Predicting Film Permeability Needs for Modified-atmosphere Packaging of Lightly Processed Fruits and Vegetables

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Sales of lightly processed produce (LPP), such as cut lettuce (*Lactuca sativa* L.), shredded cabbage (*Brassica oleracea* L. Capitata Group), and cut carrots (*Daucus carota* L.), have increased tremendously in the past few years. A large percentage of these products are packaged such that the levels of relative humidity (RH), O₂, and CO₂ are significantly modified relative to their levels in air. Although modified-atmosphere (MA) packages can potentially extend shelf life, they cannot be expected to overcome the negative effects of enhanced temperature (Kader et al., 1989). Since some form of containment is required for LPP, it should be as functional as possible. However, due to variation in respiration and permeation, limitations imposed by available polymer films, and the chance of exposure to elevated temperatures during handling and distribution, there is no assurance that atmospheres attained will be consistent among packages. Due to lack of adequate control, O₂ levels could fall below safe levels in current MA packages (Cameron et al., 1993). Risks include not only the loss of product quality through fermentative metabolism, but also the growth of potential human pathogens that thrive under anaerobic conditions (Hintlian and Hotchkiss, 1986). Accurate predictions of packaging film characteristics based on sound empirical data are important to reduce this risk.

The gas levels generated in MA packages are a function of the permeability of the film chosen, and the respiratory behavior and gas exchange characteristics of the enclosed living, breathing plant product. The traditional objective of MA packaging has been to select films with permeabilities that allow gas levels favorable for shelf life extension. Commercially, claims of MA packaging systems are plentiful, although the specific nature of the "modified" atmosphere is not generally mentioned. Several commercial MA package designs are now available, although, in practice, gases may not achieve expected levels and there are few public data available for verification.

As a preliminary test of current MA package designs, we purchased MA-packaged precut salad greens at a local supermarket and immediately measured O₂, CO₂, and ethanol partial pressures in the headspace. We found that O₂ levels were extremely low and detected significant accumulation of ethanol in the majority of packages (Fig. 1; Talasila and Cameron, unpublished results). These packages (0.12 m²) contained 0.454 kg of mixed salad, including cut lettuce, sliced carrots, and shredded red cabbage. We are unaware of any substantial exposure to elevated temperatures. The accumulation of ethanol indicated that the package designs were not capable of consistently maintaining aerobic conditions. The presence of "fermented" odors and flavors was easily detected in these packages, although the salad was still edible after adding salad dressing. This suggests that the use of MA packages for cut salads may be limited to those products that can tolerate a degree of fermentation without significant loss of quality. Products such as cut broccoli or cauliflower (*Brassica oleracea* L. Botrytis Group) that produce offensive off-odors under low O₂ levels would presumably not be suitable if there were a risk of anaerobic conditions. Plus, there remains the question of whether these low O₂ levels increase health risks (Barriga et al., 1991; Brackett, 1987; Hintlian and Hotchkiss, 1986).

The objectives of this paper are to explore some aspects related to generating modified atmospheres and discuss predictions relative to the current application of MA concepts for LPP. In particular, we wish to examine the factors that limit our ability to control gas

levels in MA packages and to explore options for improvement.

IDENTIFYING TARGET LEVELS

Appropriate target levels for O₂, CO₂, and RH are determined empirically. Traditionally, experiments are conducted in flow-through, controlled-atmosphere conditions using various combinations of mixed gases. However, results from these experiments may not always be immediately applicable to package environments where other gases and volatiles accumulate in the headspace. In particular, RH is higher in packages and can either shorten or lengthen shelf life, depending on the commodity.

Empirical studies with MA packages often take the form of "pack-and-pray" if the film permeabilities, rates of respiration, or both are not well characterized. In addition, shelf life is a qualitative measure at best and can be affected by the initial quality of the plant material and biases of the researchers. Regardless, these empirical approaches are useful for defining the lower limits for O₂ and potential harmful limits of CO₂ for LPP. For instance, cut broccoli florets stored at 0 or 5°C produced offensive off-odors only when MA package O₂ levels were

Fig. 1. Distribution of O₂ partial pressures and headspace ethanol partial pressure in 30 commercial, mixed-salad packages. The packages were sampled immediately after purchasing from a local supermarket. Each package contained 0.454 kg of mixed salad consisting of cut lettuce, sliced carrots, and shredded red cabbage. The surface area of the packaging film was 0.12 m². Five out of 30 packages had O₂ partial pressures between 1 and 6 kPa, and were not included in the distribution (Talasila and Cameron, unpublished).

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$\leq 1\%$ (Ballantyne et al., 1988b; Lipton and Harris, 1974). Cut lettuce fermented when O_2 levels were $\leq 1\%$ (Ballantyne et al., 1988a; McDonald et al., 1990).

Oxygen concentration. The traditionally stated objective of reducing O_2 levels is to retard oxidative reactions, although this may not always maintain product quality (Kader, 1986; Kader et al., 1989). For instance, it may not be possible to significantly reduce the rate of O_2 uptake without inducing fermentative metabolism, off-flavor development, or both. Low, but not anaerobic, O_2 levels apparently reduce browning and senescence for cut lettuce and broccoli florets (Ballantyne et al., 1988a, 1988b; McDonald et al., 1990). For certain fruits, most notably apple (*Malus domestica* Borkh.), low O_2 levels inhibit ethylene production and action, which combine to retard ripening. This feature has not been a significant factor for typical LPP. There seems to be general agreement that reducing O_2 to levels that are as low as possible without inducing fermentative metabolism would be desirable. However, we feel that this should not be accepted for MA packaging for nonclimacteric plant products *a priori*, since, in some experiments, we have not always observed a positive effect of low O_2 levels, particularly when molds or other disease organisms terminated shelf life. No additional benefit to shelf life was observed from low O_2 levels in MA packages of cut broccoli stored at 0C (Ballantyne et al., 1988b; Talasila and Cameron, unpublished). Additional critical comparisons are required for LPP to demonstrate the effectiveness of low O_2 levels.

Carbon dioxide concentration. Carbon dioxide can be harmful to some plant tissues at elevated levels. For instance, in lettuce, high CO_2 levels ($>2\%$) can cause the disorder brown stain. However, interestingly, in this case, cut or shredded lettuce is more tolerant than the intact product (Ballantyne et al., 1988a; Mateos et al., 1993). For products sensitive to elevated CO_2 levels, it will be necessary to design packages such that CO_2 remains below injurious levels. At levels $>20\%$, CO_2 can be fungistatic or fungicidal for plant tissue tolerant to such high levels (e.g., DeVries-Patterson et al., 1991). It has been difficult to characterize in detail the effects of CO_2 on plant tissues at different O_2 levels due to the endless number of permutations. Further empirical research is needed to better measure these effects for LPP.

Water retention. Reducing water loss is one of the most important aspects related to MA packaging of LPP despite the usual emphasis on modifying O_2 and CO_2 levels. Water loss reduces the salable weight and can induce senescence of the product (Grierson and Wardowski, 1978). It has long been known that water loss can be greatly reduced by packaging in plastic such that O_2 levels remain adequate for aerobic respiration, which usually is accomplished by leaving an opening or punching small holes in the package. In fact, this provides a simple experimental protocol for testing the postharvest response of a given product in packages with and without low O_2 levels but with high RH. When there is no difference in shelf life between products enclosed in packages designed for low but safe O_2 levels and those in the same packages but with pin holes to provide $>15\%$ O_2 , water loss reduction (or in some cases, CO_2 accumulation) is more important than reduction of O_2 levels (Cameron et al., unpublished).

One serious problem associated with high in-package humidity is condensation on the film that is driven by temperature oscillations during marketing MA packages. The amount of condensate formed is related to the difference in temperature inside and outside the package, the void volume of package, and, to some extent, the nature of the polymer barrier. Condensate is reduced to a minimum when a product is "sealed" with a shrink wrap film because this reduces void volume (Ben-Yehoshua, 1985). Condensation can also be reduced by lowering in-package humidity and temperature oscillations. For cut salads and other products with high water permeability (high transpiration coefficients), even relatively small reductions in RH could cause unacceptable water loss with time. Conversely, the presence of significant condensate could increase microbial activity and block diffusion of O_2 into submerged tissues, thus causing fermentation. For some plant products (particularly fruits), high humidity may encourage disease development (e.g., Shirazi and Cameron, 1993). Ultimately, empirical testing is needed to determine "optimal" RH in the package.

There remains limited published information on effective gas levels for LPP compared to that on entire fruits and vegetables. It is

often difficult to understand how this information can be applied during commercial packaging to different cultivars or even the same cultivars grown under different seasons or growing conditions. Given adequate resources, information should be collected for the crops at the same time they are being packaged to determine their tolerance to low O_2 levels. The development of comprehensive databases has been limited by the considerable amount of information required, lack of consistent techniques, and the sheer number of treatment combinations. Some of this information likely has been collected and not published by commercial companies since it has an inherent "value."

DEVELOPING PREDICTIVE MODELS

Plant tissues are, by definition, modified-atmosphere "packages" since O_2 , CO_2 , and water vapor levels inside the skin differ from their respective levels in the external environment. It follows that, in a typical MA package, the levels are further modified by the interaction of respiration, transpiration, and film permeability. Many researchers have recognized that gas partial pressures in the package atmosphere can be modeled (Cameron et al., 1989; Hayakawa et al., 1975; Kader et al., 1989; Kok and Raghavan, 1985; Mannapperuma et al., 1989). However, we are aware of no current model that uses information on modifying atmospheres inside the plant tissue. Although models can be used to circumvent at least some of the tedious testing process and aid in experimental design, as shown by Beaudry et al. (1992), they inherently tend to oversimplify the problem and model accuracy is limited by the quality of the empirical data incorporated.

The general form of the proposed model can be derived from mass balance equations, but it is easier to simply state the equations for steady-state O_2 uptake by the plant material, and O_2 flux through the skin, package, and total system (Table 1). The rationale behind the equations is presented in the following sections. Symbols and units used in this model are described in Table 2. In most cases, variables affecting values of physical constants were incorporated into the symbols for the sake of accuracy. For instance, notation is used to identify most of the factors that change with temperature (Table 2). In some cases, this was omitted for the sake of convenience. If practical, it would have been useful to use notation to identify those parameters that also change with time after harvest, such as

One of the limitations in modeling gas levels in MA packages has been the lack of a single accepted definition of symbols and units. Interconversion between the myriad units used by different researchers and industries that are involved in packaging fresh produce can be a cumbersome and time-consuming task. For this presentation, SI units were selected (Table 2). We express all flux, including respiration, on a mole basis rather than on volume or weight to standardize presentation and to avoid problems associated with changes in temperature. Adoption of a single set of units by researchers involved in the different areas, as proposed by Banks and Cleland (1993), would eventually simplify data comparison.

MODELING O_2 UPTAKE

The effect of O_2 partial pressure on O_2 uptake. Several models have described O_2 uptake as a linear function of O_2 partial pressure (Hayakawa et al., 1975; Mannapperuma et al., 1989). This simplification generally

Table 1. Steady-state equations for O_2 uptake and O_2 flux through the skin of the packaged product, the polymer barrier, and the skin and package. The rate of O_2 uptake is described as a function of the O_2 partial pressure inside the fruit and $k_{1/2}$ represents an apparent K_m for O_2 uptake. Symbols and units are described in Table 2.

Flux	Steady-state flux ($\text{mol}\cdot\text{s}^{-1}\cdot\text{kg}^{-1}$)
O_2 uptake	
O_2 through skin	
O_2 through package	
O_2 through package plus skin	

Table 2. Symbol descriptions and units.

Symbol	Description	Units
A^i	Surface area of barrier i	m^2
	"Total" permeability of barrier i to gas j	$nmol \cdot s^{-1} \cdot kPa^{-1} \cdot kg^{-1}$
Ea_j^i	Activation energy for gas j through barrier i	$kJ \cdot mol^{-1}$
$k_{1/2}$	Constant in Michaelis–Menton equation: Equal to internal O_2 partial pressure that results in half maximal O_2 uptake	kPa
Q_{10}	Increase in rate of respiration per 10C rise in temperature	None
	Standard measure of permeability of given barrier i to gas j at temperature T	$mol \cdot m \cdot m^{-2} \cdot kPa^{-1}$ per sec
	Maximum rate of O_2 uptake or CO_2 production at temperature T per kilogram produce	$nmol \cdot s^{-1} \cdot kg^{-1}$
R_j^T	Total rate of O_2 uptake or CO_2 production at temperature T	$nmol \cdot s^{-1}$
RH_k	Relative humidity in atmosphere k	None
RQ	Respiratory quotient: can potentially change with $[O_2]_{int}$ and temperature	None
T	Temperature in degrees Celsius	C
W	Weight of packaged produce	kg
Δx	Thickness of barrier film	m (usually 10–100 μm)
$[j]_k$	Steady-state partial pressure of gas species j in atmosphere k	kPa
i	Barrier identifier: skin; package barrier film); sum of film plus skin (total)	NA
j	Gas identifier: CO_2 , H_2O , O_2	NA
k	Atmosphere identifier: external (to package); in package (pkg); internal of produce	NA

implies that better empirical descriptions of O_2 uptake are unavailable and can cause serious prediction errors, particularly in regions of lower O_2 partial pressures.

Recently, the advantages of using a Michaelis–Menton equation have been recognized (Banks et al., 1989; Cameron et al., 1994; Lee et al., 1991; Peppelenbos et al., 1993). This approach seems more logical because it describes the enzymatic rate of O_2 uptake in plant tissues. This approach requires an accurate description of the K_m , preferably over a range of conditions. So far, these models have used the level of O_2 outside the fruit as a value of substrate availability; yet, it is the level of O_2 inside the product that limits O_2 uptake by enzyme systems. The internal and external O_2 levels differ depending on skin permeability and the rate of O_2 flux (Burg and Burg, 1965; Cameron and Reid, 1982). Thus, K_m based on external O_2 levels may not directly relate to K_m of enzymes in the tissue that use O_2 . Cameron et al. (1994) found that apparent K_m (based on external O_2 level) of blueberry (*Vaccinium corybosum* L.) fruit increased with temperature and suggested that this was because the values were based on external O_2 , not internal O_2 levels. Comparable observations have been made recently by other researchers (Dadzie et al., 1993; Peppelenbos et al., 1993).

To overcome this limitation, we have developed a model that incorporates gas diffusion through the skin and describes O_2 uptake as a function of O_2 partial pressure inside the tissue for strawberry (*Fragaria xananassa* Duch.) fruit (Cameron et al., unpublished; Joles, 1993). We assumed that the skin is the major site of resistance to gas diffusion, as has been concluded in the past (Burg and Burg, 1965; Cameron and Yang, 1982), although we recognize that gradients in the flesh could exist when the rate of O_2 uptake exceeds the ability of O_2 to diffuse through the tissue, as suggested by Solomos (1987). In addition, we have not taken into account the fact that O_2 solubility decreases $\approx 200\%$ with an increase from 0 to 30C. When the skin is the primary barrier, the internal atmosphere can be described as a function of the permeability and the O_2 gradient across the skin. A model based on internal O_2 partial pressure is potentially more representative of the variables that affect O_2 uptake in the tissue of the packaged product than a model that only considers the external conditions. However, this approach is limited by the accuracy of the values for skin and tissue permeability as well as for O_2 uptake. Eventually, when there is a better

understanding of tissue aeration processes, it will be of interest to include O_2 solubility and factors that describe O_2 movement in the tissue. In fact, it cannot always be assumed that gases are well mixed in the package atmosphere (Emond et al., 1991), and, hence, factors may be needed in some cases to describe the appropriate resistance to gas movement within the package. This may be applicable to cut salads, depending on the packing density.

The effect of temperature on O_2 uptake. Traditionally, the Q_{10} concept has been used to estimate changes in respiration with temperature (Table 3). Film permeability is usually thought to change according to the Arrhenius theory (Pauly, 1989; Table 3). Actually, changes in rate with temperature described by both functions are similar over a narrow range, such as 0 to 30C. Based on simple regression analysis, we found that the approximate relationship between Q_{10} and Ea was described as shown in Fig. 2.

The effect of CO_2 partial pressure on O_2 uptake. Lee et al. (1991) and others have modeled the inhibitory effect of CO_2 on O_2 uptake using the Michaelis–Menton equation. Although this approach appears to be a logical application of the inhibitor concept, actually, scant empirical data are in the literature to support a universal inhibition of CO_2 on O_2 uptake and/or to suggest a mechanism of the inhibition process. Beaudry (1993) found that CO_2 reduced O_2 uptake of blueberry fruit at partial pressures >20 kPa ($\approx 20\%$) CO_2 , and then only minimally. Peppelenbos et al. (1993) also noted little effect of CO_2 partial pressure on O_2 uptake by mushrooms [*Agaricus bisporus* (J.E. Lange) Imbach]. No effect of CO_2 on O_2 uptake below 20 kPa was noted for several fruits (Joles et al., 1993). Thus, a negative effect of CO_2 partial pressure on O_2 uptake cannot be assumed without adequate

Table 3. Equations used to describe the influence of temperature ($^{\circ}C$) on O_2 uptake and on permeation through polymer barriers. Theoretically, changes in skin permeation with temperature should conform to the activation energy equation. Symbols and units are described in Table 2. The approximate relationship between Ea and Q_{10} is shown in Fig. 2.

Variable	Value at 0C	Temp function	Change with temp
Respiration		Q_{10}	
Permeation			
(includes transpiration)		Ea

Fig. 2. The approximate relationship between Q_{10} and Ea . Values were obtained by nonlinear regression analysis of Q_{10} curves (at 0.1 increments of Q_{10}) by fitting to the equation for Ea between 0 to 30C. All regression coefficients were >0.98 .

confirmation. We are not aware of comparable studies for cut or shredded salad greens. If suitable values of k_i were determined, they could be incorporated into the O_2 uptake equation (Table 1).

MODELING GAS PERMEATION

Flux of gases through skin and package film has been described as a function of permeability and the gradient across the barrier according to Fick's Law of diffusion for skin (Table 1). In these equations, we have defined a term, γ , that is a function of several parameters that combine to describe the "permeability" of a barrier per unit weight of the packaged product:

[1]

is a "composite" term that inherently represents the sum of all diffusion barriers at the skin (e.g., skin plus lenticels, etc.) or at the package. γ is a function of A and W according to:

[2]

Note that we have defined γ as a function of kilogram product packaged. Thus, the ratio of surface area of film per kilogram of produce must be factored into estimating γ . This ratio is a function of the bulk density of the product and amount of film needed to enclose a given volume of product.

To calculate resistance coefficients (the inverse of permeability coefficients) of skin, some authors have estimated surface area from the weight combined with some type of mathematical formula based on the density and geometry of the product (see Cameron and Reid, 1982; Sastry et al., 1978). The same formulae are then used in reverse to compare values on a weight basis later. For this analysis, we define permeability on a per weight basis with the knowledge that changes in the surface area : weight ratio (such as cutting products into pieces) will change the relationship of γ to γ as proposed by Sastry et al. (1978). For plant tissue, there is also the assumption that each piece or organ in a population has about the same permeability. More likely, there will be some variation in permeability and, hence, internal gases, but these are difficult to predict without accurate data.

MODELING STEADY-STATE $[O_2]$

Equations that predict $[O_2]_{int}$ and $[O_2]_{pkg}$ as a function of γ and respiratory constants were obtained by solving the steady-state equations in Table 1 (Table 4). Several related predictive equations, such as γ , can be constructed as a function of either a given package or internal O_2 partial pressure. These equations can be useful tools to examine the effects of changes in each of the component variables on the resultant partial pressures. For the interested reader, the results can be visualized by using a spreadsheet program with graphics capacity. Note that the equation describing $[O_2]_{int}$ as a function of $[O_2]_{ext}$ and γ can be modified to yield a similar prediction equation for $[O_2]_{int}$ as a function of $[O_2]_{pkg}$ and γ by substituting these variables for $[O_2]_{ext}$ and γ , respectively. This, in turn, can be used to construct equations that describe O_2 uptake as a function of $[O_2]_{pkg}$ (Cameron et al., unpublished).

MODELING $[CO_2]_{pkg}$

Predictive equations for $[CO_2]_{pkg}$ can be developed as a function of $[O_2]_{pkg}$, RQ, and the ratio of CO_2 to O_2 film permeability (Cameron et al., 1993; Wade and Graham, 1987). The predictive ability under anaerobic conditions will depend on the availability of an accurate description of RQ vs. $[O_2]_{pkg}$. In some early models, the relationship between CO_2 production and O_2 uptake was not properly identified (Hayakawa et al., 1975).

The partial pressure of CO_2 in MA packages at steady-state is limited by the $CO_2 : O_2$ permeability ratio through the polymer (Table 4), which generally ranges from 2 to 8 (Kader et al., 1989; Pauly, 1989; Wade and Graham, 1987). For packages with microperforations or holes, the ratio is closer to 1 since, if anything, CO_2 diffuses more slowly in air than does O_2 because it is a larger molecule (Emond et al., 1991).

Carbon dioxide partial pressures will be higher in the internal atmosphere of the product than in the package and is related to the rate of production and the CO_2 permeability of the skin. These partial pressures could be incorporated into the current model if accurate values were available for permeability. Note that the solubility of CO_2 is many times greater than the solubility of O_2 .

MODELING RH_{pkg}

Several researchers have studied the loss of water from plant tissues, and Sastry et al. (1978) presented an excellent review of models and a compilation of transpiration coefficients. A first approxi-

Table 4. Predictive equations for $[O_2]_{int}$, $[O_2]_{pkg}$, $[CO_2]_{pkg}$, and RH based on the steady-state equations described in Table 1. Symbols and units are described in Table 2.

Gas species	Steady-state equation
$[O_2]_{int}$	
$[O_2]_{pkg}$	
$[CO_2]_{pkg}$	
RH_{pkg}

Fig. 3. The effect of package O_2 partial pressures at $0^\circ C$ on (A) rate of O_2 uptake, (B) rate of CO_2 production, (C) RQ, and (D) ethanol partial pressures in packages containing 10 to 160 g of cut broccoli florets. Each package was constructed of 0.06-m^2 , low-density polyethylene film ($26.8\text{ }\mu\text{m}$ thick). Insets show sharp increases in RQ and headspace ethanol at O_2 partial pressures below 0.15 kPa (from Talasila et al., 1994).

mation of water loss from plant tissues that conforms to the model presented above for O_2 and CO_2 is as follows:

[3]

where the terms and symbols are as described in Table 2. In a package environment, water vapor flux will be reduced depending on the relative permeability of the film compared to the skin, as suggested by the prediction equation given in Table 4. Usually, it is assumed that the RH_{int} is very nearly saturated at a given temperature (see Chau et al., 1988; Sastry et al., 1978). Note that $\dot{m}_w$ is related to $\dot{m}_O$ and $\dot{m}_{CO_2}$ in a manner analogous to the relationship given in Eq. [2]. If the rate of water loss for unpackaged produce is considered equal to one, then the relative rate of water loss equals:

[4]

For example, the water loss of packaged product would be reduced to essentially 1% of the water loss of unpackaged product if the film permeability were 100 times less than the skin permeability to H_2O . The corresponding reduction in O_2 partial pressure will depend on properties of both the film and the product.

MEASUREMENT OF RESPIRATION

The predictive ability of models is directly tied to the accuracy of the data used to construct the models. The traditional method for

measuring respiration has been to measure CO_2 production in a flow-through system under ambient or controlled levels of O_2 . Hardenburg et al. (1986) summarized typical values. Carbon dioxide production rates can be used to estimate rates of O_2 uptake when the RQ is known. However, these estimates are not accurate under fermentative conditions of increasing RQ unless the pattern of RQ increase is well characterized. Flow systems can be used to measure O_2 uptake, but it is difficult to accurately measure the small drop in O_2 against high background levels. Plus, it is time-consuming to measure O_2 uptake under many O_2 levels over a range of temperatures. An O_2 depletion method has been used to characterize O_2 uptake as a function of O_2 (Cameron et al., 1989; Hayakawa et al., 1975), but the accuracy of this technique will depend on the gas diffusion characteristics of the tissue under examination and the solubility of the gases in the plant organ.

We have developed a simple method for measuring O_2 uptake that can be used to circumvent at least some of the problems associated with other techniques (Beaudry et al., 1992; Cameron, 1990; Joles et al., 1994). The method is based on generating a nearly continuous range of O_2 levels in packages and, using measured permeability coefficients for O_2 and CO_2 , calculating respective rates based on Fick's Law of Diffusion. In addition, RQ could easily be calculated and plotted as a function of O_2 partial pressure. More recently, we have measured ethanol in headspaces of packages and correlated this information with the changes in RQ (Joles et al., 1994). The respiration information obtained from these experiments can be used to estimate many of the desired parameters described in the model presented above and hence can be used to generate predictive information. An example of the data obtained from this method for cut broccoli florets shows (Fig. 3; from Talasila et al., 1994) that the fit is reasonable for O_2 uptake with an estimated $k_{1/2}$ of $\approx 0.25\text{ kPa}$ (0.25%). In this example, no attempt was made to estimate a value for skin permeability from the respiration data because only one temperature was tested and hence the $k_{1/2}$ is based on $[O_2]_{pkg}$. The lower limit for aerobic respiration was 0.15 kPa based on both RQ and the presence of ethanol in the headspace.

This method for estimating respiration requires accurate values for permeability for the specific films used (Beaudry et al., 1992). Variations in film permeability will cause errors in estimates of respiration; thus, films that are as uniform as possible should be used. We have used low-density polyethylene because the polymerization process is well understood and within-batch variability has generally been $\approx 5\%$ or less (Beaudry et al., unpublished). However, we have measured larger variations between different batches of polyethylene. Such variation causes not only an error in respiration estimation in research applications but would cause variability in commercial applications (Talasila and Cameron, unpublished).

The effects of CO_2 removal (Joles, 1993) or CO_2 enhancement (Beaudry, 1993) on O_2 uptake and the lower O_2 limit for fermentative induction can be investigated by modifying the original method. By

Table 5. Respiration and permeability characteristics for selected plant products in units consistent with those proposed in the manuscript for describing respiration and transpiration. Values are estimated from several sources.

Characteristic	Broccoli	Lettuce	Blueberry	Strawberry	Units
	$150^{z,y}$	$75^{z,x}$	30^w	72^v	$\text{nmol}\cdot\text{s}^{-1}\cdot\text{kg}^{-1}$
Q_{10}	3.9^z	2.2^z	2.5^w	2.5^v	---
$k_{1/2}$	0.26^v	No data	0.3^w	0.3^v	kPa
Aerobic RQ	1.2^y	No data	1.2^w	1.7^v	---
	No data	No data	33^w	310^v	$\text{nmol}\cdot\text{s}^{-1}\cdot\text{kPa}^{-1}\cdot\text{kg}^{-1}$
	$>100^u$	$>100^u$			
	No data	$400,000^f$	$10,000^g$	$50,000^f$	$\text{nmol}\cdot\text{s}^{-1}\cdot\text{kPa}^{-1}\cdot\text{kg}^{-1}$

^zEstimated from values presented in Hardenburg et al. (1986).

^yFrom Talasila et al. (1994).

^xEstimated from data presented for uncut head lettuce.

^vFrom Beaudry et al. (1992) (some values were obtained by reanalysis of the original data set).

^wFrom Joles (1993).

^uEstimated empirically on the basis of the shape of the curve describing O_2 uptake vs. O_2 partial pressure at $0^\circ C$.

^fFrom Sastry et al. (1978).

^gInferred from Chau et al. (1988)

^hFrom Shirazi and Cameron (1993).

appropriate modification of package design, the desired O_2 ranges can be generated over a range of temperatures for more comprehensive characterization of respiration and response (Beaudry et al., 1992; Joles et al., 1994). Estimates of respiration based on CO_2 gradients across the package film can be directly compared with CO_2 production if packages are placed in a flow-through system (Beaudry, unpublished).

We compiled approximate values for respiration characteristics from a variety of sources (Table 5). Few data were available for LPP; therefore, a few examples have been included for small fruits. The values presented can be used for general modeling and for preliminary package designs. However, respiration measurements and package trials should be conducted to provide more accurate data for final application of the values as discussed above. It would be helpful to have additional information of this nature.

Values presented in Table 5 do not indicate inherent variability in respiration nor in permeability characteristics. This has seldom been the subject of investigations. For a single group of cut broccoli florets, Talasila et al. (1994) measured about $\pm 10\%$ variation (95% confidence interval) in respiration. However, the effect of differing field conditions, harvest conditions, or both on respiration are largely unknown. Ongoing programs at the commercial level to measure respiration are necessary if a higher level of control of O_2 levels in MA packages is required. At least one company claims to make such measurements. There is also the complication that respiration of LPP is usually elevated after cutting and then often declines (Cameron et al., unpublished). Thus, control of O_2 partial pressures is reduced since O_2 in the package will change continuously in response to these changes in respiratory activity.

MEASURING FILM PERMEABILITY

No standard technique has been accepted for determining gas permeability through polymers, and even when accurate estimates are available, it is not always clear how published values can be applied to MA package conditions when permeability may be altered by the presence of thin heat-sealed regions, print, or condensation on the film. Plus, there is the continuing problem of variation in permeability for a single polymer within and between batches (see above; Doyon et al., 1991). We expect that this variability will be even greater for more "exotic" films. Even with a common, simple polymer, such as polyethylene, where the polymerization process is well understood, we have measured significant variation in O_2 and CO_2 permeability between batches, as discussed above. Small errors in permeability can cause significant deviations between predicted and actual O_2 levels in packages (Talasila and Cameron, unpublished). Direct comparisons between reported permeabilities can vary widely and this has led to the need for more reliable permeability information, particularly as a function of temperature (e.g., Doyon et al., 1991). This dearth of data emphasizes the need for techniques to accurately measure permeability either for research or commercial application.

Table 6. Permeability data for a few common films used in modified-atmosphere packaging (adapted from Pauly, 1989). The unit for P is $\text{mol}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{kPa}^{-1}/10^{13}$, and for E_a , it is $\text{kJ}\cdot\text{mol}^{-1}$.

Gas species or ratio	Low-density polyethylene	Polypropylene	Polyvinyl chloride	Cellulose acetate
	27	9.0	0.19	10
	34.8	55.7	55.8	21
	99	58	0.65	348
	38.9	38.1	56.8	21
	868	280	3900	220,000
	33.5	42.3	22.9	0
/	3.7	6.2	3.4	34
/	32	30	20,000	21,000

Many researchers have published permeability data for pertinent gases (Gorris and Peppelenbos, 1992; Pauly, 1989; Roberts, 1990; Wade and Graham, 1987). In general, of the more common films used, those with the highest O_2 permeation include low-density polyethylene, polyvinyl chloride, and ethyl vinyl acetate (or alcohol). Approximate permeability coefficients in units we are using are given in Table 6.

Measuring and/or predicting permeation through holes is particularly difficult since small pressure changes can markedly affect mass flow through the holes (Emond et al., 1991). Improvements in the technology related to making precise and uniform holes with defined diffusion characteristics will greatly aid development of MA techniques.

Depending on the polymer, permeability to CO_2 exceeds the permeability to O_2 by 2 to 8 or more times (Pauly, 1989; Table 6). In addition, the permeability to H_2O exceeds the permeability to O_2 by 30 to 20,000 or even more (Pauly, 1989). These ratios can change with temperature, depending on respective E_a for O_2 and H_2O permeation. For diffusion through holes or microperforations, the ratio for either H_2O or CO_2 to O_2 is expected to be closer to 1 (see Emond et al., 1991).

Researchers generally accept that temperature influences permeation according to Arrhenius theory as detailed in Table 3 (Pauly, 1989). Approximate E_a values are given in Table 6. Most films used for MA packages have E_a values <40 – $50 \text{ kJ}\cdot\text{mol}^{-1}$. Doyon et al. (1991) pointed out that better descriptions of permeability at storage temperatures and E_a values are needed. Note that permeation through "holes" is expected to have an $E_a < 5 \text{ kJ}\cdot\text{mol}^{-1}$.

Water sorption into hydrophilic films can markedly increase the permeability of some hydrophilic polymers (Barrie, 1968). This action could greatly confound attempts to predict O_2 levels in MA packages with high moisture products, such as cut salads. The effects of heat-sealing and presence of print on film permeability is unexplored.

MEASURING SKIN PERMEABILITY

Methods for estimating permeability coefficients were reviewed by Ben-Yehoshua and Cameron (1989) and a few specific values were summarized by Cameron and Reid (1982). An excellent discussion of gas transport properties of cuticles was presented by Lendzian and Kerstiens (1991). To our knowledge, no information is available for gas diffusion in LPP. Transpiration coefficients have been characterized for intact products (see Sastry et al., 1978), although there is limited information for LPP. Diffusion coefficients for cut products likely will be higher than for entire ones due to the marked increase in surface area : weight ratio. For example, water vapor permeability of intact heads of lettuce is ≈ 40 times higher than for blueberry (Table 5).

The : ratio has not been investigated carefully. Cameron and Reid (1982) noted that this ratio apparently varies from 3 to 100 for a variety of fruits. The ratio is ≈ 300 and 160 for blueberry and strawberry fruit, respectively (Table 5). This ratio would be strongly influenced by the nature of the diffusion barrier in skin. For instance, if exchange of both gases occurs largely through holes, this value will be closer to 1. The high values indicate that water vapor moves preferentially through the skin.

We are aware of no published information on changes of skin permeability with temperature. The temperature sensitivity of will depend on the mechanism of gas exchange. For instance, if exchange is primarily through holes, then the activation energy for permeation will be low ($< 5 \text{ kJ}\cdot\text{mol}^{-1}$). However, the permeability coefficient for water vapor suggests that a significant proportion moves directly through the skin (since the $H_2O : O_2$ permeability ratio is far greater than 1). Thus, although E_a may be close to $5 \text{ kJ}\cdot\text{mol}^{-1}$ for O_2 and CO_2 permeation, we predict a larger E_a for permeation of water vapor.

MEASURING LOWER O_2 LIMITS

Although controlled-atmosphere experiments can be used to identify fermentation induction points (lower limit for aerobic respiration), empirical descriptions can be made in MA packages (Beaudry et al., 1992; Beaudry and Gran, 1993; Joles et al., 1994; Talasila et al., 1994). In these examples, package O_2 level was controlled by altering either

the permeability, surface area, or thickness of the film or the weight of the packaged produce, and the breakpoint was specifically identified by observed increases in RQ, ethanol, or both in the head space (e.g., see Fig. 3). Below the breakpoint, little ethanol in the headspace could be detected for any of the crops tested. Within reason, it was easy to identify a single O_2 partial pressure at the “breakpoint” (in this case, the breakpoint is expressed as the level of O_2 in the package). However, for red raspberry (*Rubus idaeus* L.), the increase in RQ with declining O_2 was not distinct (Joles et al., 1994). The lower O_2 limit increased with temperature for blueberry (Beaudry et al., 1992), raspberry (Joles et al., 1994), and strawberry (Joles, 1993). To our knowledge, little is known about changes of this nature for LPP. The lower O_2 limit for broccoli at 0C was ≈ 0.15 kPa (Talasila et al., 1994). At 0 to 5C, we found RQ breakpoints to range from 0.4 (strawberry) to 2 kPa (blueberry). Tolerance to lower O_2 partial pressures in the package environment would be related to skin and tissue resistance to O_2 movement.

Joles et al. (1994) and Peppelenbos et al. (1993) have each presented functions that describe the increase in RQ once O_2 levels have decreased below the fermentative induction point (lower limit for aerobic respiration). These functions are useful for improving the predictions of the models.

ESTIMATING PERMEABILITY REQUIREMENTS

To estimate permeability requirements to maintain high O_2 levels, the flux equations (Table 1) can be rearranged assuming $k_{1/2}$ is low such that O_2 uptake is essentially equal to RQ , and the permeability of the skin is large relative to rate of O_2 uptake:

[5]

Assume, for instance, you wish to construct a package for 0.5 kg shredded lettuce with O_2 uptake at 5C of $\approx 100 \text{ nmol} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$ and wish to target a “safe” O_2 partial pressure of ≈ 11 kPa (essentially 11% O_2). If 0.5 kg cut lettuce fits in a package of $\approx 0.12 \text{ m}^2$ and if the film needs to be at least 25 μm thick for adequate durability, then:

$$= 1 \times 10^{-3} \text{ nmol} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{kPa}^{-1} \text{ per sec}$$

By substitution in Eq. [5], if actual respiration exceeded the predicted value by 50%, then O_2 would drop to 6 kPa in the packages. Such variation would cause product fermentation if lower levels of O_2 had been targeted. If the $H_2O : O_2$ permeability ratio of the film used were $\approx 100:1$, then $k_{1/2}$ would be ≈ 1000 and the relative rate of water loss would be reduced to far less than 1% of the rate in air according to Eq. [4] (values for $k_{1/2}$ are given in Table 5).

PREDICTING GAS LEVELS IN MA PACKAGES

Predictions of levels of O_2 , CO_2 , and RH in packages as a function of film resistance (inverse of $1/\beta_{O_2}$) can be derived from the equations given in Table 4 and the values given in Tables 5 and 6 (Fig. 4). Any factor that alters the value of $1/\beta_{O_2}$, such as changes in the weight of packaged product or surface area of the film (Eq. [1]) should cause gas levels to change according to these predictions. Note that RH is not 100% in packages of all film combinations and is related to O_2 levels in packages (Fig. 4). This outcome confirms empirical observations that describe wilting of produce packaged in high-water-vapor permeable films, such as cellulose acetate. It is also apparent that it is possible to maintain very high RH, yet maintain aerobic conditions, for products, such as lettuce, that have high water vapor permeability (Fig. 4). Note that water vapor and CO_2 accumulation relative to O_2 depletion

Fig. 4. Model predictions for steady-state levels of RH_{pkg} , $[CO_2]_{pkg}$, and $[O_2]_{pkg}$ for lettuce based on the equations presented in Table 4 and using values given in Tables 5 and 6. Since no data were available, it was assumed that $k_{1/2} = 0.3$ kPa, $k_{H_2O} = 400 \text{ nmol} \cdot \text{s}^{-1} \cdot \text{kPa}^{-1} \cdot \text{kg}^{-1}$ and $RQ = 1.0$. The predictive curves were generated by incorporating equations into a spreadsheet program.

are greatest when diffusion occurs through holes (Fig. 4). This can be either an advantage or a detriment depending on the situation. Condensation would be more prevalent in a package that uses “holes” as a major site of gas exchange. Holes would be inappropriate as a mechanism for MA packaging for crops sensitive to high CO_2 levels.

TEMPERATURE EFFECTS ON GAS CONCENTRATIONS IN MA PACKAGES

It has long been recognized that increases in temperature during shipping, handling, or retailing MA packages could cause a decrease in package O_2 levels because respiration tends to increase more than permeation through polymers (see Kader et al., 1989). Using trucks that are not pre-cooled, improper handling at transfer points, and retail display under nonrefrigerated conditions contribute to this problem. One powerful advantage of the present model is that it can be used to predict changes in package O_2 , CO_2 , and H_2O partial pressures with increasing or decreasing temperature. In the past, models describing

Fig. 5. Model predictions for changes in $[O_2]_{pkg}$ (solid lines) as a function of temperature and film permeability characteristics for blueberry fruit. The dashed line on each graph represents the lower O_2 limit for blueberry fruit as determined by the increase in RQ. For polyethylene films and holes, E_a was assumed to be 40 and 5 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. Each prediction curve was generated by setting O_2 to a given level at a given temperature (e.g., 5 kPa at 25C in the top two graphs).

temperature effects have been severely limited by inadequate respiration data.

Using data collected via Beaudry et al.'s technique (1992), we are just beginning to make reasonable predictions of O_2 partial pressure changes with temperature for MA-packaged blueberry (Cameron et al., 1994), raspberry, and strawberry (Cameron et al., unpublished). We have modeled predictions for O_2 and CO_2 partial pressure changes in MA-packaged blueberry fruit over a range of starting conditions (Fig. 5; from Cameron et al., 1993). The dashed line on each graph represents the lower O_2 limit for blueberry as determined by the increase in RQ (Beaudry et al., 1992). For a "safe," low-density polyethylene package at 25C, $[O_2]_{pkg}$ will need to be >10 kPa at 0C (Fig. 5). Conversely, if a package were designed to give 2 kPa at 5C, the fruit would be anaerobic with a very small increase in temperature (Fig. 5). For a hypothetical film with a large $E_a = 60 \text{ kJ}\cdot\text{mol}^{-1}$, the fruit could remain aerobic between 0 to 25C (Fig. 5). Packages that use holes or microperforations for gas exchange are particularly vulnerable to increased temperatures because gas diffusion through holes increases little with increasing temperature (Fig. 5). To remain aerobic over 0 to 25C, package O_2 would need to be $\approx 18 \text{ kPa}$ at 0C. Predictions from these models emphasize the difficulty in designing MA packages with adequate control over O_2 levels. Comprehensive models for LPP cannot be constructed until further respiratory information is collected.

These models can help direct research toward safer package designs and at least reduce the need for extensive testing. For instance, we predict that a film with an activation energy of $\geq 60 \text{ kJ}\cdot\text{mol}^{-1}$ will maintain aerobic conditions between 0 to 25C for blueberry fruit (Cameron et al., 1994). This result would presumably apply to lettuce, as the Q_{10} of lettuce is nearly equal to the Q_{10} of blueberry (Table 5).

An even higher film activation energy ($\approx 100 \text{ kJ}\cdot\text{mol}^{-1}$) would be required for broccoli, considering its high Q_{10} (Table 5). Currently, films with activation energies $>50 \text{ kJ}\cdot\text{mol}^{-1}$ are rare for MA application, although the possibility of temperature-compensating films has been reported recently (Stewart et al., 1993). Other possible solutions have been discussed (Cameron et al., 1993, 1994).

One limitation is that the models predict only the final steady-state O_2 levels achieved in the packages, yet the rate of change and the time to reestablish the new steady-state levels are also important considerations. Talasila et al. (1992) have modeled the rate of change in product temperature in MA packages under changing external conditions and it should be possible to combine this with the current model to predict the rate of change of O_2 partial pressure following a shift in temperature. The rate of change depends not only on the void volume (Cameron et al., 1989), but also on temperature as demonstrated for sample packages of blueberry (Fig. 6). Note that it can take 2 to 3 weeks to attain steady-state at low temperatures. These slow rates could be an important factor. If low O_2 levels are truly needed for shelf life extension, then N_2 flushing will be required for products stored at low temperatures unless the void volume can be reduced to a minimum. In contrast, a slow decline in O_2 levels could be beneficial if packages are not designed to provide adequate O_2 at steady-state.

FILM REQUIREMENTS FOR MA PACKAGING

Polymer films currently used in the industry for MA packaging have been selected primarily on the basis of applied research and practical considerations. Only a limited number of films are available with adequate O_2 permeability to prevent anaerobic conditions (Roberts, 1990). This situation is in contrast to the number of high-barrier films that are used for MA packaging of meats and other products that require a totally anaerobic environment. Barmore (1987) states that most films used have been polyvinyl chloride and perforated, thin, low-density polyethylene for bagged products. Perforations can greatly enhance permeability but are very unresponsive to temperature increases (see earlier discussion). Actually, most films are proprietary in nature, and it is difficult to ascertain the composition and obtain accurate determinations of permeability. In addition to high O_2 permeation, films suitable for MA packages should have a predictable permeability (e.g., not overly affected by the presence of water), and be consistent, inexpensive, easy to use, workable, pliable for moving through packaging machines, sealable (heat sealable is preferred), resistant to tears and punctures, and transparent for a view of the package interior. Ultimately, it will be desirable to use recyclable materials, which could eventually preclude the use of colaminates or other nonrecyclable polymers.

Currently, films with adequate O_2 permeability, adequate response to increases in temperature, or both are few. However, even if they

Fig. 6. Predicted $[O_2]_{pkg}$ changes in MA packages of blueberry as a function of temperature using parameter values given in Table 5 and assuming constant at each temperature based on initial optimization to 4 kPa at each temperature. The data were generated by numerical integration of equations given in Tables 3 and 4. Film permeability was assumed to respond to temperature in a standard Arrhenius function.

were available, variation in respiration of the packaged produce can cause significant variability in the O₂ levels attained in MA packages (Talasila and Cameron, unpublished).

SENSE-AND-RESPOND PACKAGES

Labuza and Breene (1989) reviewed the concept of active packaging. Active packaging has been used to describe the addition of O₂ scrubbers, CO₂ scrubbers and emitters, ethanol emitters, etc. Various possibilities exist, although precise control of O₂ levels in MA packages is still not possible. Most of the active packaging applications have been developed for meats and other products. Fewer applications have been introduced for LPP, although many new possibilities are being tested (Roberts, 1990). However, there appears to be marked resistance from the industry to add to the cost of packaging materials.

Cameron et al. (1993) introduced the concept of sense-and-respond technology. They proposed that some component of the package would sense a signal, such as an increase in temperature or an increase in headspace ethanol, and initiate a marked increase in permeability to compensate for the change. A system for increasing permeability in response to increasing temperature was proposed by Patterson and Cameron (1992). The system is based on opening holes originally blocked by solid hydrocarbons with melting points between 10 to 30°C. Once the melting point is exceeded, permeability increases dramatically as the hydrocarbons melt and are wicked from the hole(s). The objective is to provide adequate O₂ levels to prevent excessive fermentative induction during inadvertent exposure to elevated temperatures. Although irreversible in its current form, this system could be useful for certain MA applications. Handling the active portion of the package before packaging could be a problem, however.

We are also developing a system that could sense and respond to fermentation of the packaged product. During periods of exposure to low O₂ levels, plant products will produce ethanol. In many cases, it is only after extended periods that off-flavors become significant and, in fact, small amounts of ethanol may be desirable (Saltveit and Sharaf, 1992). We have postulated that an active component of a package could be designed to sense ethanol and respond by increasing film permeability, perhaps in a manner analogous to the system described above for temperature. Ethanol appears in the headspace a short time after the lower O₂ limit is exceeded (Joles et al., 1994; Saltveit and Ballinger, 1983). Joles, Patterson, and Cameron (unpublished) have developed a simple biosensor system that changes color in response to an increase in headspace ethanol. However, we have not yet linked this change to an increase in O₂ permeability. A package design based on ethanol detection could be valuable in that it could be analogous to a one-size-fits-all.

Development of other types of sense-and-respond systems is an interesting possibility. For instance, it eventually may be realistic to identify the presence of specific human pathogens in packages if appropriate (and inexpensive) biosensors can be constructed to detect specific volatiles (e.g., Phillips, 1990).

CONCLUSIONS

Modified-atmosphere packaging is being used commercially for LPP such as cut lettuce, carrots, and cabbage, although current designs are not sufficient to prevent the onset of fermentation under normal marketing conditions (Fig. 1). In these cases, fermentation alters the flavor and quality of the product but apparently does not render it inedible to the average consumer compared to the increased convenience. This approach will not work for products such as broccoli that produce offensive off-odors and off-flavors under low-O₂ conditions. Proper MA package designs for these products will require better control of package O₂ levels. However, better control of O₂ requires better fundamental knowledge of respiratory behavior of packaged products plus implementation of precise temperature control during commercial handling and marketing. The development of sense-and-respond packages may help overcome at least some of these problems, particularly if they are used in conjunction with detection or indicator systems that provide color changes to advise consumers against eating the enclosed product.

There remains a great need for research and innovation to determine the most appropriate gas levels for extending shelf life and methods for consistently obtaining these levels in MA packages. At the least, it is necessary to determine the relative importance of low O₂ levels for extending shelf life and to determine if it is worth the risks to product quality, human health, or both. Research has been hampered by the lack of control of O₂ partial pressures in packages since it is difficult to conclude that a given combination of O₂ and CO₂ partial pressures will prolong the shelf life of a product if it cannot be repeatedly attained in packages. Beaudry et al.'s (1992) approach for generating information on respiration and on the response of plant products to a range of O₂ levels in MA packages helps overcome at least part of this difficulty. Refined models generated from respiratory data are useful to circumvent some pack-and-pray research but must be viewed with some caution since they have a tendency to oversimplify the problem. We strongly recommend further research on the variability of O₂ levels and other gases in MA packages in an effort to better understand the control (or lack thereof) of gas levels using semipermeable films.

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