration rate of the selected fresh produce to temperature and concentrations of O_2 and CO_2.

Little research has been done on respiration rate models. Large experimental errors in the determination of the respiration rate are a barrier to the development of predictive models; consequently, a constant respiration rate is sometimes considered in MAP modeling reported in the literature. However, this approach can only be accepted as a simplified model, as in fact MAP relies on the ability to control the respiration rate by changing the atmosphere composition. The models in the literature are either empirical (Henig and Gilbert, 1975; Yang and Chinnan, 1988; Cameron *et al.*, 1989; Beaudry *et al.*, 1992; Emond, 1992; Talasila *et al.*, 1992b) or based on the Michaelis–Menten equation (Lee *et al.*, 1991; Cameron *et al.*, 1994; Joles *et al.*, 1994). In general, the studies on respiration rates are oriented for studying the influence of temperature or for analyzing the effect of gas concentrations, but rarely are both factors considered simultaneously. Temperature may vary significantly along the distribution chain. A package is designed for a specific outside temperature; therefore, it may not be properly designed for other temperatures, hence the importance of knowing the influence of temperature on the respiration rate. Another limitation is that most available data are either oxygen consumption or carbon dioxide production rates, thus assuming the respiratory quotient to be unity. If the RQ were greater than unity, the model would underestimate CO_2 production and if the RQ were smaller it would overestimate it. The influence of CO_2 concentration on O_2 and CO_2 respiration rate is another study that has not been sufficiently investigated.

The usual methods of respiration rate determination are the closed or static system; the flow or flushed system; and the packed system. In the static system a gas-tight container of known volume called a respirometer is filled with product and flushed with a known gas mixture. Changes in the concentration of O_2 and CO_2 over a certain period of time are measured to estimate respiration rates. In the flow system, the product is enclosed in an impermeable container through which a known mixture of gases flows at a known rate. The respiration rates are calculated from the difference in gas concentrations between the outlet and the inlet. By contrast to the static system, in which it is sometimes difficult to estimate accurately the gas volume, in dynamic systems it is often difficult to estimate accurately the rate of gas flow. In the flow system the flow rates must be well chosen in order to measure accurately the difference in the gas concentrations between the inlet and the outlet. The packed system consists of analyzing the changes in concentration inside a package of known permeability characteristics (Beaudry *et al.*, 1992; Joles *et al.*, 1994).

Fonseca *et al.* (1995) studied the influence of storage temperature, O_2 concentration and CO_2 concentration on O_2 consumption rate and CO_2 production rate of shredded cabbage, a potential product for perforated MAP. The static method was chosen to measure the respiration rate (consumption of O_2 and release of CO_2). The influence of storage temperature (1, 12, 20 °C), O_2 concentration (5–10%) and CO_2 concentration (10–15%) on the oxygen consumption rate and carbon dioxide production rate was assessed. Additional experiments were performed in atmospheric air at 1, 12 and 20 °C. A factorial design at two levels was used. The levels considered for each variable were: temperature (1–20 °C), O_2 concentration (5–10%) and CO_2 concentration (10–15%). No significant effects of O_2 and CO_2 concentrations on the O_2 consumption and CO_2 production rates were found. Respiration rates when the product was exposed to atmospheric air were higher when compared with the results obtained with the other O_2/CO_2 mixtures tested. The expected effect of O_2 and CO_2 concentration appears to be too low to be distinguishable from experimental variability. Future experiments should be conducted with a wider range of O_2 and CO_2 concentrations. Temperature was the only variable with a significant effect on the O_2 consumption and CO_2 production rates at the 95% confidence level. The Q_{10} value (the increase in the respiration rate for a 10 °C temperature increase) ranged from 3.5 to 7.2 between 1 and 12 °C and from 1.4 to 3.0 between 12 and 20 °C. The respiratory quotient ranged from 0.4 to 1.2, with an average value of 1.0.

Gas exchange through a perforation

Emond *et al.* (1991) studied the O_2 and CO_2 exchange through a perforation drilled in a Plexiglas box. Silva (1995) had also studied the O_2 and CO_2 exchange through a perforation, but in this work the perforation was a tube inserted in a glass jar lid. Both works developed an empirical additive model relating oxygen and carbon dioxide coefficients with temperature, diameter and length of the perforation. Silva (1995) did not identify an influence of temperature on the coefficients. Emond *et al.* (1991) and Silva (1995) concluded that the β ratio was 1.0 ± 0.2 and between 0.72 and 0.98, respectively, while the previous work of Mannapperuma *et al.* (1989) reported the value of 0.8 for holes, as well as for microperforations in films. In a preliminary study of the influence of some factors on the gas exchange though a tube inserted in a glass jar lid, Caldas *et al.* (1995) concluded that the diameter and length of the tube influenced the O_2 and CO_2 transfer coefficients at a significance level of 95%, while temperature and depth of penetration of the tube had no significant effect. The β ratio was not influenced by any of the factors studied, and therefore this parameter cannot be controlled by changing the tube characteristics. In a more detailed study, Fonseca *et al.* (1996) presented a multiplicative equation (Equation 6) relating the O_2 transfer coefficient with the diameter and length of the tube; the CO_2 transfer coefficient was related with the O_2 transfer coefficient by the β ratio (Equation 7), in the range of lengths 5 mm $< L <$ 30 mm and range of diameters 8 mm $< D <$ 17 mm. This study has also shown that the lumped mass capacitance model developed by Emond *et al.* (1991) provided an adequate description of O_2 and CO_2 exchange process through a perforation. Temperature also had no significant effect on the mass transfer coefficients and it was further verified that the positive effect of diameter and the negative effect of length of perforation on O_2 and CO_2 mass transfer coefficients were lower than that which would be expected from Fick's law of diffusion, highlighting that some end effects might be present. It is essential to note that this β ratio consistently obtained by the various authors is approximately equal to the square root of the ratio between molecular weight of O_2 and molecular weight of CO_2. We therefore believe that for perforations, the size of the molecules is the single controlling factor of the relative mass transfer rates.

$$K_{O_2} = (9.12 \pm 3.53) \times 10^{-6} \times D^{1.47 \pm 0.08} \times L^{-0.55 \pm 0.03} \quad (6)$$

$$K_{CO_2} = (0.82 \pm 0.04) \times K_{O_2} \quad (7)$$

Gradient of concentrations inside a package

A major goal in the design of a modified atmosphere bulk package is to minimize the gas concentration profile inside the package. The magnitude of this problem and the remedy for it through package design has to be fully investigated.

Emond and Chau (1990a) compared experimental gas concentrations of O_2 and CO_2 at steady state with blueberries in a single perforated package with the predicted values, using two different models: the lumped model used in literature and the distributed system model. The lumped model assumes the gas concentration inside the package to be uniform. The distributed system model considers a concentration profile inside the package. The authors concluded that gas concentrations predicted by the distributed system model are very close to the experimental values. The values predicted by the lumped model were more similar to those measured near the perforation. Emond and Chau (1990a) concluded that: (i) reducing package length reduces gas concentration differences inside the package; (ii) the diffusion window permeability does not significantly affect gas concentration differences but does (iii) affect the absolute value of gas concentration; and (iv) increasing the free volume inside the package decreases gas concentrations profiles but conversely increases the time necessary to reach steady state.

Application of perforated modified atmosphere packaging to shredded cabbage

It is important to verify the potential applicability in real-life situations of perforated packages as a suitable modified atmosphere package. Shredded cabbage is an interesting minimally processed product in the Portuguese market with potential to be packaged in perforated MAP due to its high respiration and transpiration rate, high CO_2 levels for optimal preservation and high commercial value. This product was selected for presenting a case study. The optimal concentrations for shredded cabbage were taken as 5–10% O_2 and 5–15% CO_2 (Kaji *et al.*, 1993).

In order to know if the atmosphere inside the perforated package may achieve the gas concentrations desired to preserve the produce in a reasonable period of time, a simplified model can be developed in order to simulate the process. This simplified model considers a constant respiration rate, a constant temperature and a uniform concentration inside the package. With these assumptions, Equations (1) and (2) can be integrated, yielding the history of concentrations of both gases in the package (Equations (8) and (9)).

$$\frac{y_{O_2} - \left(y^{x}_{O_2} - \frac{R_{O_2} W}{NK_{O_2}}\right)}{y^{0}_{O_2} - \left(y^{x}_{O_2} - \frac{R_{O_2} W}{NK_{O_2}}\right)} = e^{-\frac{NK_{O_2} t}{V}} \quad (8)$$

$$\frac{y_{CO_2} - \left(y^{x}_{CO_2} + \frac{R_{CO_2} W}{NK_{CO_2}}\right)}{y^{0}_{CO_2} - \left(y^{x}_{CO_2} + \frac{R_{CO_2} W}{NK_{CO_2}}\right)} = e^{-\frac{NK_{CO_2} t}{V}} \quad (9)$$

At steady state these equations reduce to:

$$y^{eq}_{O_2} = y^{x}_{O_2} - \frac{R_{O_2} W}{NK_{O_2}} \quad (10)$$

$$y^{eq}_{CO_2} = y^{x}_{CO_2} + \frac{R_{CO_2} W}{NK_{CO_2}} \quad (11)$$

Equations (8) and (9) show that the variables that affect the time required to reach the equilibrium are: (i) the O_2 and CO_2 mass transfer coefficients; (ii) the number of perforations; (iii) the free volume inside the package; (iv) the concentrations of O_2 and CO_2 at the beginning and at equilibrium; and (v) the product weight. Usually the initial concentrations are those in atmospheric air and the concentrations at equilibrium are the ones for optimal preservation of the produce, thus the variables that can be manipulated are only the mass transfer coefficients, the number of perforations and the free volume (which relates to package dimensions and produce weight).

Equations (10) and (11) indicate that the variables that affect the concentrations at equilibrium are: (i) the O_2 consumption rate; (ii) the CO_2 production rate; (iii) the O_2 and CO_2 mass transfer coefficients; (iv) the number of perforations; (v) the produce weight; and (vi) the initial concentrations of O_2 and CO_2. We had determined the respiration rates of shredded cabbage at 1 °C for low O_2 and high CO_2 in an earlier study, being $8.0 \pm 3.2 \times 10^{-6}$ $m^3O_2/(kg.h)$ and $6.1 \pm 2.5 \times 10^{-6}$ $m^3CO_2/(kg.h)$ (Fonseca *et al.*, 1995). From the knowledge that β is constant and equal to 0.82 (previously mentioned), K_{CO_2} in Equation (11) can be replaced by $0.82 \times K_{O_2}$ and therefore if one assumes constant respiration rates, the O_2 and CO_2 concentrations at equilibrium are a linear function of $W/(NK_{O_2})$ (Figure 1). The range of values of the

$W/(NK_{O_2})$ ratio for obtaining simultaneously the optimal O_2 and CO_2 concentrations for shredded cabbage is 13670 to 19913 kg h/m^3 (Figure 1). From this range and from Equation (6) it is easy to determine the minimum and maximum value of the perforation diameter for obtaining the optimal concentrations for preservation of shredded cabbage, once the produce weight is specified, for any value of the perforation length. This can be done graphically from Figure 2, where for the lengths 0.5, 1, 2 and 3 cm, the minimum and maximum diameters can be read for any value of the product weight, up to 14 kg. Instead of a single perforation, multiple perforations can be used in the package. Figure 3 allows for a simple graphical calculation of the diameter of each perforation (D_N) from the diameter of a single perforation (D_1) calculated from Figure 2, for different numbers of perforations up to 50 (note that we are assuming that there are no interactions resulting from the use of multiple perforations).

The free volume of the package can be calculated from the diameter of a single perforation with the equation of the transient period for CO_2 (because the CO_2 process is slower than the O_2 process, it is used as the limiting step for achieving equilibrium) for any value of the equilibration time that is specified. Figure 4 shows this relation

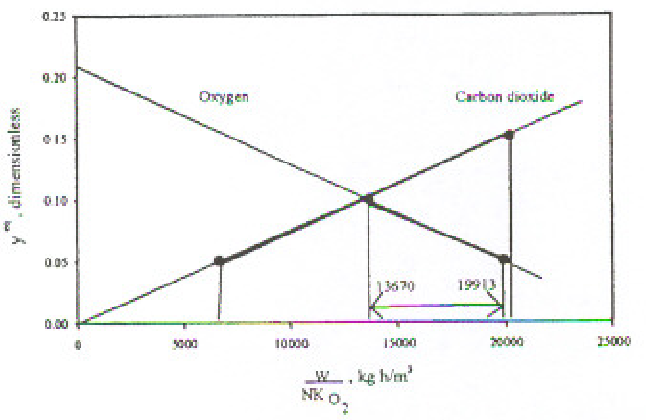

Figure 1. Concentrations of O_2 and CO_2 at equilibrium as a function of the ratio of produce weight to number of perforations and O_2 mass transfer coefficient. The arrow indicates the values for achieving optimal concentrations for preservation of shredded cabbage.

Figura 1. Concentraciones de O_2 and CO_2 en el equilibrio en función de la relación de peso frente al número de perforaciones y el coeficiente de transferencia de materia. La flecha señala los valores para obtener las concentraciones óptimas de conservación de la col troceada.

graphically for 0.5, 1, 2 and 3 cm of perforation length. The graphs allow for a good visualization of the effect of specifying a lower time for equilibration in the free volume. In principle it is preferable to have an equilibration time as small as possible, to avoid detrimental changes during the equilibration, which obviously occur at faster rates. However, small overhead volumes lead more easily to composition stratification, which we are neglecting in this procedure. It is necessary to note that Figure 4 was not drawn for the time required to achieve actual equilibrium, but for a dimensionless concentration of 0.05 (5% from equilibrium), because the transient equation does not have a real solution for a dimensionless concentration of 0 (zero).

An example of calculation can be given to clarify how Figures 1 to 4 can be used very easily by any producer. Taking the case of wishing to pack 5 kg of this shredded cabbage, we start by determining the optimum range of values of $W/(NK_{O2})$ from Figure 1. Since the CO_2 dimensionless concentration must be between 5 and 15% and that of O_2 between 5 and 10% (Kaji *et al.*, 1993), the optimum range is 13670–19913. The range of diameters of a single perforation is taken from Figure 2 for 5 kg. If the perforations available have a 5 mm length, the minimum diameter is 5 mm and the maximum 6.5 mm; for L = 10 mm, the diameter range is 6.5 to 8.4 mm; for L = 20 mm, the diameter range is 8.4 to 10.9 mm; for L= 30 mm it is 9.8 to 12.6 mm. In real situations, that is the diameter of the perforations that is normally fixed and plugs can be cut with any required length. It is possible to use smaller diameters, by having more than one perforation. The diameter of N perforations which give the same effect as one single perforation with the diameter specified in Figure 2 can be determined using Figure 3. For example, for L= 5 mm where the diameter of a single perforation ranges from 5 to 6.5 mm, the diameter of two perforations ranges from 3.12 mm to 4.03 mm and for 10 perforations diameters smaller than 2 mm could be used. The free volume inside the package can be determined using the range of diameters of a single perforation and the time considered adequate to achieve equilibration with Figure 4 (time for reaching 5% of equilibrium). For the example of L = 5 mm, the free volume ranges between 1.65 dm^3 and 2.40 dm^3 for an equilibration time of 24 h.

Unfortunately, shredded cabbage is a material with a very large bulk porosity. Without pressing the cabbage, a bulk porosity of the order of 80% and higher would occur. This means that in order to have such a small free volume as indicated in the above calculations, the cabbage would have to be significantly pressed, which would have many detrimental effects. Furthermore, a large bulk porosity means the possibility of significant stratification

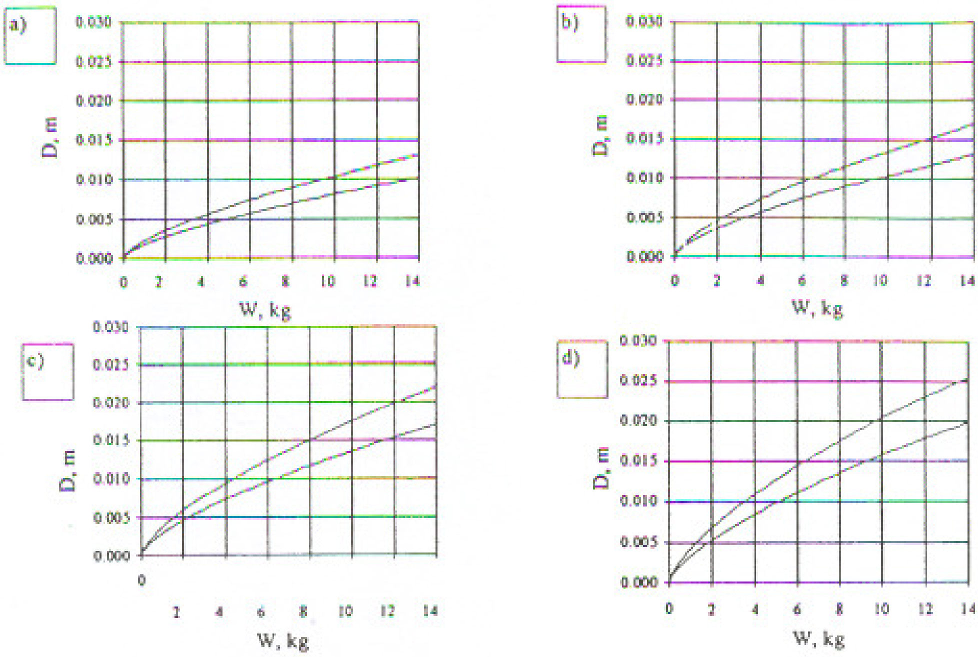

Figure 2. Diameters of a single perforation as a function of produce weight. Perforation lengths: (a) 0.005 m; (b) 0.01 m; (c) 0.02; (d) 0.03 m.

Figura 2. Diámetros de una perforación en función del peso del producto. Altura de la perforación: (a) 0,005 m; (b) 0,01 m; (c) 0,02; (d) 0,03 m.

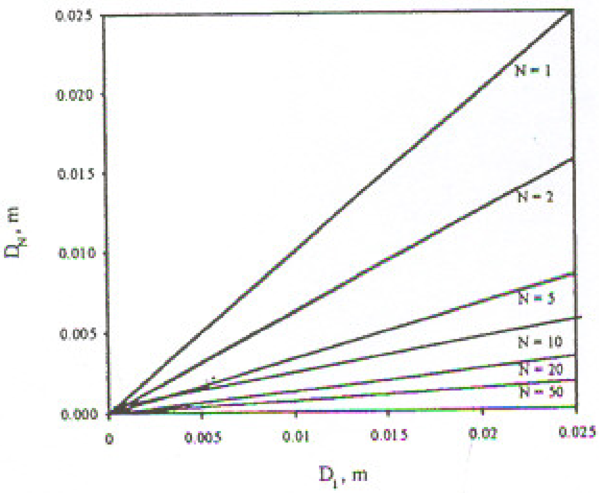

Figure 3. Relationship between the diameter of a single perforation and the diameter of each of *N* perforations (assuming no interactive effects).

Figura 3. Relación entre el diámetro de una perforación y el diámetro de cada una de las *N* perforaciones (sin efectos interactivos).

of the gas compositions within the bulk material. A time of 24 h may also be excessive for this type of material. The final conclusion is that although a perforated package is suitable for storing shredded cabbage under MAP in terms of equilibrium conditions, it is unlikely that the equilibration can proceed satisfactorily. It is therefore advisable to flush the package with the required gas concentration when packing.

It is interesting to compare the use of polymeric films (in smaller packages) for this type of produce. The equations of O_2 and CO_2 concentrations at equilibrium using a film are:

$$y^{eq}_{O_2} = y^{\infty}_{O_2} - \frac{R_{O_2} WL}{AP_{O_2}} \tag{12}$$

$$y^{eq}_{CO_2} = y^{\infty}_{CO_2} + \frac{R_{CO_2} WL}{AP_{CO_2}} \tag{13}$$

For a common low density polyethylene (LDPE) film, Mannapperuma and Singh (1994) reported the O_2 permeability as 2.39×10^{-12} m^2/s and the CO_2 permeability as 10.45×10^{-12} m^2/s, thus the β ratio is 4.17. Illustrating the O_2 and CO_2 concentrations at equilibrium as function of $WL/(AP_{O_2})$ in Figure 5, it is possible to conclude that there are no $WL/(AP_{O_2})$ values that allow us to obtain simultaneously the optimal O_2 and CO_2 concentrations for shredded cabbage. The minimum β ratio for

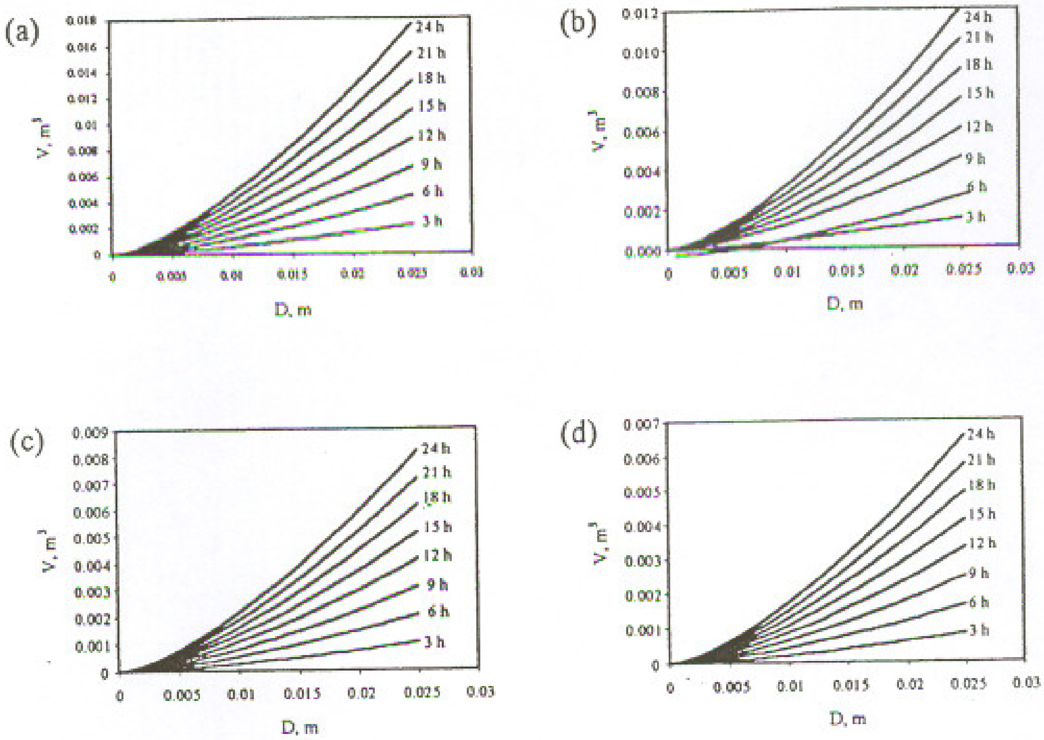

Figure 4. Free volume inside the package as function of the diameter of a single perforation and of the time required to reach a dimensionless concentration of 0.05. Perforation lengths: (a) 0.005 m; (b) 0.01 m; (c) 0.02; and (d) 0.03 m.

Figura 4. Volumen libre del envase en función del diámetro de una perforación y el tiempo necesario para alcanzar una concentración adimensional de 0,05. Altura de la perforación: (a) 0,005 m; (b) 0,01 m; (c) 0,02; (d) 0,03 m.

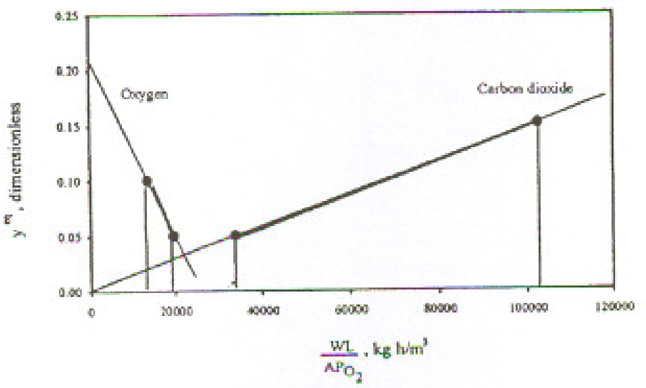

Figure 5. Concentrations of O_2 and CO_2 at equilibrium as a function of the ratio of produce weight and thickness of the film to surface area of film and O_2 mass transfer coefficient for an LDPE film.

Figura 5. Concentraciones de O_2 and CO_2 en el equilibrio en función de la relación entre el peso del producto y el espesor de la película con respecto a la superficie de la película y el coeficiente de transferencia de materia para una película LDPE.

polymeric films found in literature (Marcellin, 1974; Anzueto and Rizvi, 1985; Zagory and Kader, 1988; Nakhasi *et al.*, 1991; Talasila *et al.*, 1992a; Exama *et al.*, 1993; López-Briones *et al.*, 1993; Mannapperuma and Singh, 1994; Cameron *et al.*, 1995) was 2.2 for a hydrochloride film (Exama *et al.*, 1993). This value is sufficiently low to allow for a range of $WL/(AP_{O_2})$ where both concentrations can be optimized, which is 17970 to 19913 kg h/m³ (Figure 6). The range of values is much narrower than with perforations which implies that the flexibility of the system is greatly limited.

Future trends

The possibility of changing the ratio of CO_2 and O_2 permeabilities of perforations should be explored. This involves studying the effect of using molecular sieves or materials that interact with the gases and delay their movement (as in gas chromatography columns). By selectively impairing the movement of one of the gases, it would be theoretically possible to adjust the β ratio. The simultaneous use of polymeric windows is another area

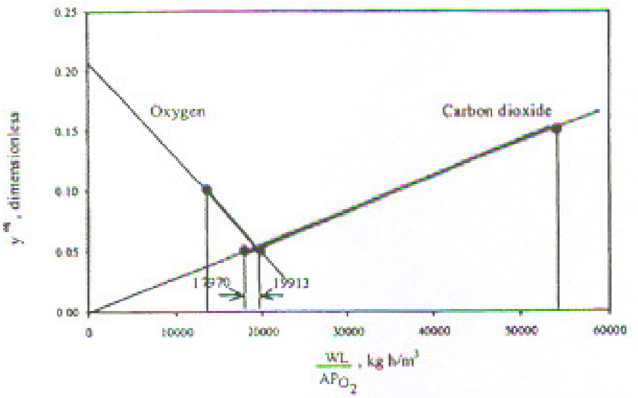

Figure 6. Concentrations of O_2 and CO_2 at equilibrium as a function of the ratio of produce weight and thickness of the film to surface area of film and O_2 mass transfer coefficient for a rubber hydrochloride film. The arrows indicate the narrow range of values for the optimum concentrations.

Figura 6. Concentraciones de O_2 and CO_2 en el equilibrio en función de la relación entre el peso del producto y el espesor de la película con respecto a la superficie de la película y el coeficiente de transferencia de materia para una película de cloruro de caucho. La flecha indica el estrecho margen de concentraciones de los gases para el valor óptimo.

of research that would expand the flexibility and applicability of these systems.

More knowledge is required on the interaction between different perforations, on the effect of their location (which may be dependent on the package geometry) and on the gas stratification inside a package. These issues require experimental work but also advanced numerical modeling.

NOMENCLATURE

- A Surface area of a film, m^2
- D Diameter of perforation, m
- K_i Gas mass transfer coefficient, m^3/s
- L Length of perforation or thickness of the film, m
- N Number of perforations
- P_i Gas permeability coefficient, m^2/s
- R_i Consumption/production rate, $m^3/(kg \cdot h)$
- RQ Respiratory quotient, dimensionless
- t Time, s or h
- V Free volume inside package, m^3
- v Gas volume, m^3
- W Weight of produce, kg
- y_i^* Outside volumetric gas i concentration (v/V), dimensionless
- y_i Volumetric gas i concentration (v/V), dimensionless
- y_i^0 Initial volumetric gas i concentration (v/V), dimensionless
- y_i^{eq} Volumetric gas i concentration at equilibrium (v/V), dimensionless
- β Ratio of CO_2 to O_2 mass transfer coeffients

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