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MODIFIED-ATMOSPHERE PACKAGING OF APPLE SLICES: MODELING RESPIRATION AND PACKAGE OXYGEN PARTIAL PRESSURE AS FUNCTION OF TEMPERATURE AND FILM CHARACTERISTICS

By

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ABSTRACT

MODIFIED-ATMOSPHERE PACKAGING OF APPLE SLICES: MODELING RESPIRATION AND PACKAGE OXYGEN PARTIAL PRESSURES AS A FUNCTION OF TEMPERATURE AND FILM CHARACTERISTICS.

By

Ruomwadee Lakakul

A systematic approach was taken to acquire information for the design of a modified-atmosphere packaging (MAP) system for apple slices. Initially, various combinations of O_2 and CO_2 were assessed for their control of tissue browning, thereby generating target gas concentrations for package design. Reduced O_2 and elevated CO_2 atmospheres were applied to sliced apples and while some gas concentrations significantly reduced browning relative to air controls, none of the treatments prevented browning to a sufficient level to be acceptable. MAP was used as a tool for obtaining respiratory data needed to calculated permeability characteristics of packaging films that will obtain and achieve and maintain desired gas levels in the package headspace at 0, 5, 10 and 15C. The lowest O_2 patial pressure to which fruit could be exposed without fermentation increased with increasing temperature. A mathematical model was developed to characterize the relationship between steady-state O_2 partial pressure ($p_i^{O_2}$) and O_2 uptake and film permeability to O_2 of packages. The $p_i^{O_2}$ model was used for predicting the effect of P_{O_2}, activation energy (Ep^{O_2}), temperature, film type, and film thickness on $p_i^{O_2}$.

"And whatever you do, whether in work or deed,
do it all in the name of the Lord Jesus,
giving thanks to God the Father through him."
Colossians 3:17.

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The journal paper format was chosen for this thesis in accordance with departmental and university regulations. The thesis is divided into 2 chapters in which Chapter II has been prepared according to format requirements for Journal of the American Society for Horticultural Science.

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LIST OF SYMBOLS

a,b,c,m,n	Parameters
A	Surface area of polymer, cm^2
$Ea^{R_{O_2}}$	Activation energy of O_2 uptake by fruit, $kJ \cdot mol^{-1}$
Ep^{O_2}	Activation energy of polymer O_2 permeation, $kJ \cdot mol^{-1}$
F_{O_2}	Total O_2 flux into the package, $mmol \cdot h^{-1}$ (Fick's law)
K_T	O_2 partial pressure at half-maximal O_2 uptake, kPa
l	Thickness of polymer, cm
P	Permeability constant
P_{O_2}	O_2 Permeability coefficient, $mmol \cdot cm^1 \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$
P_{CO_2}	CO_2 Permeability coefficient, $mmol \cdot cm^1 \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$
$p_i^{O_2}$	O_2 partial pressure inside the package, kPa
$p_i^{CO_2}$	CO_2 partail pressure inside the package, kPa
$p_o^{O_2}$	O_2 partial pressure outside the package, kPa
$p_o^{CO_2}$	CO_2 partial pressure outside the package, kPa
Q_{10}	R_{O_2} at $(T+10)/R_{O_2}$ at T

LIST OF SYMBOLS (cont.)

R	The gas constant 0.0083144 $kJ \cdot mol^{-1}\ K^{-1}$
R_{O_2}	O_2 uptake of fruit per unit weight, $mmol \cdot kg^{-1}\ h^{-1}$
$R_{O_2}^{total}$	Total O_2 uptake of packaged fruit, $mmol \cdot h^{-1}$
T	Temperature in celsius or kelvin
V_{max}	Maximum R_{O_2} as a function of T, $mmol \cdot kg^{-1} \cdot h^{-1}$
W	Weight of packaged fruit, kg

INTRODUCTION

Lightly processed vegetables which include lettuce, cabbage, broccoli, cauliflower, etc., have found widespread acceptance and have been readily incorporated into food service offerings. Fruit products, such as apple slices, have potential for successful entry into a precut fruit market. The purpose of this research was to determine necessary packaging characteristics (e.g. package dimensions, film permeability to O_2 and CO_2, temperature sensitivity of O_2 and CO_2 permeability, etc) to generate acceptable atmospheres within packages for sliced apple fruit. The first goal was to determine target O_2 and CO_2 to control the browning reaction of sliced fruit. The second goal was to collect respiratory data for the development of a respiratory model for sliced apple such that package characteristics needed to achieve and maintain target gas concentrations could be identified. To this end, the model was used to predict the steady-state package oxygen partial pressure as a function of temperature and film permeability.

Apple slices undergo rapid tissue browning. Atmosphere with reduced O_2 or elevated CO_2 concentrations have been commonly used to reduce apple respiration and extend storage life. In addition, certain proportions of these gases have also been found to reduce browning reaction in some commodities. Controlled-atmosphere

technique was used to target O_2 and CO_2 concentration for controlling browning reaction in apple slices.

For model development, the respiration of apple slices described by O_2 uptake as function of temperature and package O_2 partial pressure was defined using a package approach. A respiratory model was developed by empirically fitting the data with Michaelis-Menten type model (Lee et al., 1991; Cameron et al., 1994) or Langmuir's equation (Hernadez and Gavara, 1994). Maximal O_2 uptake and the package O_2 partial pressure at half maximum O_2 have temperature sensitivity and can be defined by the model. The package O_2 model can be developed from respiratory model related with permeability characteristics according to Fick's law. The O_2 partial pressure inside the package can be predicted according to the model as a function of temperature and permeability characteristics.

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CHAPTER I

LITERATURE REVIEW

Browning in apples and modeling of Modified-atmosphere packaging

Lightly processed produce, also known as precut, value-added, fresh-processed or fresh-cut produce, are packaged produce items that comprise the most rapidly growing segment of the fresh produce industry. In January, 1994 issue of the trade journal, Packer reported that within the $57 billion/year produce industry in 1992, lightly processed products comprised approximately $2 billion. Retail sales of fresh-cuts, or lightly processed produce, an unknown category a few years ago, commanded a 6% of retail produce sales nationally, and up to 11% in California. Recent sales figures indicate sales of refrigerated prepared salads and coleslaw increased almost 93% from 1992 to 1993 (anonymous, 1994). The primary driving force behind their use is the convenience offered to food service industry and consumers. Consumers (retail and institutional users) have demonstrated that they are willing to pay substantially more for ready-to-use lightly processed produce than whole produce.

Lightly processed vegetables which include among other lettuce, cabbage, broccoli, and cauliflower have found widespread acceptance or readily incorporated into food service offerings. On the other hand, lightly processed fruit products, unlike their vegetable counterparts, have been slower to develop. Sliced fruits with higher sugar and water contents which contributes to significantly problems with moisture loss, decay and tissue softening. Another important impediment to a lightly processed fruit product is rapid tissue browning. New technology to protect processed lightly processed fruits from physical and physiological damage are being developed. Once these processing methods are developed, significant market outlets should soon open for fruit, especially since lightly processed vegetables are so widely

accepted. Perhaps the most likely and successful lightly processed fruit product is apple slices.

I. Browning in cut apples

As indicated above, browning of the cut tissue of apple slices is a major quality concern. Enzymatic browning develops easily in cut fruits such as apples, pears, peaches, bananas, and grapes, and vegetables such as potatoes, mushrooms and lettuce. Coloration reactions can occur after bruising or cutting and they affect significantly the produce shelf-life.

The browning process constitutes a complex set of reactions between the product tissue and environment factors. To a large extent, browning in apples involves the oxidation by polyphenol oxidase (PPO). Its substrates include phenols such as caffeic acid derivatives, chlorogenic acid, (+)-catechin, and (-)-epicatechin (Nadudvari-Markus and Vamos-Vigyazo, 1984), and atmospheric oxygen. In the browning reaction, monophenolic compounds are hydroxylated to o-diphenols, and these latter are oxidized to o-quinones (Mayer and Harel, 1979; Vamos-Vigyyazo, 1981; McEvily et al., 1992). On the other hand, o-quinones are highly reactive compounds and can polymerize spontaneously to form high-molecular-weight compounds such as the brown pigment melanin, or react with amino acids and proteins (non-enzymatic reaction) that enhances the brown color produced (McEvily et al., 1992). A variety of phenolic compounds are oxidized by PPO; the most common substrates are catechins, cinnamic acid esters, 3,4-hydroxyphenyl-alanin (DOPA), and

tyrosine (Sapers G.M., 1993). PPO takes the name of tyrosinase, o-diphenol oxidase, catechol oxidase, etc., depending upon the substrate. In apple peel (Red delicious), 4-methyl catechol, chlorogenic acid, catechol and catechin are substrates of PPO (Vamos-Vigyyazo, 1981).

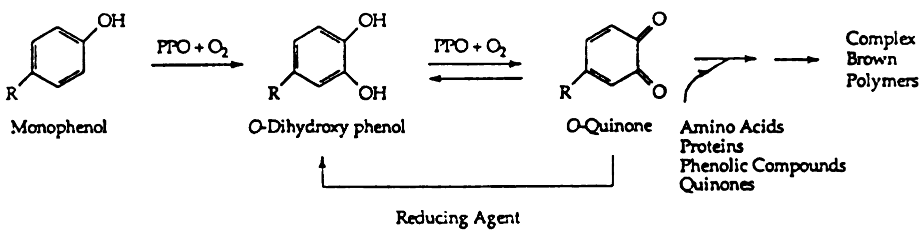

Illustration 1: Enzymatic browning reaction, showing site of action of reducing agents which include such browning inhibitors as sulfiting agents and ascorbic acid.

The severity of enzymatic browning on cut surfaces of apple slices will depend partly on the extent of the damage done to surface tissues by the peeling or cutting procedure. A water-jet cutting system was found to produce more subsurface cellular damage in sliced potato than a sharp stainless steel knife blade, as judged by scanning electron microscopic observation and measurement of protein extractability at the cut surface (Backer and Gray, 1992).

The degree of browning is also dependent on the amount and activity of PPO and substrate. Cultivars of apples differ in their tendency to brown due to variation in PPO activity and substrate content. For instance, NY674 apples are lower in polyphenol oxidase and polyphenols content compared to other cultivars (Lee and McLellan, 1990). The cut surface of NY674 tissue showed least low degree change

of browning change in 'L' values among 12 cultivars tested (Kim et al, 1993). Such differences can be used in the selection of cultivars that give the condition to minimize browning.

Senescent browning (SB); a common feature of product deterioration, can be prevented or reduced by using CO_2 enriched atmosphere. The brown pigments of senescent browning are generated by the oxidation of phenolic compounds by PPO. These phenolic compounds come from the hydroxylation of cinnamic acid which is formed by the deamination of phenylalanine catalyzed by phenylalanine ammonia-lyase (PAL) (Mateos, 1993). Under environmental with high concentration of CO_2, PAL activity is induced whereas phenolic production and browning is inhibited. Control of low degree of browning is lost when lettuce tissue is transferred from CO_2 to air which cause rapid increase in soluble phenolic content (Siriphanich and Kader, 1985). Elevated value of CO_2 concentration can reduce browning of mechanically damaged green beans by inhibiting formation of phenolic compounds and phenolase activity (Buesher and Henderson, 1977).

II. Browning Inhibition

A.) Controlled Atmosphere storage

As browning is the product of complex oxidative reactions and therefore a direct function of oxygen concentration, it can be retarded by the decreasing O_2 in direct contract with the cut surface of the fruit. Atmospheres with reduced O_2 and/or elevated CO_2 concentrations have been commonly used to reduce apple respiration and

extend storage life. Studies have shown that there are optimal values of O_2/CO_2 rater in preventing browning (Rolle and Chism, 1987). For example, elevated CO_2 levels delay brown discoloration of lettuce (Siriphanich and Kader, 1985).

However, minimum percentage of (1-3%) O_2 is necessary for maintenance of aerobic respiration. Usually O_2 concentrations of less than 1% create anaerobic conditions for the living cells, whereby energy requirements of tissues are supplied via glycolysis and fermentation rather than through the TCA cycle. The by-products of fermentation include ethanol and acetaldehyde, which can contribute to off flavor development (Rolle and Chism, 1987).

Although the use of elevated CO_2 treatments has been shown to have desirable effects, controlling the environment, influencing respiration and controlling browning for some commodities, negative effects may occurs if concentrations exceed certain critical levels. High values of CO_2 concentrations decrease energy supplied to tissues by inhibiting various respiratory enzymes (Shipway and Bramlage, 1973). Where cut apples are treated with high CO_2 concentration, areas around the core are injured producing a dry and brown surface. CO_2 treatments can also induce the development of off-flavors and cause physical damage if the level is too high.

Barrett (1989) found that apples stored under typical CA conditions; 1-3% O_2 and 3-5% CO_2, and analyzed immediately did not have a trace of brown discoloration in their tissues. On the other hand, the cortical tissue of apples stored under varying CO_2 conditions (8%, 9%, 10% and 12%) was observed to be both browner initially and to darken faster after 30 minutes in air than apples stored under typical CA

conditions. This finding agrees with the results of Liu and Pan (1989) who found that 'Delicious' apples stored under the same varying high CO_2 conditions had significantly greater flesh browning than normal CA stored apples after 6 months.

Since O_2 is required for enzymatic browning, reducing oxygen from contact with product can delay the reaction. MAP has the potential to be used to control gas concentrations in the package. However, excessive reduction of oxygen must be avoided to prevent anaerobic conditions that can damage the tissue by inducing anaerobic metabolism, leading to tissue breakdown and off-flavor formation. Further more, anaerobic condition in the package are also favorable for the growth of *Clostridium botulinum*, very dangerous microorganism.

B.) Chemical treatment

A number of chemical treatments exist that are able to control browning. These treatment are commonly based of sulfiting agents. Sulfur dioxide, sodium sulfite, potassium bisulfite and potassium metabisulfites are highly effective in controlling not only both enzymatic and non-enzymatic browning but also the growth of microorganisms (Sapers, 1993). However, sulfites are subject to regulatory restrictions by the FDA because of adverse effects on human health. FDA restrictions on the use of sulfites in certain fruit and vegetable products have prompted researchers to develop sulfite substitutes. Ascorbic acid (vitamin C) is probably the best known alternative to sulfite. It reduces quinones back to phenolic compounds before they can undergo further reaction to form pigments. Ascorbic acid

and its isomer erythorbic (*d*-isoascorbic) acid have been used to inhibit enzymatic browning in fresh-cut apples. As reported by El-shimi, 1993; Tressler and Dubois, 1944, these two compound can be added to syrups solution, sometimes in combination with citric acid and calcium salt, for dipping of the fruits.

Sulfites inhibitors present greater chemical stability and better penetration than ascorbic acid-based inhibitors, for these reasons the latter are less effective. To improve the performance of the ascorbic acid more stable derivatives have developed. Stable formulations include, ascorbic acid-2-phosphates, ascorbyl palmitate and other fatty acid esters of ascorbic acid, α-glucosyl ascorbic acid. The rate of penetration can be increased by treating the fruit under pressure or vacuum instead of dipping or spraying (Sapers et al., 1990).

The use of PPO inhibitors such as cinnamic acid and benzoic acid in combination with ascorbic acid (Sapers et al., 1989), carbon monoxide and kojic acid [5-hydroxy-2-(hydroxymethyl)- -pyrone] (Chen et al., 1991) has been reported. Dudley and Hotchkiss (1989) reported that cysteine prevents brown pigment formation by reacting with quinone intermediates to form stable, colorless compounds. Molnar-Perl and Friedman (1990) suggested that reduced glutathione and N-acetylcysteine are nearly as effective as sulfites in controlling browning in apple, potato, and fresh fruit juices. Bromelain, an enzyme present in pineapples, proved to be effective for inhibiting browning in refrigerated apple slices (Lozano-de-Gonzalez et al., 1993). Further studies by Lozano-De-Gonzalez (1993) has confirmed that pineapple juice and ion exchanged pineapple juice (pineapple juice where organic acids and amino acids

and small peptides were removed) are a good alternatives to sulfites for preventing browning in fresh and dried apple products.

Interestingly, honey has been shown to inhibit enzymatic browning on white grapes and cut fruits. Indeed, honey found effective in retarding flesh color change of MA packaged apple slices (Lee et al., 1994). This effect appears to be associated more with the presence in honey of a small peptide weight of about 600 Datton than to the reduction of dissolved oxygen due to the sucrose (Oszmianski and Lee, 1990).

C.) Edible coating

An edible coating was reported to prevent enzymatic browning of mushroom slices (Nisperos-Carriedo et al.,1991) and sliced apples. The USDA researcher Attila Pavlath has developed a FDA approved, tasteless seaweed-based gel coating that can prevent browning for fourteen days on apple slices (personal communication). Pavlath has also created a spray formulated with the calcium salt of vitamin C which can be found in many green vegetables. It can keep a cut apple fresh for two or three days. John Krochat, a researcher at the University of California Davis, is attempting to develop a transparent coating derived from components of milk on sliced apples (Krochat, personal communication). A cellulose-based coating, called 'Nature seal', now has been used for carrots, papaya, and pears by acquired by EcoScience of Worcester, Mass. (Stephens, 1994).

III. Decay Concern

Physiological decay, in addition to browning, is still a major obstacle remaining to the commercial production of sliced apple and other fruit. Two diseases, the blue mould rot and grey mould rot in apples which are caused by *Penicillium expansum* Link and *Botrytis cinerea* Pers. respectively, commonly affect stored apples (Snowdon, 1990). These microorganisms penetrate wounded tissue causing physiological damages and decay development. So it seems plausible that they may be responsible for the decay in sliced apples too. Possibly there are other species that can grow in the surface of slice apple. The control of these species is achieved by a combination of chemical and physical methods. Chemical control methods, (pre- and post-harvest), are directed at eliminating, or substantially reducing, the primary inoculum input into stores and in certain crops. Chemical control can be accomplished by washing and applying fungicide in sprays, aqueous washes, as dusts, or by fumigation. Physical control methods often affect the activity of both host and pathogen and include atmosphere modification, low and high temperature, heat treatment and irradiation, and are generally intended to retard the onset of decay in storage (Maude, 1980).

Modified-atmospheres have been found to effectively retard the growth of some microorganisms. High carbon dioxide (10-20%) or low oxygen (1-0.25%) reduced decay of strawberries caused by *B. cinerea* (Couey and Wells, 1970). Carbon dioxide storage was preferred by Couey and Wells (1970) because insufficient oxygen results in anaerobic respiration leading to 'invasive alcohol poisoning' or off-flavors.

Fungi, in general, are more sensitive to elevated carbon dioxide than to low oxygen. However, injuries caused by carbon dioxide limit the level of CO_2 that can be used.

Decay control can also be achieved through the application of chemical food additives such as SO_2, irradiation or fungicide. However, the use of this type of additives poses health hazards to human consumption such as in the case of the allergic response to sulfites. For these reasons, the use of 'natural' preservative compounds and techniques has a greater appeal to most consumers. At present, no chemical materials are applied to lightly processed products.

There have been investigations into the possibility of using biological control of the fruit decay. Janisiewicz (personal communication) has described a pink yeast, *Sporobolomyces roseus*-occurring naturally on the surface of pears, that reduces blue mold on apples up to 100% and gray mold up to nearly 80%. Furthermore, by adding a sugar (2-deoxy-d-glucose) to the antagonistic yeast *Candida saitoana*, Wilson and El Ghaouth (personal communication) have discovered a new biocontrol agent to protect peaches and apples from postharvest rots of apples treated with this yeast-sugar combination, 80% completely resisted the *Botrytis cinerea* rot pathogen after 16 days. Ecogen (Langhorne, PA) & Ecoscience (Falmoth, MA) companies are now commercially making a new biocontrol agent.

Decay control using volatile antifungal compounds holds some promise as an alternative to materials and techniques discussed so far. This technology 'fits well' with packaging applications where the volatile material can be incorporated in the packaging material for treating the commodity right at the time of consumption.

Antifungal volatile materials such as benzaldehyde, 1-hexanol, E-2-hexanal and 2-nonanone, released by red raspberries and strawberries during ripening can control decay in package fruit (Vaughn et al. 1993). Among those compounds, 2-nonanone has surfaced as a likely candidate due to its relatively low toxicity to the fruit, very low mammalian toxicity, a pleasant fruity odor and commercial availability. 2-nonanone is also a generally recognized as safe (GRAS) compound and is listed for food application under Synthetic Flavoring Substance and Adjuvants (FDA, 172.515).

Levels of volatile compounds other than O_2, CO_2 and H_2O can accurately be modeled based on their production rate within the package (Beaudry et al.,1993). The implication is that the steady-state approach can be used for manipulating headspace concentration of a number of volatiles, including that may have antifungal properties. Maintenance of continuous volatile concentrations will probably be necessary due to the fact that most volatiles are fungistatic rather than fungicidal. Advances in controlled-releases/delivery technology for volatile materials such as pheromone suggest that a continuous release system can be developed for packages. Prior to this advance, a model is need to predict the necessary film characteristics to maintain acceptable levels of O_2 and CO_2 inside the package as a function of oxygen partial pressure.

III. Modified Atmosphere Packaging (MAP)

MAP is a process to extend the shelf-life of fresh fruits and vegetables. Target gas compositions surrounding a product is dependent upon the product's

requirements, gas exchange and sensitivity of desirable physiological processes to gas levels. Most fresh fruits and vegetables can be stored longer in low O_2 and high CO_2 atmosphere than in air (Kader, 1989). For apple slices, MAP can possibly be used to facilitate the use of volatile antifungal compounds, maintain aerobic conditions and maintain sterile conditions.

Modification of the internal atmosphere is attained through respiration of the product within the sealed package and depends on the interaction of respiratory characteristics of the product and the permeability properties of packaging film. The natural process of respiration of products is used to reduce O_2 and increase CO_2 under restricted gas exchange through a barrier. Permeable films are usually used and available as a barrier to create modified atmosphere (Talasila et al., 1992). The reduction in O_2 concentration and increase in CO_2 concentration create gradients causing O_2 to enter and CO_2 to exit the package. When O_2 consumption equals O_2 diffusion into the package and CO_2 production equals CO_2 diffusion out of the package, steady-state conditions are achieved (Kader,1989).

One approach for designing an MA package that generates a physiologically effective package O_2 partial pressure is to match the total respiratory O_2 uptake of the packaged product with the total O_2 permeation through the film according to the following equation (Kader,1989; Beaudry et al., 1992; Cameron et al., 1994):

$$R_{O_2}^{total} = R_{O_2} W = \frac{P_{O_2} A}{l} [p_o^{O_2} - p_i^{O_2}] \qquad (1)$$

Where $R_{O_2}^{total}$ is total O_2 uptake of package fruit ($mmol \cdot h^{-1}$), R_{O_2} is O_2 uptake of fruit per unit weight ($mmol \cdot kg^{-1} \cdot h^{-1}$), P_{O_2} is O_2 permeability coefficient ($mmol \cdot cm^{1} \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$), $p_i^{O_2}$ is O_2 partial pressure of inside the package (kPa), W is fruit weight (kg), A surface area of the package (cm^2) and l is the thickness of the film (cm).

As can be seen from the equation 1, the total O_2 uptake by the product is a function of the fruit weight, surface area, thickness of the film and type of film that will be used (permeability coefficient). If the O2 level inside the package falls below that supporting aerobic respiration, anaerobic condition or fermentation may occur. Although the tissue can tolerate anaerobic conditions, extended exposure to these conditions leads to browning, off-flavors and loss of economic value. MA packages should be designed to maintain safe and effective partial pressures of O_2 and CO_2 over a wide range of temperatures (e.g. 0 to 30C) because there is a risk of temperature abuse during shipping, handling, and marketing. Therefore, the need for an accurate determination of the lower O_2 limit is required for MAP. Gran and Beaudry (1993) described a method for determining the lower O_2 limit as defined by the O_2 level at the upswing in the respiratory quotient (RQ) or RQ breakpoint, as O_2 levels become limiting to aerobic respiration.

Selection of a film that will result in a favorable atmosphere should be based on the expected respiration rate at the transit and storage temperature and the known optimum O_2 and CO_2 concentrations. The O_2 level in the package should be higher than lower O_2 limit and CO_2 level should be lower than harmful CO_2 levels. A suitable film requires much more permeability to CO_2 than O_2. Fortunately, most commercially available films are about 4 to 5 times more permeable to CO_2 than O_2.

In addition to differential O_2 and CO_2 permeabilities, some desirable characteristics of plastic films for MAP of fresh produce include having required permeabilities for the different gases, good transparency and gloss, low weight, high tear strength and elongation, low temperature heat-sealability, lack of toxicity, nonreactivty with produce, good thermal and ozone resistance, good weatherability, commercial suitability and, ease of handling, printing and labeling (Kader, 1989).

There are few kinds of polymers routinely used for packaging fresh produce such as PVC, polystyrene, polyethylene, and polypropylene. Polyolefins; polyethylene, polypropylene, and polybutylene as well as their copolymers, are typified by their good water vapor barrier properties, their relatively high gas permeabilities, and their favorable response to heat sealing. Among those, LDPE (specific gravity = 0.910 to 0.925) has high ratio of CO_2 to O_2 permeability which allow O_2 concentrations to decrease without an associated excessive buildup of CO_2 inside the package (Kader, 1989). Some PVC films can have very high CO_2/O_2 permeability ratios (4-5) as well, making them well suited for MAP.

IV. Modeling Atmosphere Modification within the package

Respiration of apple slices described by R_{o_2} and $p_i^{o_2}$ as function of temperatures has not been shown. The effect of temperature on respiratory rate has been measured for tomato, blueberry, and raspberry fruits (Cameron et al., 1989; Beaudry et al., 1992; Joles et al., 1994). The permeability of the film to O_2 and CO_2 and it's temperature sensitivity have to be also experimentally defined so that the living produce will be able to respire and maintain aerobic condition through out the temperature range.

A.) Respiratory Models

Respiration rates have been measured for a number of fruits and vegetables under various conditions as either O_2 consumption or CO_2 production rates. Talasila (1992) gives a comprehensive list of the available models. Henig and Gilbert (1975) fitted regression equations for rates of O_2 consumption and CO_2 production as functions of O_2 and CO_2 concentrations for tomato fruits by assuming that there was negligible influence of CO_2 concentration on O_2 consumption and O_2 concentration on CO_2 production. This assumption was not considered valid after the data was analyzed again by Hayakawa et al. (1975). However, a number of studies have shown that CO_2 has little influence on respiratory activity at levels below 20 kPa (Beaudry et al., 1992; Joles et al., 1994).

Cameron et al. (1989) developed empirical models for O_2 consumption rate as a function of O_2 concentrations from the O_2 depletion data from tomato fruit sealed in jars. Cameron et al., (1989), Mannapperuma and Singh (1987) estimated respiration rates only at 20C. Talasila et al. (1992) developed a model to predict respiration rate of strawberries as a function of temperature and a function of gas concentrations. He found that the influence of CO_2 concentration on respiration rate of strawberries is

minimal.

Lee et al. (1991) developed a semi-empirical model for cut broccoli based on a enzyme approach. In this model, the dependence of respiration on O_2 was assumed to follow a Michaelis-Menten type equation, the effect of CO_2 on respiration was thought to follow an uncompetitive inhibition model. This model was later used to predict gas concentrations inside MA packages of cut broccoli.

A Michaelis-Menten type respiratory model can be well fitted with respiratory data of several commodities and has been used with various commodities such as blueberry, tomato, raspberry and strawberry (Banks et al., 1989; Beaudry et al., 1992; Cameron et al., 1994; Joles et al., 1994; Lee et al., 1991; Talasila et al., 1994). In these studies the Michaelis-Menten type respiration model is as follows.

$$R_{O_2} = \frac{V_{max}\, p_i^{O_2}}{K_T + p_i^{O_2}} \tag{2}$$

From the above equation, O_2 uptake (R_{O_2}) depends on O_2 partial pressure inside the package ($p_i^{O_2}$) and temperature which can be expressed in two parameters; K_T ($p_i^{O_2}$ at half-maximal R_{O_2}) and V_{max} (maximal R_{O_2}). This model, developed by Lee et al. (1991), was proved to fit well with the real respiratory data of blueberry fruit (Cameron et al., 1994). This model appears to have general applicability and has been shown to be suitable for incorporation into models for predicting the level of $p_i^{O_2}$ over a range of temperatures.

B.) Modeling Package Atmospheres

For packaged produce, it was recognized by Tomkins (1961) that several factors affect O_2 and CO_2 conditions within packages. Factors identified were the size of package, surface area and weight of contents and the production, escape and equilibrium concentration of CO_2 (Tomkins, 1961). Based on this early knowledge, there were many attempts to find the relationship between polymer film characteristic and respiration of commodity in MAP.

Several attempts have been made to model MAP systems for each constant surrounding temperatures (Cameron et al., 1989; Deily and Rizvi, 1981; Hayakawa et al., 1975; Henig and Gilbert, 1975; Jurin and Karel, 1963; Mannapperuma and Singh, 1987; Veeraju and Karel, 1966). Kader (1989) and Talasila (1992) give the comprehensive list of the available models. The first steady state model to predict gas concentrations inside a package for apples at constant temperature was developed by Jurin and Karel (1963). This is simply a form of Fick's law and a rearrangement of equation 1.

$$p_i^{O_2} = \left[p_o^{O_2} - \left(\frac{R_{O_2}\, l}{P_{O_2}} \right) \frac{22.414\, W}{A} \right] \tag{3}$$

$$p_i^{CO_2} = \left[p_o^{CO_2} - \left(\frac{R_{CO_2}\, l}{P_{O_2}} \right) \frac{22.414\, W}{A} \right] \tag{4}$$

Where $p_i^{O_2}$ and $p_o^{O_2}$ are O_2 partial pressure inside and outside the package, respectively in kPa. R_{O_2} R_{CO_2} are O_2 uptake and CO_2 production of fruit per unit weight ($mmol \cdot kg^{-1} \cdot h^{-1}$). P_{O_2} and P_{CO_2} are O_2 and CO_2 permeability coefficient, respectively in $mmol \cdot cm \cdot cm^{-2} \cdot h^{-1} \cdot kPa^{-1}$. W is fruit weight in kg. l is thickness of film in cm. A is surface area of the package in cm^2.

From the steady-state respiratory model (equations 3 and 4), the relationship between the rate of O_2 uptake and O_2 concentration for tomato fruit was described as a continuous mathematical function which was utilized to develop the model for optimization of oxygen concentration in the sealed package of tomato fruits (Cameron et al., 1989; Gong and Corey, 1994). Beaudry et al. (1992) measured the effect of temperature on package O_2 and CO_2 and empirically fitted the relationship between O_2 uptake and steady-state O_2 of blueberry fruit with exponential equations at each temperature (0-25C).

The blueberry fruit data generated by Beaudry et al. (1992) was further evaluated by Cameron et al. (1994), who developed the model for prediction of steady-state package O_2 for MA systems over a wide range of temperature (0-25C). The model developed has been used to predict the effect of altering the Ea of the film on $p_i^{O_2}$ across the temperature range of 0-25C. Predicted O_2 levels agree quite well with original package O_2 data of Beaudry et al. (1992).

The purpose of this research was to determine necessary packaging characteristics (e.g. package dimensions, film permeability to O_2 and CO_2, temperature sensitivity of O_2 and CO_2 permeability, etc) to generate acceptable atmospheres within packages for sliced apple fruit. The first goal was to determine target O_2 and CO_2 to control the browning reaction of sliced fruit. The second goal

was to collect respiratory data for the development of a respiratory model for sliced apple such that package characteristics needed to achieve and maintain target gas concentrations could be identified. To this end, the model was used to predict the steady-state package oxygen partial pressure as a function of temperature and film permeability.

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CHAPTER II

Modified-atmosphere packaging of apple slices: Modeling respiration and package oxygen partial pressure as function of temperature and film characteristics.

ABSTRACT

A systematic approach was taken to acquire information for the design of a modified-atmosphere packaging (MAP) system for apple slices. Initially, various combinations of O_2 and CO_2 were assessed for their control of tissue browning, thereby generating target gas concentrations for package design. Reduced O_2 and elevated CO_2 atmospheres were applied to sliced apples and while some gas concentrations significantly reduced browning relative to air controls, none of the treatments prevented browning to a sufficient level to be acceptable. Modified-atmosphere packaging (MAP) was used as a tool for obtaining respiratory data needed to calculated permeability characteristics of packaging films that will obtain and achieve and maintain desired gas levels in the package headspace at 0, 5, 10 and 15C. The lowest O_2 partial pressure to which fruit could be exposed without fermentation increased with increasing temperature. A mathematical model was developed to characterize the relationship between, steady-state O_2 partial pressure ($p_i^{O_2}$) and O_2 uptake and film permeability to O_2 of packages. Maximum O_2 uptake (V_{max}) and the $p_i^{O_2}$ at half-maximal O_2 uptake (K_T) were both increased with temperature. The $p_i^{O_2}$ model was used for predicting the effect of P_{O_2}, activation energy (Ep^{O_2}), temperature, film type, and film thickness on $p_i^{O_2}$ for apple slices. It can also be used to predict the minimum ratio of W*l*/A of LDPE that can achieve aerobic condition throughout the temperature range.

INTRODUCTION

Lightly processed produce, also known as precut, value-added, fresh-processed or fresh-cut produce, are packaged produce items that comprise the most rapidly growing segment of the fresh produce industry. Precut vegetables which include lettuce, cabbage, broccoli, cauliflower, etc., have found widespread acceptance and have been readily incorporated into food service offerings. Fruit products, unlike vegetable counterparts, have been slower to develop. Sliced fruit with higher sugar and water contents, have significantly more problems than vegetables because of rapid tissue browning, moisture loss, decay, and tissue softening. Apple slices has the potential to be successful lightly process fruit product.

Browning is a major quality concern and, for apple, is primarily. Discoloration can occur after bruising, cutting or during storage and is often the limiting factor in shelf life. Browning in a sliced product results from a series of complex oxidative reactions in part catalyzed by polyphenol oxidase (PPO) (McEvily et al., 1992). Browning can be retarded by decreasing O_2 or increasing CO_2 in contact with the cut surface of the product (Siriphanich and Kader, 1985; Kader, personal communication). Atmospheres with reduced O_2 or elevated CO_2 concentrations have been commonly used to reduce apple respiration and extend storage shelf life (Rolle and Chism, 1987; Siriphanich and Kader, 1985).

A minimum percentage of (1-3%) O_2 is necessary for maintenance of aerobic respiration. Induction of fermentation results in ethanol and acetaldehyde synthesis, which can contribute to off flavor development (Rolle and Chism, 1987). Although

the use of elevated CO_2 treatments has been shown to have the desirable effects of influencing respiration and controlling browning for some commodities, if concentrations exceed a certain level, injury is likely to occur. Although range of non-damaging O_2 and CO_2 levels have been published for a numbers of commodities (Kader, 1989); the safe levels of O_2 and CO_2 are unknown for apple slices.

Modified atmosphere packaging can be used to achieve target gas compositions surrounding a product. The natural process of respiration of the enclosed products reduces O_2 and increases CO_2 under restricted gas exchange through the polymer film barrier. Steady-state gas levels achieved in the package depend on the interaction of respiration of the product and the permeability properties of packaging film.

MA packages should be designed to maintain safe and effective partial pressures of O_2 and CO_2 over a wide range of temperatures because there is a risk of temperature abuse during shipping and handling. The need for an accurate determination of the lower O_2 limit is required for modeling and designing MAP systems. MA package should be able to provide O_2 levels higher than the lower O_2 limit and CO_2 levels below harmful CO_2 levels across the temperature range likely to be encountered.

One approach for designing an MA package that generates desirable package O_2 partial pressures is to match total respiratory O_2 uptake of the packaged product with the total O_2 permeation through the package according to Fick's law (Kader, 1989; Beaudry et al., 1992; Cameron et al., 1994). Respiration and film permeability to O_2 and CO_2 vary differentially with temperature. The respiratory process has the

added complexity of also being dependent on the package O_2 partial pressure.

The effect of temperature on the respiration rate has been measured for tomato, blueberry and raspberry fruits (Cameron et al., 1989; Beaudry et al., 1992; Joles et al., 1994). Respiration of apple slices described by O_2 uptake as a function of temperature and O_2 partial pressure has not been defined. However the dependency of respiration on O_2 and temperature has been found to be reasonably well described by a Michaelis-Menten type equation for tomato (Cameron et al., 1994), blueberry (Beaudry et al., 1992), raspberry (Joles et al., 1994), strawberry (Talasila et al., 1994) and cut broccoli (Lee et al., 1991). The respiratory models have been successfully combined with describing the temperature sensitivity of P_{O_2} to develop model for predicting package O_2 as a function of temperature, fruit weight, surface area, film thickness.

The purpose of this research was to determine necessary packaging characteristics (e.g. package dimensions, film permeability, etc) to generate acceptable atmosphere within packages of sliced apple fruit. The first goal was to determine if there were O_2 and CO_2 combination that controlled browning reaction of sliced fruit. These gas combinations would then serve of target for package design. The second goal was to collect respiratory data for the development of a respiratory model for sliced apple. Finally, package permeability characteristics were combined with the respiratory model to develop a model that can be used to predict the effects of various parameters (temperature, film thickness, fruit weight. etc) in package O_2 such that target gas concentrations could be achieved.

MATERIALS AND METHODS

I. Measuring browning in apple slices

A.) Apples

Apple fruit of the cultivar 'Ida Red' were harvested in an early October from Clarksville, Michigan at a stage of maturity suitable for long-term storage under controlled-atmospheres (CA). They were stored in CA at 1.5 $\pm$ 0.1 kPa O_2 and 3 $\pm$ 0.5 kPa CO_2 at 1 $\pm$ 0.2C. After two months, fruit were removed from CA storage and held for 1 day in air at 3C prior to the experiment.

B.) Rate of Browning

The rate of tissue discoloration was measured in order to gauge the time when antibrowning treatments need to be applied at 0, 5, 10, and 15C. Two apples were sliced into wedges (width 2-3 cm) using a stainless steel knife and placed into jars with small holes for aeration. The jars were held at 0, 5, 10, and 15C for 3 days. Browning of the cut surfaces was assessed using the method of Barrett (1989) using the change in reflectance over time. Measurements were made using the Model CR-300 Minolta Chroma Meter, (Minolta camera Co.,Ltd, Ramsey, NJ). The 'L' value signifies the degree of lightness from 60 white to -60 (black), 'a' and 'b' values signify the color; 'a' value varies from 60 (green) to -60 (red), 'b' value varies from 60 (yellow) to -60 (blue). Prior to measurement, the Chroma Meter was calibrated using a white calibration plate.

C.) Inhibition of Browning with CA storage

A flow-through CA system, as described by Liu and Samelson (1986) was used to generate various gas mixtures of O_2 and CO_2. In the study, ten different mixtures were prepared containing 1 or 20 kPa O_2 and 0, 5, 10, 15 or 20 kPa CO_2. Apple fruits were cut into wedges (2-3 cm in width) while at 5C using a stainless steel knife. Bruised tissue was avoided. Four pieces were randomly selected and sealed into an air-tight 473.2 ml (1 pint) glass container. The jars were flushed immediately with one of the ten different gas mixtures, and the levels of O_2 and CO_2 in the jar were measured to confirm that they had reached the desired concentration. Atmosphere modification was completed within 90 seconds after slicing. The jars were placed in a storage room maintained at 5C and humidified (Liu and Samelson, 1986) gas mixtures were supplied, having a flow rate of 15 ml per minute. Fruit slice color was determined immediately after cutting and after 1, 2, 3, 5, 7, 10 and 14 days under CA conditions. In each instance, color was determined in three locations on each face of the four slices for each treatment/time combination.

D.) CO_2 injury index

A CO_2 injury rating system was developed based on visual analysis. Ratings were on a 1-4 scale (1=none, 2=slight, 3=moderate, and 4=severe) (Barrett, 1989). CO_2 injury was assayed after treatment with the various gas combinations for 14 days. CO_2 injury may be seen as brown and moist surface near core tissue (Lidster et al., 1990)

II. Modeling apple respiration and package oxygen partial pressures as a function of temperature.

A.) Apples

Apple fruit of the numbered selection 'NY 674' were obtained from plantings in Geneva, New York and Clarksville, Michigan. Kim et al. (1993), and Lee and McLellan (1990) reported 'NY 674' tissue showed less decline in 'L' values than other apple varieties and they attributed this resistance to browning as being a result of lower polyphenol oxidase activity and polyphenol content relative to the other cultivars tested. This characteristic makes 'NY674' a product which should make treatments to control browning more efficient. Harvested fruits were held under elevated humidity at 3C for 7 days prior to use. Apples were cut into wedges using stainless steel knife. The core of each piece was removed. Each piece was approximately 1-2 cm wide measured at the skin side.

B.) Package design

Fruit slices were sealed in pouches made of 0.00762 and 0.01016 cm (3 and 4 mil, respectively) thick low-density polyethylene (LDPE; LDF 550) (Dow chemical company, Midland, MI). The range of steady-state O_2 concentrations from 0.1 to 16 kPa were generated at 0, 5, 10, and 15C (Cameron et al., 1989). The initial step in the designing process involved determining respiration rates for apples at an elevated O_2 partial pressure (20.7 kPa) and 20C. From this valve, the R_{O_2} was estimated to be 0.1, 0.6, 0.05 and 0.02 mmol kg^{-1} h^{-1} at 15, 10, 5,and 0C, respectively. Using these

estimates of R_{O_2}, the needed film thickness, area and fruit weight was calculated to generate 16 kPa O_2. From these high O_2 settings, film thickness and fruit weight were increased and package area decreased in order to achieve a wide range of lower O_2 levels. Four replications of each package configuration were made for each temperature (Table 1). Film thickness were either 3 or 4 mil and package area either 800 or 1250 cm^2. Fruit weight ranged from 19 to 587 g.

C.) Permeability of Film:

The O_2 and CO_2 permeability of 3 mil and 4 mil LDPE films were determined on three random film samples at 0, 10 and 20C according to the method of Beaudry et al. (1992). A specially-built stainless steel permeability cell was submerged in a water bath (Lauda RC20; Brinkman Instrument Co., West Bury, N.Y.), and temperature was measured using thermocouple and mercury thermometers. The permeability cell contained two circular 25-ml chambers separated by the film sample and sealed in place by an O-ring. The cell chambers were 8 cm in diameter and 0.5 in depth and surface area 50 cm^2. Stainless steel and copper coils tubing were attached to the inlet for the N_2 carrier supply line. The passage of the gas through the coils before entering the cell allowed the system to be isothermic, i.e. the entering gas had the same temperature as the cell. The permeant mixture of O_2 and CO_2 (65 and 35 kPa, respectively) was introduced to one chamber of the cell and N_2 carrier gas was introduced to the other chamber. The rate of O_2 and CO_2 permeation through the film was calculated from the steady-state partial pressure difference between the two

streams. The partial pressure of O_2 and CO_2 in the carrier gas stream was determined from concentration measurements obtained using a sequential combination of O_2 and CO_2 analyzers. To measure the O_2 concentration, an analyzer with a Ametek S3A/II a calcia-zirconia electrochemical detection cell was used (Ametek Co., Thermox Instrument Div., Pittsburgh, Pennsylvania). CO_2 was measured with a ADC 225-MK3 analytical infrared gas analyzer (Analytical Development Co., Hertfordshire, England). Concentrations were calculated relative to a certified standard gas mixture (106 μL/L O_2 and 100 μL/L CO_2 in N_2 gas). Flow rates were maintained between 110 and 130 ml/min for all gases, and the chamber pressures were equalized and maintained at about 0.4 kPa H_2O above atmospheric.

Concentration data were converted to partial pressures using the ideal gas law to determine the permeability coefficients. Values of the permeability as a function of the temperature were fitted by an Arrhenius equation or indicated by the following equation:

$$P_i = P_c\, e^{-\frac{Ep}{RT}} \tag{1}$$

Where P_i is permeability coefficient at any temperature in kelvin. P_c is permeability constant. R is gas constant (0.0083144kJ·mol^{-1} K^{-1}). Ep is activation energy in kJ·mol^{-1}. T is temperature in Kelvin. This equation can be converted to:

$$\ln(P_i) = \frac{Ep}{RT} + \ln(P_c) \tag{2}$$

E.) Respiration rate of apple slices

Apples were cut into wedges and placed on a plastic tray in order to avoid cut surface contact with the film. The tray with the slices were placed in LDPE pouches and heat sealed. A gas-sampling septum, made of Dupont Silicone II tub/tiling glue on a short strip of electrical tape was attached to the surface of the package (Boylan-Pett, 1986).

In order to accelerate the achievement of steady-state gas concentrations, a portion of the headspace air was removed by vacuum and replaced with N_2 gas. Packages having obvious holes or containing fruit with decay lesions were discarded. No fungicide treatment was used.

Gas samples were drawn from each package through the self-sealing silicone septum using a 0.5 ml insulin syringe. Two gas samples were analyzed from each package at each evaluation using the O_2 analyzer (Servomex Paramagnetic O_2 Transducer, Series 110, Servomex Co., Sussex, England) and CO_2 analyzer (ADC analytical infra red CO_2 Analyzer 225-MK3, Analytical Development Co., Hoddesdon, England) connected in series, with N_2 as the carrier gas (flow rate = 100 ml/min). A third gas sample was taken if any difference was noted between the first two samples.

The gas composition of individual packages was monitored until the internal gas partial pressure, $p_i^{O_2}$ and $p_i^{CO_2}$ reached steady-state values. For steady-state conditions the following equations can be written:

$$R_{O_2} = \left(p_o^{O_2} - p_i^{O_2}\right) \frac{P_{O_2}A}{Wl} \tag{3}$$

$$R_{CO_2} = \left(p_i^{CO_2} - p_o^{CO_2}\right) \frac{P_{CO_2}A}{Wl} \tag{4}$$

The respiratory quotient (RQ) was calculated as R_{co_2} divided by R_{o_2}. Data were plotted as the dependence of O_2 uptake and CO_2 production on O_2 partial pressure in the package ($p_i^{o_2}$) at four temperatures. The RQ breakpoint indicating lower O_2 limit was determined from the curve between RQ and O_2 partial pressure using the approach of Beaudry et al. (1992) and an increase in ethanol vapor in the package.

RESULTS

I. Browning under controlled-atmosphere

Compared rate of browning for cultivar 'Ida Red' at 0C and 'NY674' at room temperature, 'NY674' even at high temperature (23C) has much slower browning rate than 'Ida Red' at low temperature (Figure 1). The browning of apple slices in air as determined by 'L', 'a', and 'b' value were plotted versus times at five temperatures (0, 5, 10, 15, and 20C) (Figure 2, 3, and 4). Based on subjective evaluations by laboratory personnel, changes in 'L', 'a', and 'b' values were 2.8, 1.7, and 4.2, respectively could be detected. If the value decreased ('L' and 'a') and increased ('b' value) by more than this margin point it was considered to have undergone an undesirable levels of browning. 'L' and 'a' values decreased rapidly, while the 'b'

value increased rapidly for all temperatures. The relationship between the time ($T_{1/2}$) required for the reading to reach half way between initial and final value and temperature was estimated from the best fit curves (Figure 5). Browning occurred with such rapidity at all temperatures, it was evident that flushing of the mixture gas would be needed immediately after cutting. 'L' and 'b' trends indicated the browning rate was slower at lower temperature. the rate of change in the 'a' value was not much influenced by temperature in the range from 0 to 15C however, it increased at 20C.

There are significant treatment effects (α=0.05) for on 'L', 'a', and 'b' values (Table 1; Appendix A). CO_2 and time (the duration of exposure to treatment atmosphere) had a significant effect on all 'L', 'a', and 'b' values. Only O_2 had a significant effect on 'b' value (Table 2; Appendix A). Exposure to 5, 10, 15, and 20% CO_2 caused an increase in 'L' value and 'a' value relative to CO_2 control ($\leq$ 0.03% CO_2) (Table 2) but 5, 10, 15, and 20% CO_2 did not differ. 5, 10, 20% CO_2 caused a decrease in 'b' value. The exception being 15% CO_2 which didn't differ from 5, 10 and 20% CO_2. There was no apparent pattern to effect of date on 'L', 'a', and 'b' values although there were some differences.

CO_2 treatment had a significant effect on the severity of CO_2 injury of apple slices (Table 3; Appendix A). CO_2 injury was encountered for 20, 15 and 10% CO_2 treatments, it was most severe for the 20% CO_2 treatment and there was no significant difference between 10 and 15% CO_2 (Table 3).

II. Film Permeability

As previously shown (Beaudry et al., 1992), P_{O_2} and P_{CO_2} of LDPE 3 and 4 mil increased exponentially with increasing temperature (Figure 6). An Arrhenius plot of the data indicates that the natural log of the permeability coefficient for both gases depended linearly on the reciprocal of temperature in Kelvin (Figure 7) with r^2 = 0.99 according to the equation 2, where Ep/R is the slope of the fitted line and $\ln(P_c)$ is the y-intercept.

Activation Energy (Ep^{O_2}) is a measure of temperature sensitivity for O_2. The higher the activation energy, the greater the temperature effect. The degree to which relative permeability increases in response to temperature (Figure 8) is associated with its Ep^{O_2} according the following equation.

$$\frac{P_i}{P_o} = \exp\left\{\frac{Ep^{O_2}}{R}\right\}\left[\frac{(T_i - T_o)}{(T_i * T_o)}\right] \qquad (5)$$

Where P_i and P_o are permeability constants at any temperature (T_i) in Kelvin and 273.15 K (T_0).

The change in the rate of O_2 diffusion with temperature for free diffusion is proportional to the relative change in temperature in Kelvin. The Ep^{O_2} of free diffusion through holes is approximately 5 kJ/mol. This low Ep^{O_2} confers essentially no change in gas exchange across the temperature range of this experiment (Figure 8).

Equations for predicting P_{O_2} and P_{CO_2} for 3 and 4 mil film at any temperature (Kelvin) were determined to be:

4 mil film

$$P_{O_2} = 0.077 * \exp(-4396/T) \quad (6)$$

$$P_{CO_2} = 0.132 * \exp(-4157/T) \quad (7)$$

3 mil film;

$$P_{O_2} = 0.104 * \exp(-4485/T) \quad (8)$$

$$P_{CO_2} = 0.167 * \exp(-4230/T) \quad (9)$$

Regression analysis was performed on transformed data to estimate values of Ep and, the permeability constant (P_c). When the curves are plotted together, they are not significantly different for P_{CO_2} and are nearly identical for P_{O_2}. The equations describe essentially the same curve within the temperature range of 0 to 15C.

III. Respiratory model

Steady-state $p_i^{O_2}$ was reached for all packages for each temperature. Steady-state $p_i^{O_2}$ ranged from approximately 0.1 to 16 kPa. R_{O_2} and R_{CO_2} was calculated for each package using equation 3 and 4, respectively. R_{O_2} and R_{CO_2} of apple slices with $p_i^{O_2}$ were plotted as a function of temperature (Figures 9, 10, and 11). The R_{O_2} and R_{CO_2} increased with increased temperature at all steady-state $p_i^{O_2}$. The data tended to be more variable at 10C and 15C.

As $p_i^{O_2}$ declined, RQ increased above its aerobic values (Figure 12). The O_2 level at which this increase took place decreased with temperature. The increase in RQ with declining $p_i^{O_2}$ has been taken as representing the lower O_2 limit (Gran and Beaudry, 1992) variously referred to as the RQ breakpoint, extinction coefficient and fermentation point. The low O_2 limits for each temperature were determined by marked increases in RQ values above the aerobic RQ value (approximately 1) which occurred for packages with declining $p_i^{O_2}$ (Table 4). Ethanol concentration in the package headspace increased linearly with RQ above 1 (Figure 13) indicating fermentative metabolism.

The lower O_2 limit estimates for 0, 5, 10, and 15C (T) were empirically fitted with an exponential equation for graphical depiction (r^2 0.99):

$$\mathit{Lower}\ O_2\ \mathit{limit} = 0.195\, e^{(0.047 \cdot T)} \qquad (10)$$

The data describing the relationship between R_{O_2} and steady-state $p_i^{O_2}$ were fitted with the Michaelis-Menten type model (Lee et al., 1991; Cameron et al., 1994) with two temperature-dependent functions V_{max} and K_T as indicated in the following equation:

$$R_{O_2} = \frac{V_{max}\, p_i^{O_2}}{K_T + p_i^{O_2}} \qquad (11)$$

V_{max} and K_T were found to vary with temperature according to the follows:

$$V_{max} = a e^{bT} + c \tag{12}$$

$$K_T = mT + n \tag{13}$$

Data were fitted simultaneously at four temperatures using statistical analysis software (SAS) to estimate values for a, b, c, m, and n as in Table 5. Substituting these constants in equation 11 yields:

$$R_{O_2} = \frac{(0.602 e^{0.069T} - 0.377)\, p_i^{O_2}}{(0.05T + 0.662) + p_i^{O_2}} \tag{14}$$

The relationship between R_{O_2} and $p_i^{O_2}$ for 0, 5, 10, and 15C was depicted (Figure 15). At high $p_i^{O_2}$, R_{O_2} is considered equal to V_{max}. This model was well fitted by the data in Figure 11 with R^2 0.944. V_{max} and K_T were calculated from the model (Table 6, Figures 16 and 17, respectively).

According to the model, R_{O_2} increased more rapidly with temperature as $p_i^{O_2}$ increased (Figure 18). At 0.3 kPa, R_{O_2} increased approximately 3-fold, while at 16 kPa, R_{O_2} increased nearly 6-fold. The change in the rate of respiration due to temperature can be characterized using Q_{10}. Like $Ea^{R_{O_2}}$, Q_{10} can be used as a measure the relative temperature sensitivity of a physiological process. As Q_{10} increases, temperature sensitivity increases. Q_{10} was determined at temperature range between 0-15C at different $p_i^{O_2}$ (Figure 19). For every 10C increase in temperature, the

respiration rate decrease approximate 1.7 to 3.6 times depending on the $p_i^{O_2}$ inside the package.

IV. The $p_i^{O_2}$ model

The total O_2 uptake of the packaged fruit is given by the multiplication of R_{O_2} times the weight, W.

$$R_{O_2}^{total} = R_{O_2} W = \left[\frac{V_{max}\, p_i^{O_2}}{K_T + p_i^{O_2}} \right] W \tag{15}$$

For a package in which gas exchange is at steady-state, O_2 flux into the package (F_{O_2}, mmol h^{-1}) can be calculated from

$$F_{O_2} = \frac{P_{O_2} A}{l} \left[p_o^{O_2} - p_i^{O_2} \right] \tag{16}$$

At steady-state, F_{O_2} (total O_2 flux into the package) is considered equal to respiration rate total; We can therefore solve for O_2 partial pressure inside the package as from the following equation:

$$\frac{P_{O_2} A}{l} \left[p_o^{O_2} - p_i^{O_2} \right] = \left[\frac{V_{max}\, p_i^{O_2}}{K_T + p_i^{O_2}} \right] W \tag{17}$$

which can be rearranged to

$$2p_i^{O_2} = -\left[K_T + \frac{Wl}{P_{O_2}A}V_{max} - p_o^{O_2}\right] + \left[\left[K_T + \frac{Wl}{P_{O_2}A}V_{max} - P_O^{O_2}\right]^2 + 4\,p_o^{O_2}K_T\,)\right]^{1/2} \quad (18)$$

DISCUSSION

While some gas concentrations significantly reduced browning relative to air controls, none of the treatments prevented browning to a sufficient level to be acceptable. Kader (personal communication) suggested that O_2 levels of 0.5% and CO_2 levels of more than 20% would started to have some effect of controlling browning on cut fruits. However 0.5% O_2 is dangerously close to the lower O_2 limit for apple fruit slices (0.1 to 0.3%) and a concentration of CO_2 greater than 10% can cause CO_2 injury.

There are many possible anti-browning treatments that retard tissue browning apple slices, for example, the combination of sporix; an acidic polyphosphate, with ascorbic acid (Sapers et al., 1989), pineapple juice and ion exchange pineapple juice (Lozano-de-Gonzalez et al., 1993), the combination of 1% ascorbic acid solution with heat treatment (El-shimi, 1993) as well as honey (Lee et al., 1994). An edible coating, such as the seaweed-based coating developed by Attila Pavlath (personal communication) also has potential control browning for 8-14 days. One of these methods may prove commercially viable depending on the practical processes of slicing and packing, period of distribution and cost. Anti-browning agents extracted

from natural sources may gain favor with some consumer groups. None of them are successfully used for MA fresh apple slices package in the market.

The anti-browning treatment should be applied to the slices immediately after it is cut since color changes rapidly. The optimal concentration and duration of chemical treatment for apple slices will probably be cultivar dependent due to differing browning rates, polyphenol oxidase activities and native antioxidant levels. It will be important to apply an anti-browning agent in a way that consumes little time, is of low cost and has high production rate.

Use of this seaweed-based coating is potentially practical way to control browning in sliced apple. Pavlath (personal communication, 1994) sprayed apple slices with a seaweed-based coating on surface within 20 seconds. This seaweed-based formulation has some commercial promise. However, the layer of coating material (100th of an inch in thickness) may affect consumer's preference.

Maintenance of an acceptable texture after cutting, treating with anti-browning agent and storage needs to be studied. Loss of firmness of apple slices in atmosphere can be easily detected by consumer. However, the study of texture changes has not been done for apple slices in MA package.

Due to the susceptibility of the cut surface of apple slices to decay, a sealed package or pouch may be necessary. Atmosphere modification is apt to occur once a package is sealed. Modification of the atmosphere is attained through respiration of the fruit within the sealed package and depends on the interaction of respiratory characteristics of the fruit and the permeability properties of packaging film.

Therefore, the respiratory data, permeability properties and the levels of $p_i^{O_2}$ and $p_i^{CO_2}$ limit must be reported.

The lower O_2 limit for apple slices was about half (or less) that of whole fruit (Gran, 1993). The low O_2 tolerance of apple slices can be explained by the fact that whole apple fruit have a skin resistance to O_2 movement that is significantly higher than tissue resistance (Trout et al., 1942; Burg and Burg, 1965). Without the skin apple tissue (wound tissue) respire more and has higher an internal O_2 than whole fruit at the same $p_i^{O_2}$ so it needs less O_2 to maintain aerobic conditions, thereby resulting in a decrease in the lower O_2 limit.

The low O_2 limit of whole apples is temperature dependant (Grans, 1993). Like whole fruit, the lower O_2 increased with temperature for apple slices. While the lower O_2 limit was defined by an elevated RQ and associated fermentation, there are also limits imposed by CO_2 injury. The data suggest the $p_i^{CO_2}$ limit was near 10 kPa as determined by CO_2 injury. An optimal package design therefore, will maintain $p_i^{O_2}$ in the range of aerobiosis and $p_i^{CO_2}$ below the range causing injury. The $p_i^{O_2}$ model, based on the respiratory model, can be used to design a package that will predict the makeup of the atmosphere for sliced apple in any package size, by any polymer film of known thickness, for any given fruit weight (equation 18). In addition to providing a suitable atmosphere during storage, packages should maintain safe and, if possible, effective $p_i^{O_2}$ and $p_i^{CO_2}$ over a range of temperatures because of the risk of temperature abuse during the process of handling and marketing.

Optimal package designs will allow sufficient O_2 in such that $p_i^{O_2}$ is higher than the lower O_2 limit throughout the temperature range. The Ep^{O_2} of LDPE (Figure 8) is lower than the apparent $Ea^{R_{O_2}}$ of apple slices (Appendix B) throughout the range of temperatures from 0 to 15C. Thus, the permeation of O_2 gas through the package has a lower temperature sensitivity than fruit respiration, meaning that as temperature increased, the respiration rate of the fruit increased relatively more than P_{O_2}. The lower O_2 limit at which anaerobiosis within the LDPE packages was induced also increased with temperature ranging from 0 to 15C, thus enhancing the temperature sensitivity of the system.

Cameron et al. (1993) measured variation in product respiration and package permeability and modeled the effect on $p_i^{O_2}$. They determined there is an estimatable risk of the $p_i^{O_2}$ falling below lower O_2 limit and resulting in fermentation. They showed that for broccoli, packages need to be designed to generate $p_i^{O_2}$ levels well above the lower O_2 limit in order to ensure aerobic conditions. Target $p_i^{O_2}$ concentrations 3-fold higher than the lower O_2 limit reduced the risk of a package becoming anaerobic 1 in a 1,000,000 (Talasila, personal communication).

The $p_i^{O_2}$ model developed from apple slice data was used to determine how changing $Ea^{P_{O_2}}$ affects the potential risk of temperature-induced anaerobiosis. Predictions were made for packages optimized to 0.6 kPa at 0C which provides a buffer (3X) relative to the lower O_2 limit (Figure 20). No Ep^{O_2} can provide $p_i^{O_2}$ above 3X buffered low O_2 limit at the higher end of the temperature range. This can be

explained by the fact that respiration rate of apple slices increased more rapidly than the increase in O_2 flux through the film.

For packages designed to generate 1.2 kPa at 15C (Figure 21), the lower the Ep^{O_2}, the higher $p_i^{O_2}$ a package will attain at 0C. Polymer films that have lower temperature sensitivities are predicted to develop greater declines in $p_i^{O_2}$ when the temperature increased from 0C to 5C and less flexibility in package design. Therefore, for package system, the higher the Ep^{O_2} the better for the temperature abuse of the system.

The $p_i^{O_2}$ model can also be used to demonstrated the effect of film thickness on $p_i^{O_2}$ (Figure 22). The predicted curves are for an LDPE package system with fruit 0.1 kg and a surface area of 120 cm^2. Films of 0.227 mil thickness or less are predicted to provide aerobic $p_i^{O_2}$ levels within the 0 to 15C temperature range. The thicker films are predicted to risk fermentation over some portion of the temperature range.

A more generally applicable form of the model can be derived using a ratio of the Wl/A of each polymer film. From our data, an apple slice package can be designed to maintain aerobic conditions within the temperature range from 0 to 15C when the Wl/A ratio is less than 5.65×10^{-7} kg·mil/cm^2 (Figure 23). This ratio is easily used in designing packages. For example, if a company wished to develop a 100 gram fruit pack and the machines could handle 0.5 to 2 mil thickness of LDPE, the film dimensions would therefore have to fall within the range of 225 cm^2 to 899 cm^2 to avoid the risk of fermentation.

Ratio 3.575E-07 and 2E-07 were chosen to validate the model at 0, 3, 5, 10, and 12C. The package pouches were designed for surface area, thickness and fruit weight according to the predicted ratio. $p_i^{O_2}$ of packages were measured and plotted as a function of temperature (Figure 24). The data points were reasonably close to the predicted value (represented by the solid line). However, there were some packages that were eliminated due to holes in package as determined by an elevated RQ at steady-state. More packages at each temperature (0 to 15C) should be tested and a statistical evaluation performed for a more through validation of the model.

Another concern for apple slices package is the package dimension and design. The primary package needs to be strong enough to prevent the damage from transportation and distribution that can happen after packing or before consuming. This design should be appropriate for the process of packing and handling.

There are many kinds of polymer film available in the market that can be used for MAP of fresh produce. If company wants to design package that has surface area 120 cm^2 exposed to atmosphere and contain 0.1 kg (6 or 7 pieces of 2-3 width wedge), they model can be used to predict the range of film thicknesses to be used (Figure 25) to maintain aerobic conditions between 0C and 15C. Among these polymers, Saran has a high Ep^{O_2}, but low P_{O_2} so it can achieve a large range of aerobic $p_i^{O_2}$. However P_{O_2} is very low, so film thickness must be extremely thin. Since machining has the limitation that the thinnest film that they can produce is 0.4 mil (Steve Jenkins, Dow Chemical, Midland, personal communication) Saran use is not an option. Moreover, a thin monolayer film may not provide enough strength for

the package. Film that has low P_{O_2}, for example LDPE (P_{O_2} = 8.85E-09 mmol·cm·cm^{-2}·h^{-1}·kPa^{-1}) or lower, can not be used for product apple slices in this designed package.

Affinity 1140, an experimental film for Dow Chemical company, is a new LDPE formulation having precisely controlled frequencies of aliphatic side chains of specific lengths that has P_{O_2} about 3 times higher than that of LDPE with the similar Ep^{O_2}. The elevated P_{O_2} allows the use of greater film thickness than standard LDPE. For example, 1 mil film will yield p^{O_2} of 6 kPa at 0C (film area 120 cm^2 and apple slices 0.1 kg) and will safely remain aerobic until 15C. Affinity 1140 has also has the advantages of being polyolefin which include high tear strength, high resistance to chemical degradation, good water barrier, high ratio of P_{CO_2}/P_{O_2} and good heat seal, with higher O_2 and CO_2 permeability (Appendix C).

Decay is one of the major obstacles remaining to the commercial production of apple slices. Decay was observed on the apple slices in packages within 5 days at 15C and 8 days at 10C. Maximizing this duration will probably be a major goal marketing to provide sufficient retail and home shelf life after distribution. Types of microorganisms at each temperature can also be studied.

Decay control can be achieved through the application of chemical food additives, irradiation or fungicide however, consumer may prefer the use of natural preservative compounds. Leepipatanawit (personal communication) is attempting to use the volatile antifungal compound, 2-nonanone released by red raspberries and strawberries during ripening (Vaughn et al., 1993) to control decay in apple slices package. Levels of release of volatile antifungal compounds to maintain target headspace concentrations can be modeled. An extension of the present model can be developed which predicts release rate requirements for 2 nonanone or other compound on the film recommendation generated by the present $p_i^{O_2}$ model.

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Table 1: Weight of fruit(gram), thickness (mils), and surface area (cm^2) of pouches were used to generated range of O_2 partial pressure inside the package at 0, 5, 10, and 15C, calculated from equation 9.

Temperature	0C			5C		
pkg	Weight(g)	Thickness(mil*)	Area(cm^2)	Weight(g)	Thickness(mil)	Area(cm^2)
1	475	4	800	578	4	800
2	232	4	800	432	4	800
3	150	4	800	248	4	800
4	107	4	800	118	4	800
5	90	4	800	87	4	800
6	72	4	800	66	4	800
7	54	4	800	48	4	800
8	38	4	800	74	3	800
9	53	3	800	54	3	800
10	42	3	800	40	3	800
11	47	3	1250	30	3	800
12	27	3	1250	19	3	800

Temperature	10C			15C		
pkg	Weight(g)	Thickness(mil)	Area(cm^2)	Weight(g)	Thickness(mil)	Area(cm^2)
1	437	4	800	236	4	800
2	250	4	800	115	4	800
3	139	4	800	76	4	800
4	80	4	800	53	4	800
5	61	4	800	40	4	800
6	90	3	800	73	3	800
7	67	3	800	56	3	800
8	50	3	800	46	3	800
9	36	3	800	52	3	1250
10	27	3	800	35	3	1250
11	31	3	800	28	3	1250
12	20	3	800	21	3	1250

*1 mil = 0.00254 cm

Table 2: Effect of O_2, CO_2 and time on 'L', 'a', and 'b' values of slice apple tissue of cultivar 'Ida Red' held at 5C. The values of 'L', 'a', and 'b' immediately after cutting were 84.98, 2.55, and 14.90, respectively.

O_2 (%)	'L' value	'a' value	'b' value
1	78.236a	2.38b	23.78a
20	78.05a	2.37a	22.95b
CO_2 (%)	'L' value	'a' value	'b' value
0.03	77.22b	2.35b	24.06a
5	78.47a	2.39a	22.91c
10	78.36a	2.38a	23.27bc
15	78.36a	2.38a	23.70ab
20	78.31a	2.38a	22.88c
Day	'L' value	'a' value	'b' value
1	78.75ba	2.39ba	22.95b
2	77.82cd	2.37cd	22.95b
3	78.75a	2.40a	23.08b
5	78.54ba	2.39ab	23.04b
7	78.26cb	2.38bc	23.16b
10	77.26d	2.35d	24.01a
14	77.26d	2.36d	24.33a

Table 3: Effect of CO_2 concentration on CO_2 injury of apple slices rating from 1-4 scale (1=none, 2=slight, 3=moderate, and 4=severe) on cultivar 'Ida Red' held at 5C.

CO_2 (%)	CO_2 injury
0	1.00c
5	1.00c
10	2.00ba
15	1.75b
20	2.63a

Table 4: Lower O_2 limit for apple slices held at 0, 5,10, and 15C. The p_{O_2} were estimated from the curve describing the relationship between RQ and O_2 partial pressure (Figure 13) O_2 partial pressure below which a sharp increase of RQ took place.

Temperature (°C)	Lower O_2 limit (kPa)
0	0.2
5	0.25
10	0.3
15	0.4

Table 5: Values for a, b, c, m, and n in equation 17 describing the relationship between O_2 uptake and O_2 partial pressure inside the package were fitted simultaneously for 0, 5, 10, and 15C and standard error calculated by using SAS.

Parameters	Estimate	Asymptotic Std. Error
a	0.602	0.257
b	0.069	0.019
c	-0.377	0.264
m	0.050	0.033
n	0.662	0.398

Table 6: V_{max} and K_T for 0, 5, 10, and 15C calculated from the fitted model; $V_{max} = 0.602e^{0.069T}-0.377$ mmol kg^{-1} h^{-1} and $K_T = 0.05T + 0.662$ kPa.

Temperature (°C)	V_{max} (mmol kg^{-1} h^{-1})	K_T (kPa)
0	0.23	0.66
5	0.50	0.91
10	0.80	1.16
15	1.32	1.41

Figure 1: Effect of time on the 'L' value, 'a' value, and 'b' value of sliced apple tissue of cultivar 'Ida Red' at 0C (closed circle) and cultivar 'NY674' at room temperature (23C) (open circle). Data were fitted with exponential $y = ae^{bx}+c$.

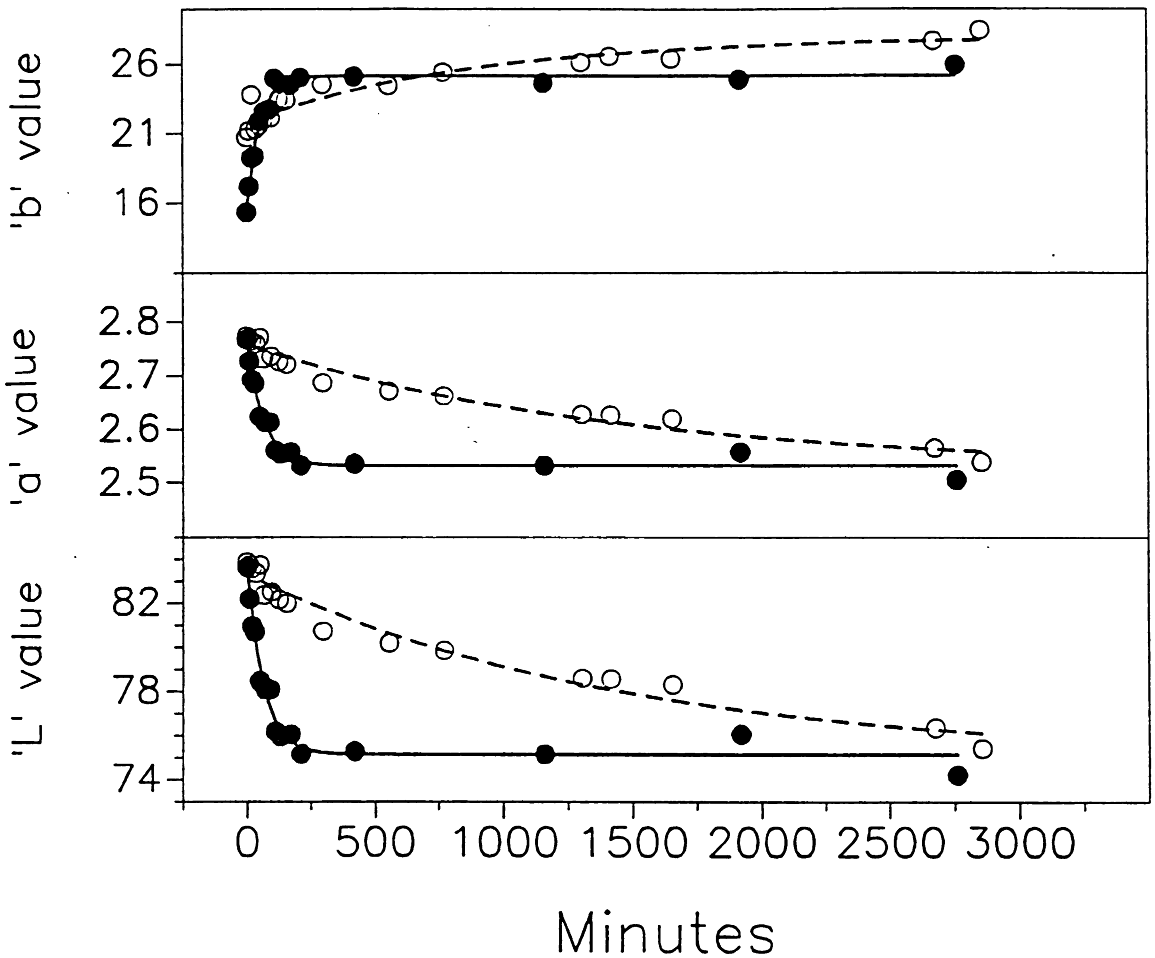

'b' value
26
21
16
'a' value
2.8
2.7
2.6
2.5
'L' value
82
78
74
0
500
1000
1500
2000
2500
3000
Minutes

Figure 2. Effect of time and temperature on the 'L' value of sliced apple tissue of the cultivar 'Ida Red' in air. Data were fitted with exponential equation $y=ae^{bx}+c$.

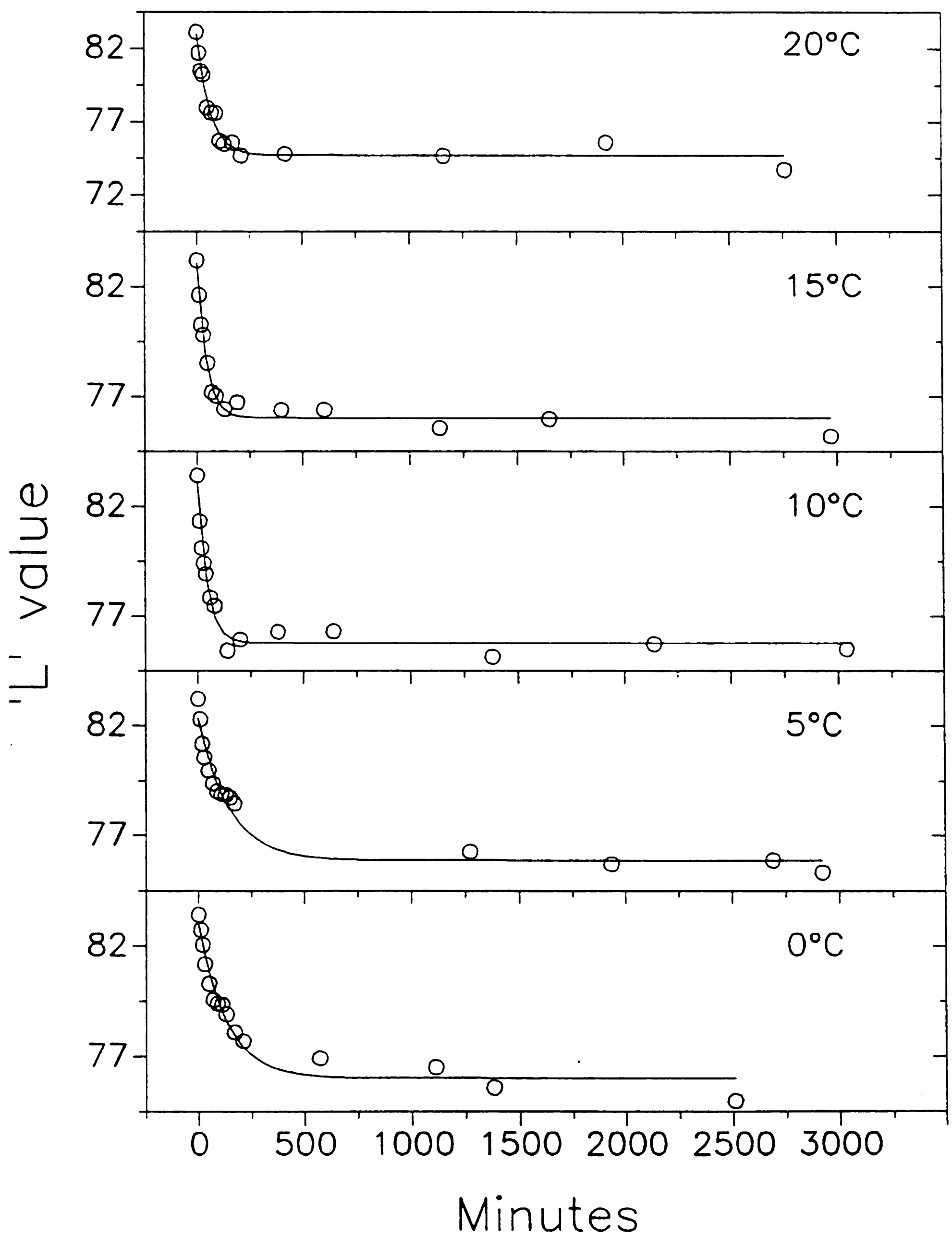

20°C
15°C
10°C
5°C
0°C
82
77
72
'L' value
0
500
1000
1500
2000
2500
3000
Minutes

Figure 3. Effect of time and temperature on the 'a' value of sliced apple tissue of the cultivar 'Ida Red' in air. Data were fitted with exponential equation $y=ae^{bx}+c$

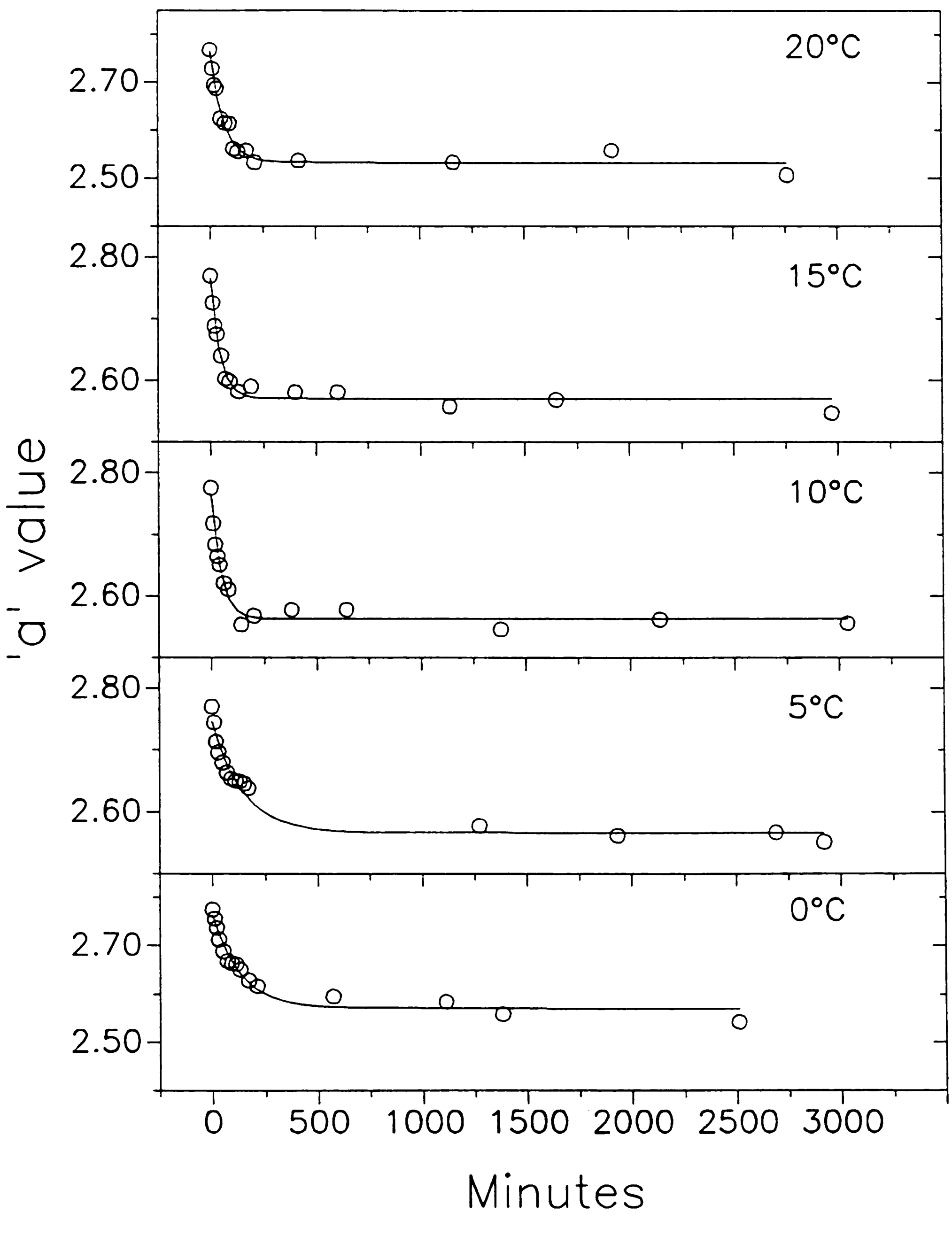

20°C
15°C
10°C
5°C
0°C
2.70
2.50
2.80
2.60
'a' value
0
500
1000
1500
2000
2500
3000
Minutes

Figure 4. Effect of time and temperature on the 'b' value of sliced apple tissue of the cultivar 'Ida Red' in air. Data were fitted with exponential equation $y=ae^{bx}+c$

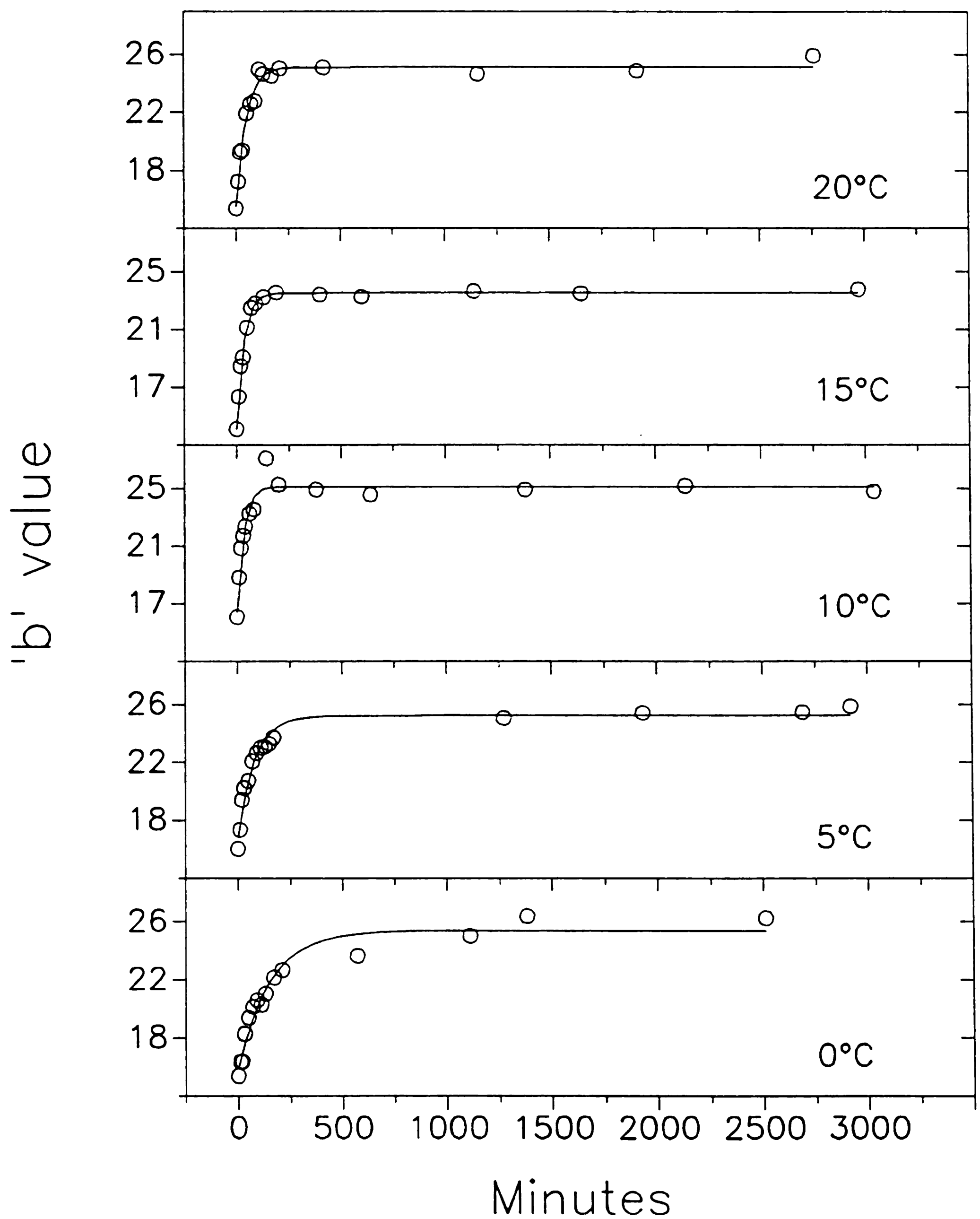
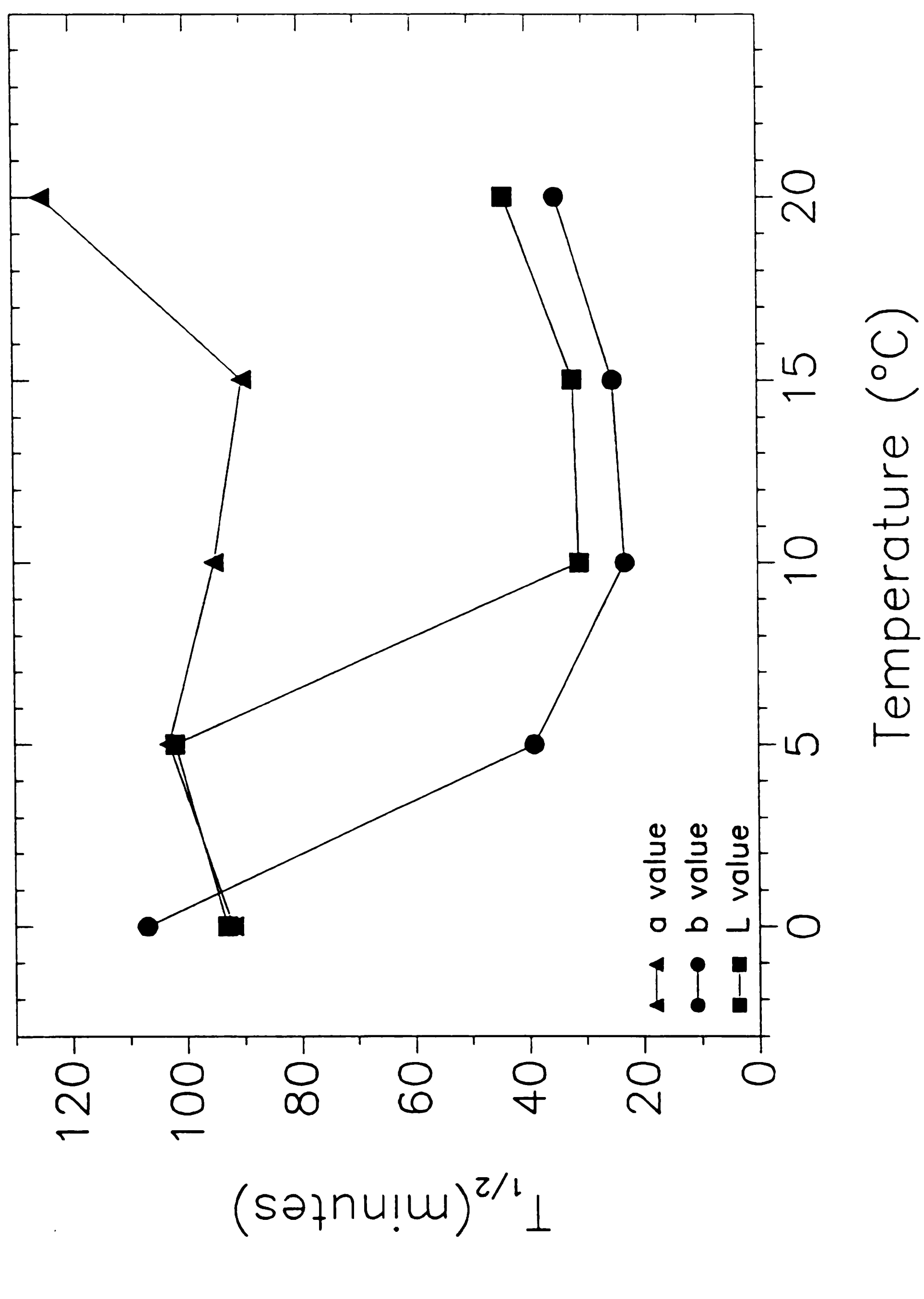
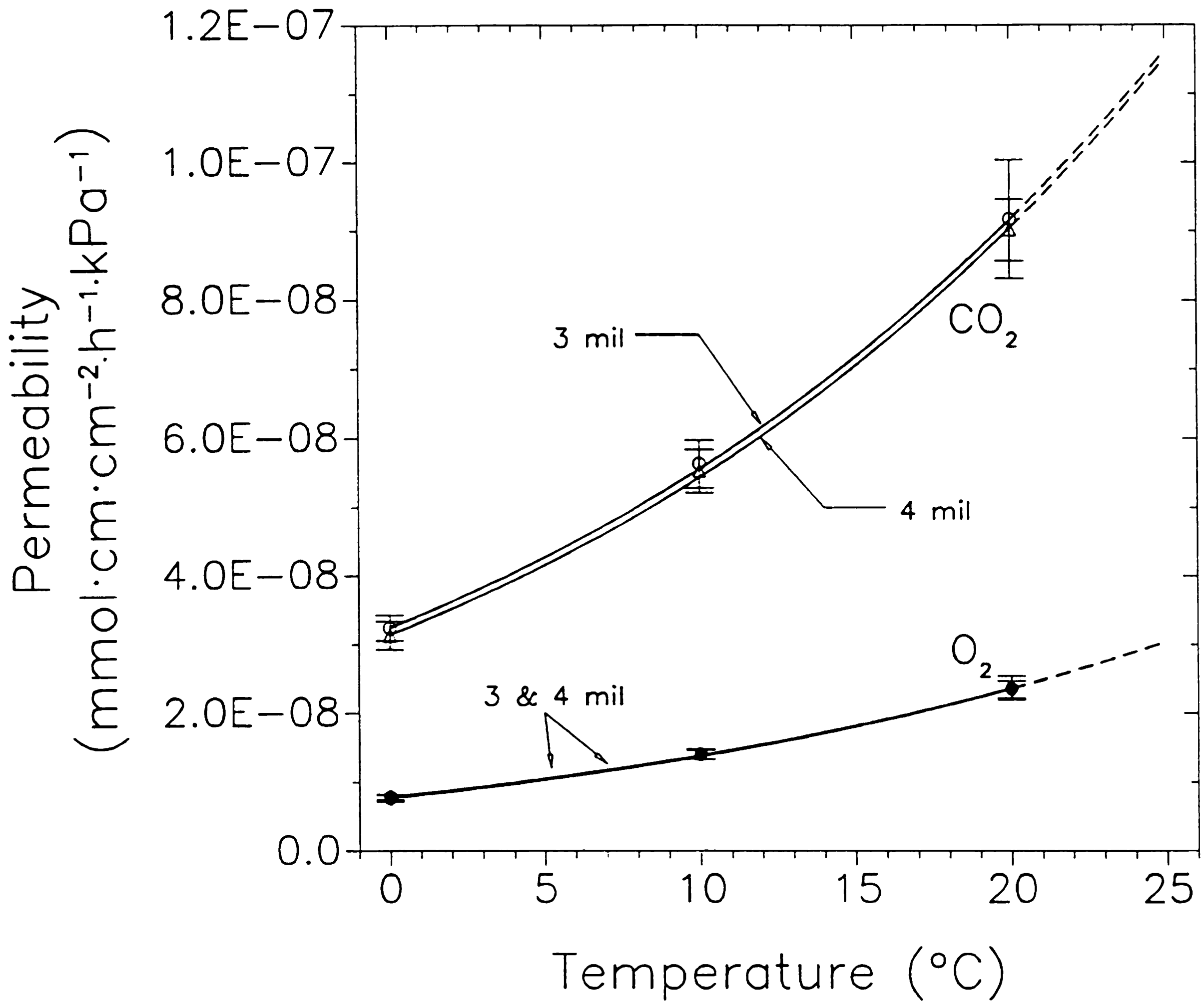

'b' value
Minutes
20°C
15°C
10°C
5°C
0°C
26
22
18
25
21
17
0
500
1000
1500
2000
2500
3000

Figure 5. The time ($T_{1/2}$) required for 'L', 'a' and 'b' values to reach half way between initial and final value of sliced apple tissue of cultivar 'Ida Red' in air from using the best fit curves of Figures 2, 3, and 4.



$T_{1/2}$(minutes)
Temperature (°C)
a value
b value
L value
0
20
40
60
80
100
120
0
5
10
15
20

Figure 6. Effect of temperature on film permeability to O_2 and CO_2 for 3 mil and 4 mil (0.00762 cm and 0.01016 cm) LDPE films used in packaging



1.2E-07
1.0E-07
8.0E-08
6.0E-08
4.0E-08
2.0E-08
0.0
Permeability
(mmol·cm·cm⁻²·h⁻¹·kPa⁻¹)
0
5
10
15
20
25
Temperature (°C)
CO2
O2
3 mil
4 mil
3 & 4 mil

Figure 7. Arrhenius plot of O_2 and CO_2 permeability for 3 and 4 mil LDPE film used in packaging experiments with r^2 = 0.99.

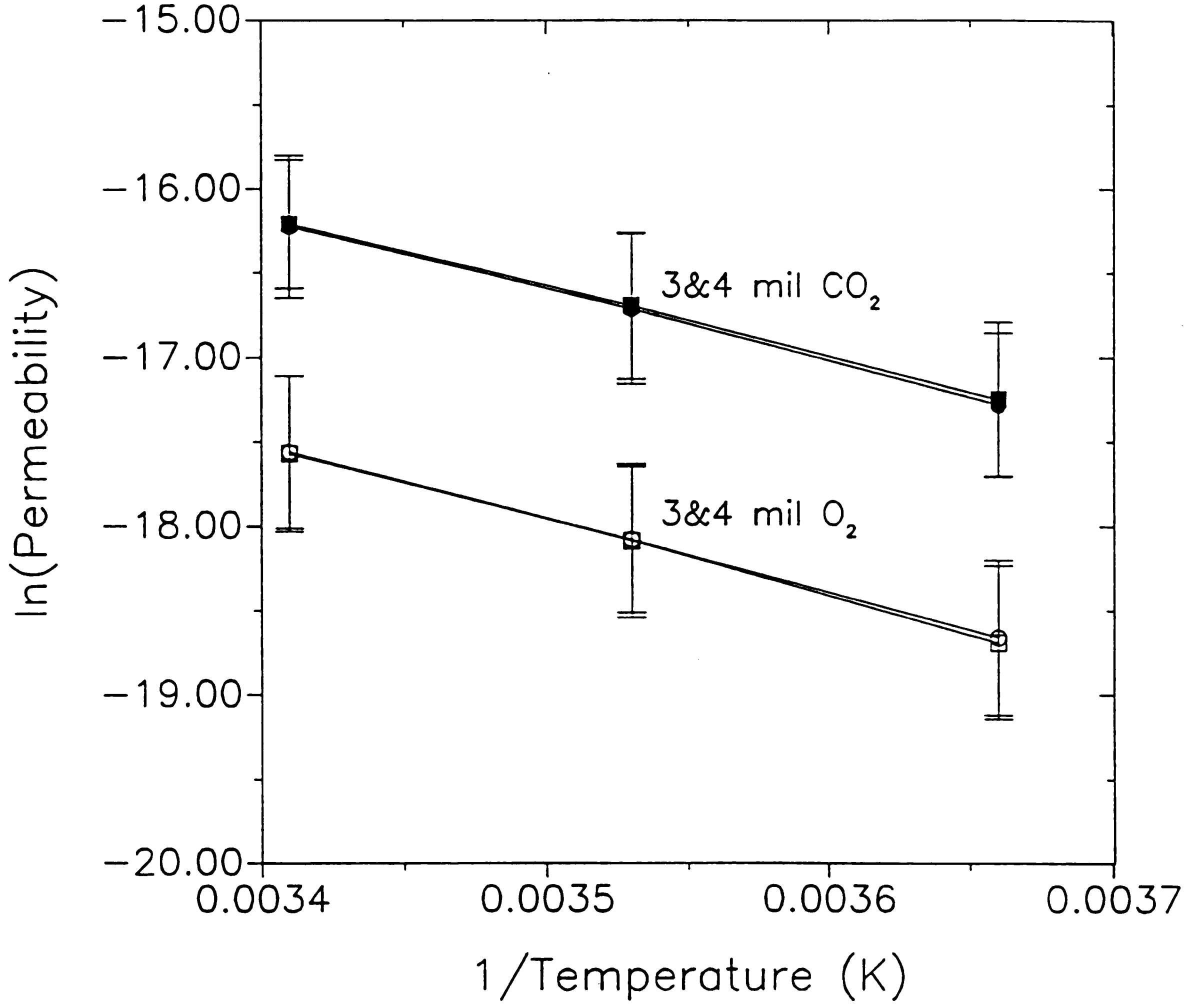
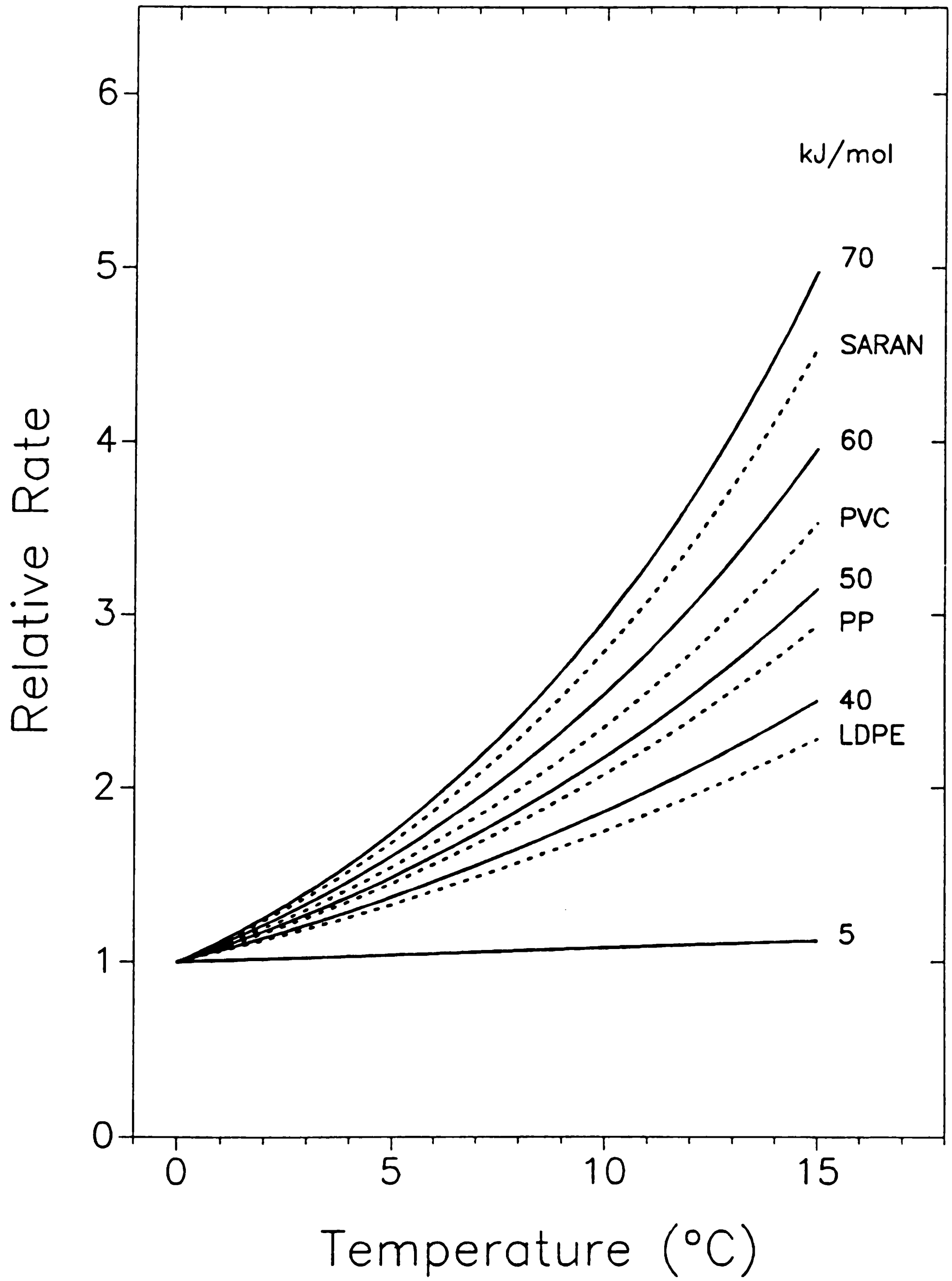

-15.00
-16.00
-17.00
-18.00
-19.00
-20.00
ln(Permeability)
3&4 mil CO_2
3&4 mil O_2
0.0034
0.0035
0.0036
0.0037
1/Temperature (K)

Figure 8. Effect of temperature on relative rate for rates of reaction possesing range of activation energies including those of the P_{O_2} of some films (Saran, PVC, PP, and LDPE). Data were generated using the Arrhenius equation (equation 5) and before transformed to a relative rate of 1 at 0C.



Relative Rate
Temperature (°C)
kJ/mol
70
SARAN
60
PVC
50
PP
40
LDPE
5
0
1
2
3
4
5
6
0
5
10
15

Figure 9. The effects of steady state O_2 partial pressure and storage temperatures (0, 5, 10, and 15C) on the rate of O_2 uptake of apple slices cultivar 'NY674' in sealed LDPE packages.

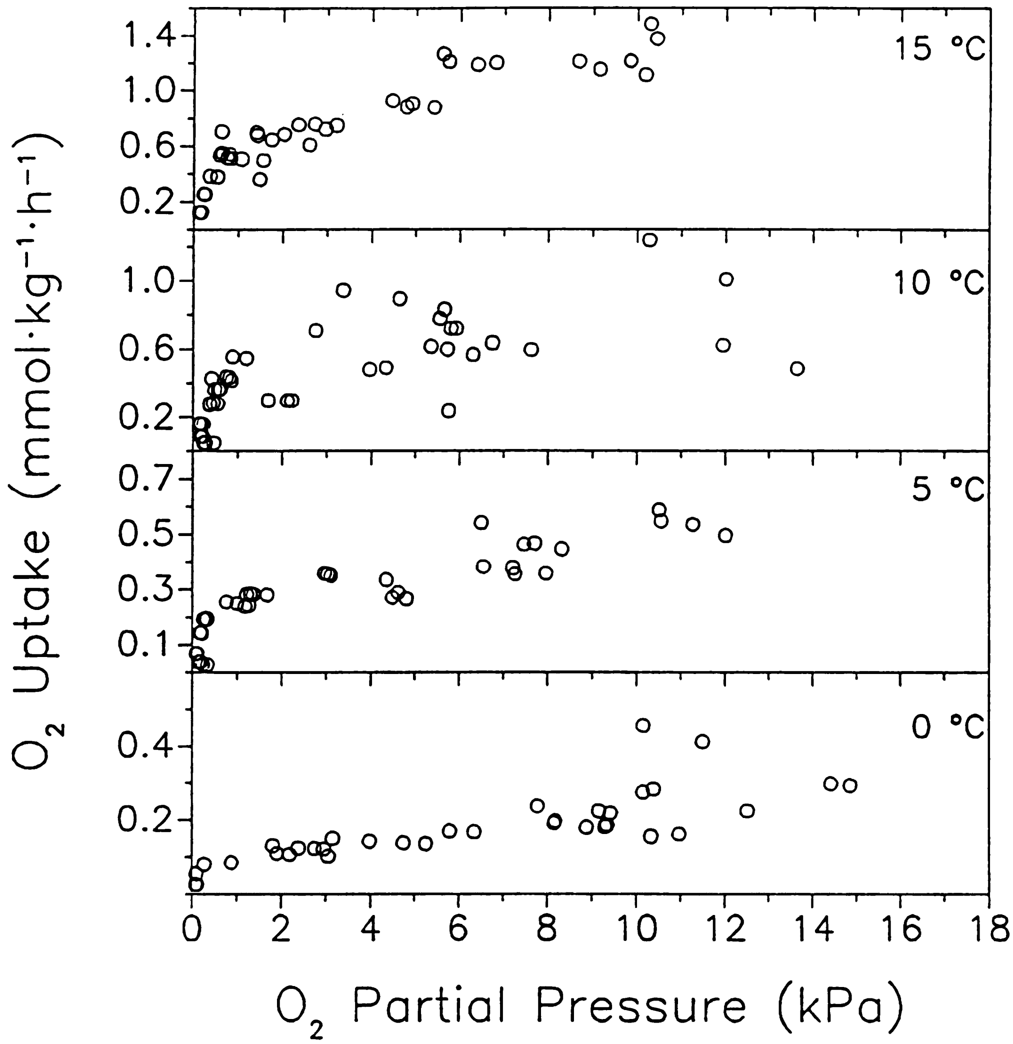
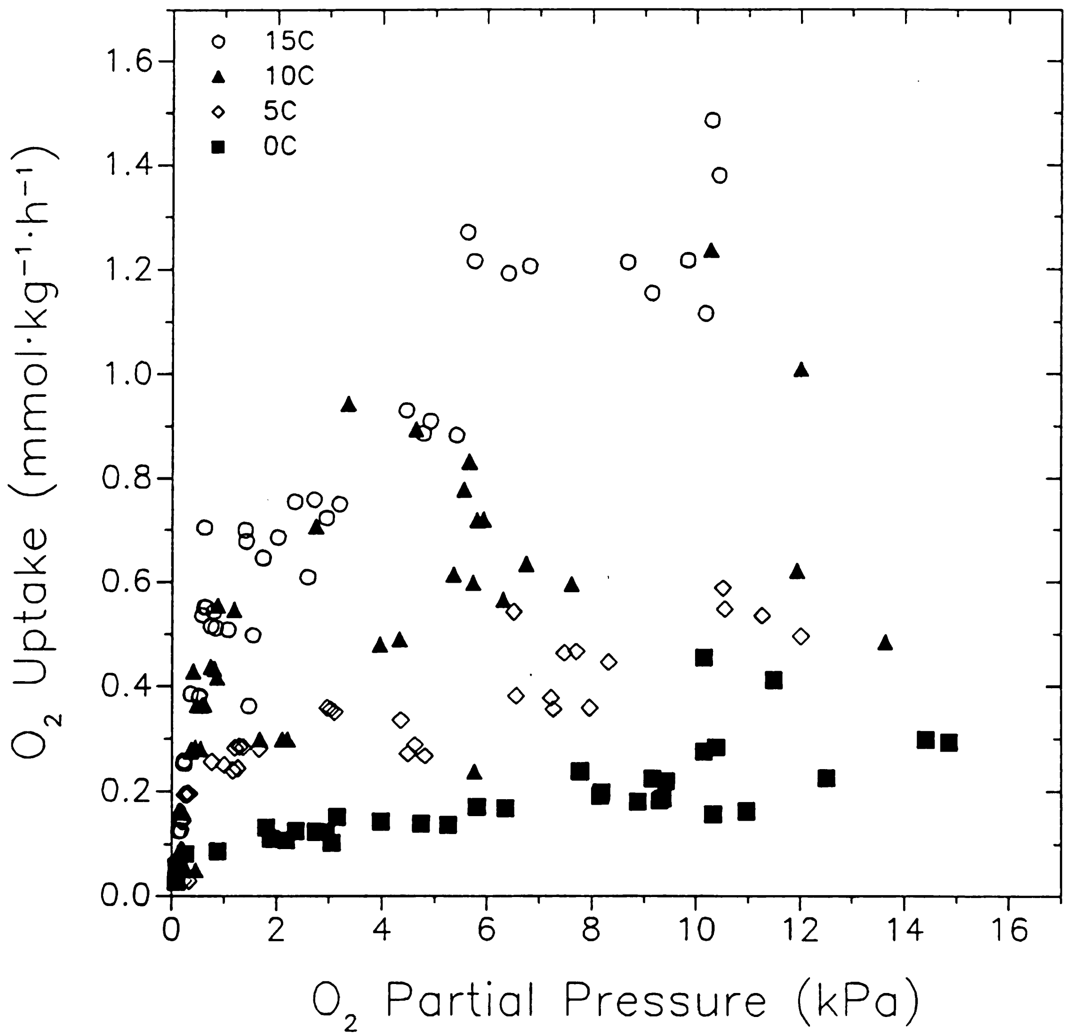

15 °C
10 °C
5 °C
0 °C
1.4
1.0
0.6
0.2
1.0
0.6
0.2
0.7
0.5
0.3
0.1
0.4
0.2
0 2 4 6 8 10 12 14 16 18
O_2 Uptake (mmol·kg⁻¹·h⁻¹)
O_2 Partial Pressure (kPa)

Figure 10. Composite curves demonstrating the effects of steady state O_2 partial pressure and storage temperatures (0, 5, 10, and 15C) on the rate of O_2 uptake of apple slices cultivar 'NY674' in sealed LDPE packages.



15C
10C
5C
0C
O_2 Uptake (mmol·kg⁻¹·h⁻¹)
O_2 Partial Pressure (kPa)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0
2
4
6
8
10
12
14
16

Figure 11. Effect of steady state O_2 partial pressure and storage temperatures (0, 5, 10, and 15C) on the CO_2 production of apple slices cultivar 'NY674' in sealed LDPE packages.

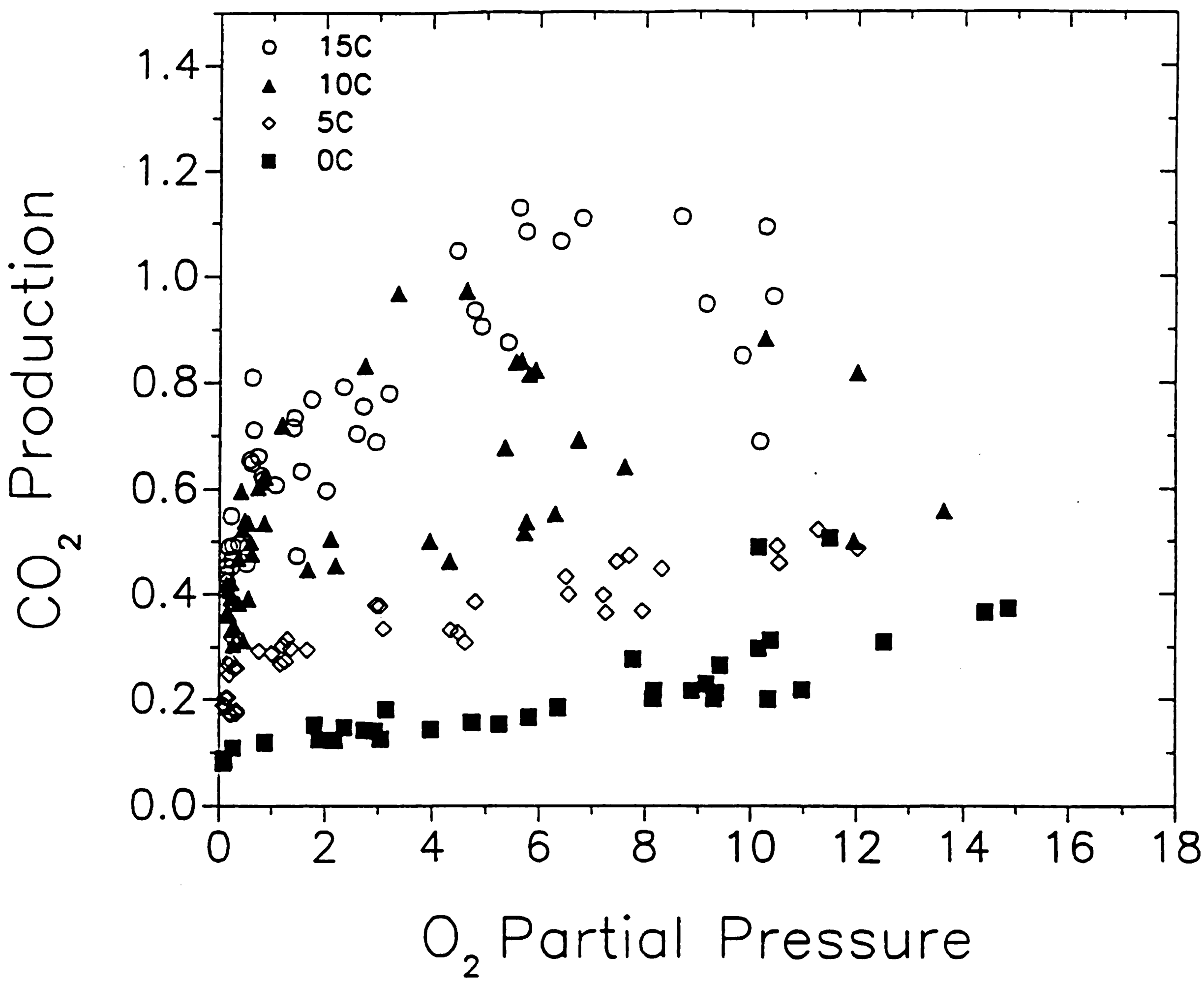

15C
10C
5C
0C
CO_2 Production
O_2 Partial Pressure
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
2
4
6
8
10
12
14
16
18

Figure 12. Effect of steady-state O_2 partial pressure on the respiratory quotient of apple slices in sealed LDPE packages held at 0, 5, 10, and 15C.

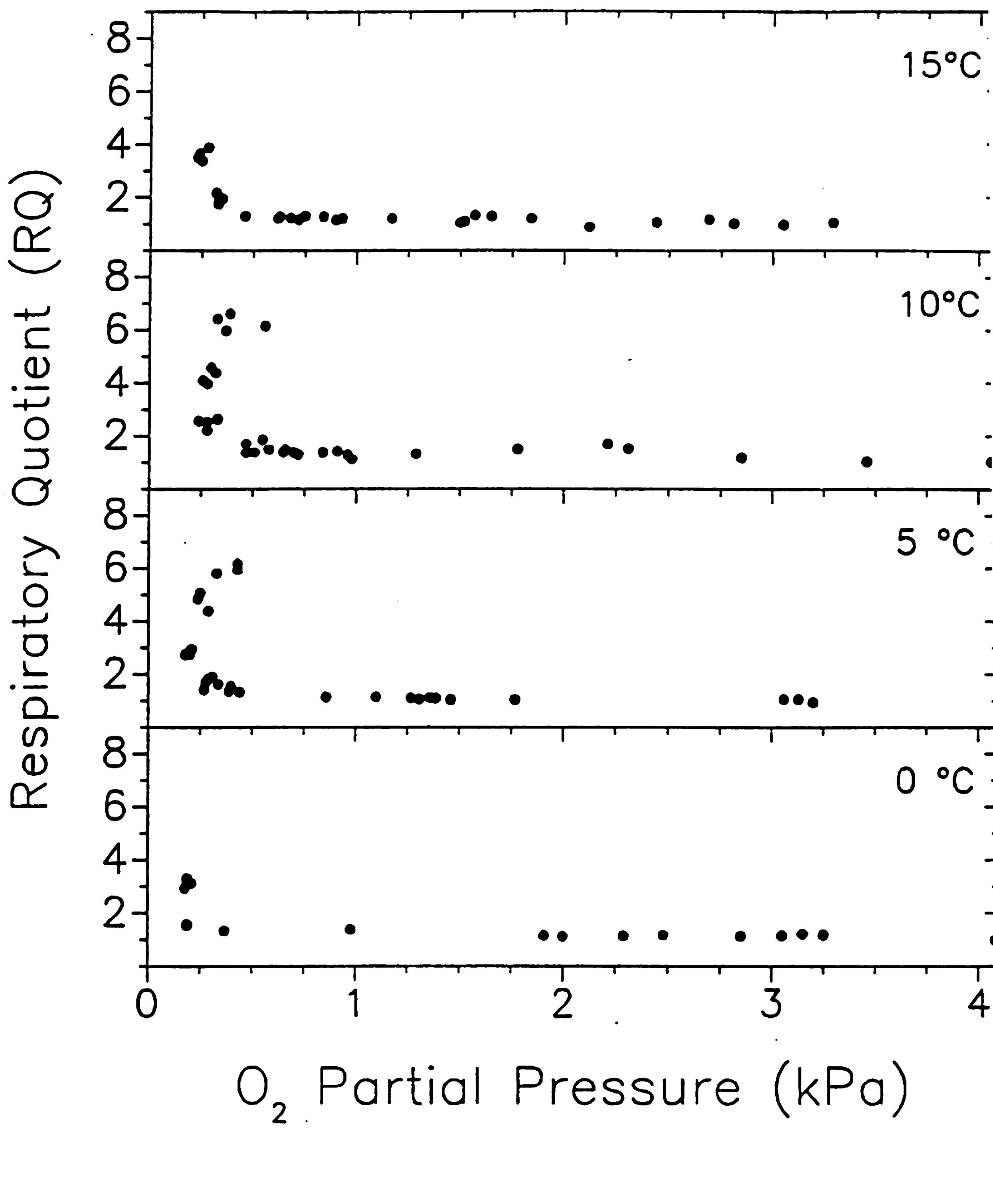

15°C
10°C
5 °C
0 °C
Respiratory Quotient (RQ)
O2 Partial Pressure (kPa)
8
6
4
2
0
1
2
3
4

Figure 13. Relationship between headspace ethanol vapor partial pressure and the respiratory quotient of apple slices in LDPE sealed packages at four temperatures.

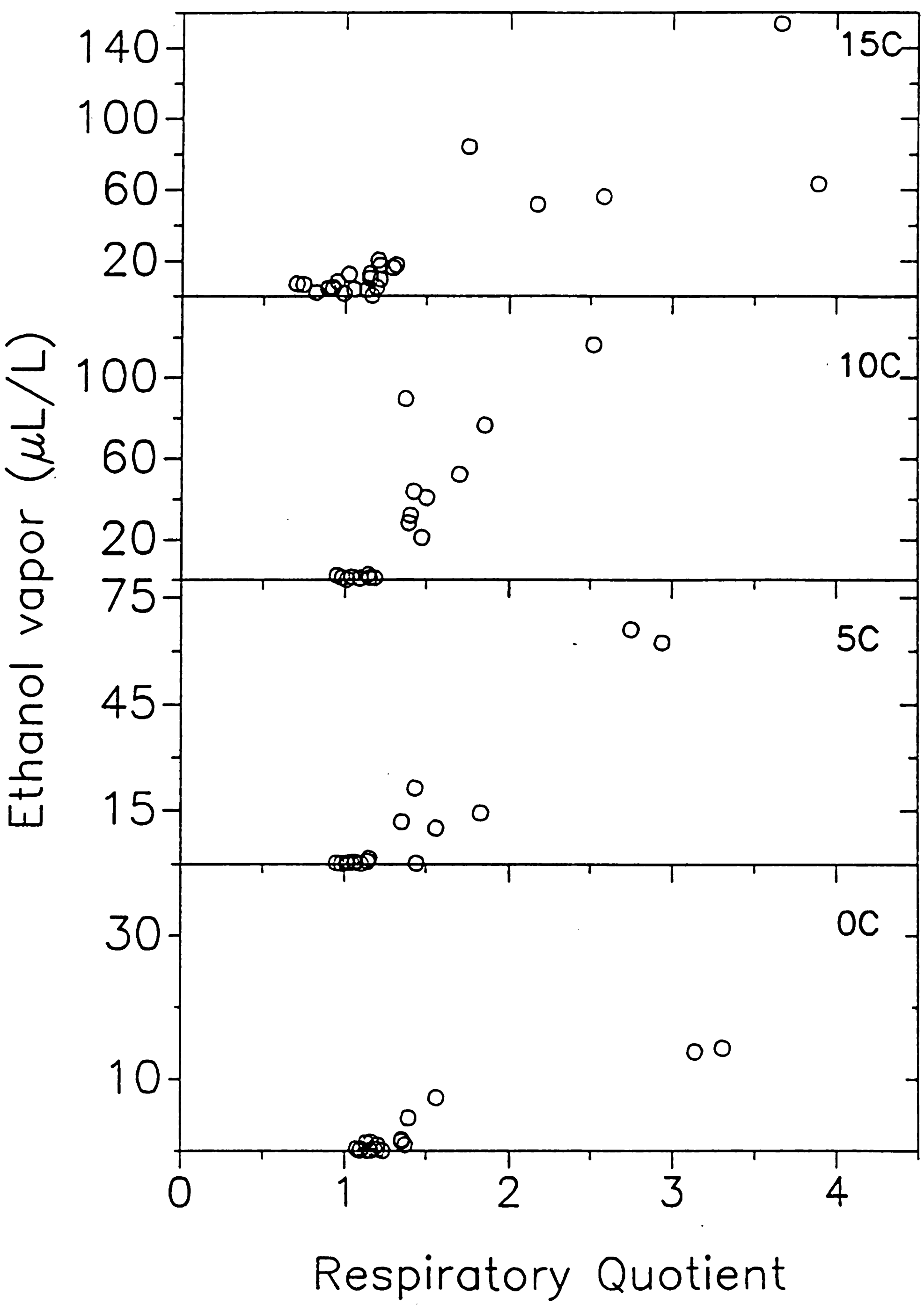
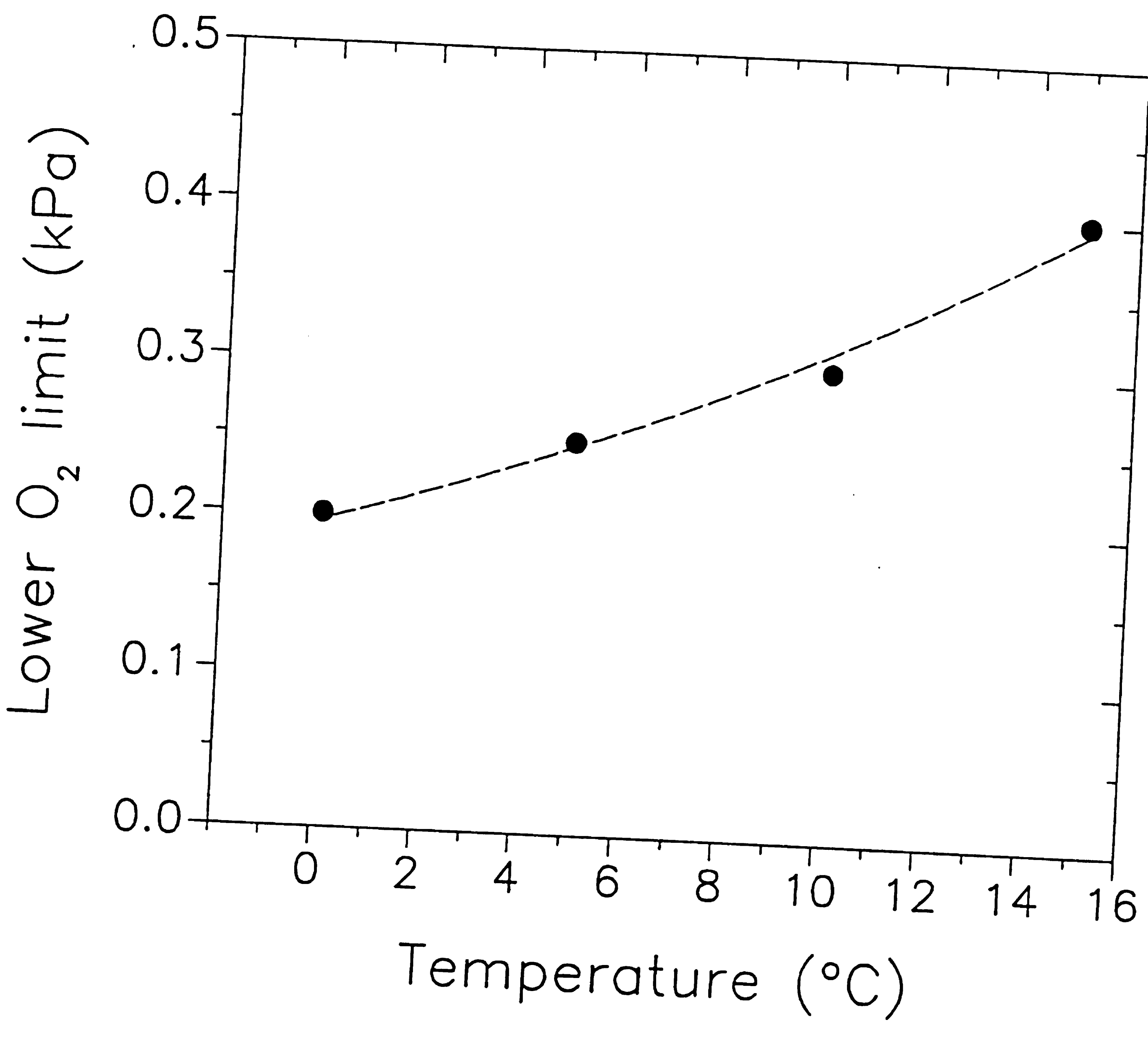

15C
10C
5C
0C
140
100
60
20
100
60
20
75
45
15
30
10
0
1
2
3
4
Ethanol vapor (µL/L)
Respiratory Quotient

Figure 14. Lower O_2 limit of apple slices cultivar 'NY674' over a range of temperatures as determined by RQ breakpoint.



Lower O_2 limit (kPa)
0.5
0.4
0.3
0.2
0.1
0.0
0
2
4
6
8
10
12
14
16
Temperature (°C)

Figure 15. Effect of steady state O_2 partial pressure and storage temperatuer on the rate of O_2 uptake of apple slices cultivar 'NY674' in sealed LDPE packages. Curves are depict the best-fit respiratory model for 0, 5, 10, and 15C (equation 14).

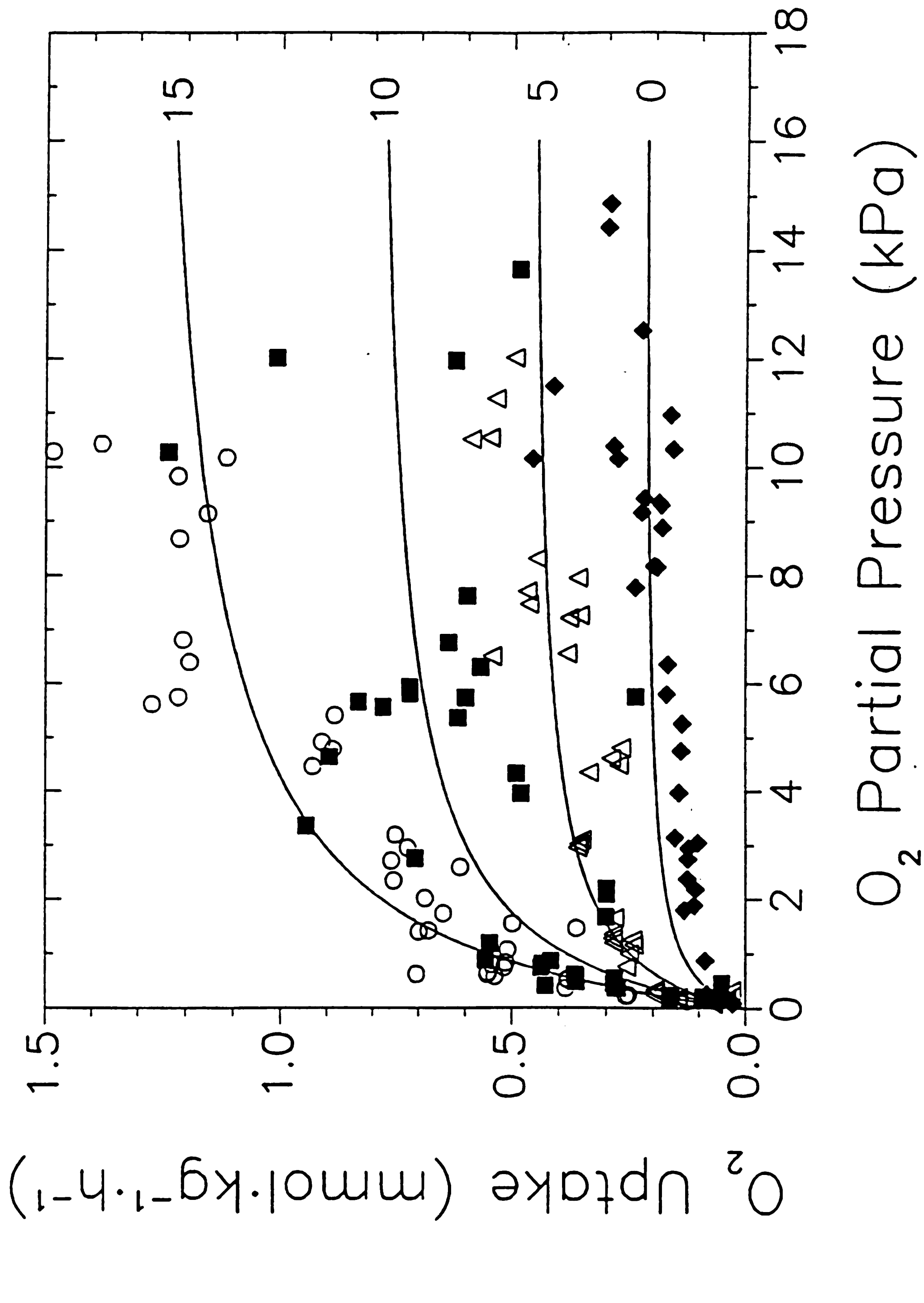
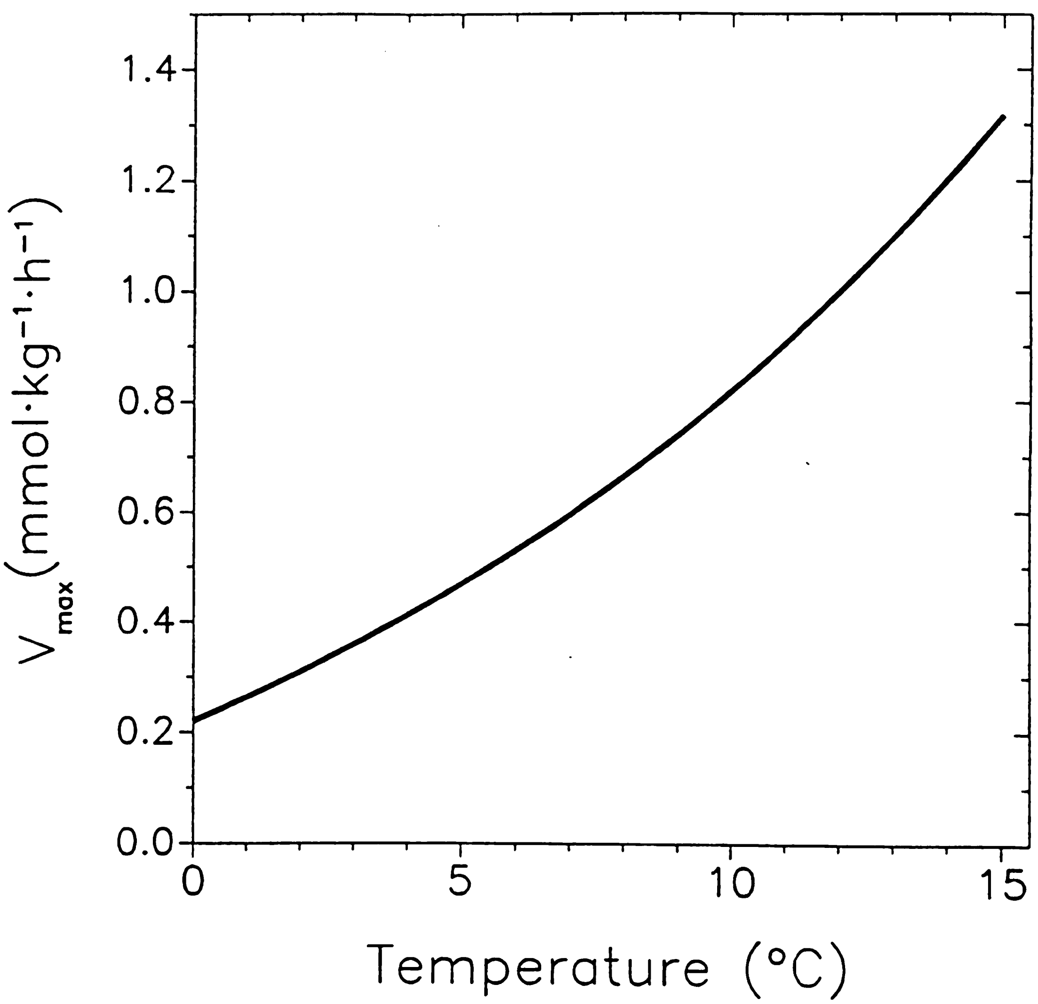

O2 Uptake (mmol·kg−1·h−1)
0.0
0.5
1.0
1.5
O2 Partial Pressure (kPa)
0
2
4
6
8
10
12
14
16
18
15
10
5
0

Figure 16. Effect of temperature on for V_{max} as determined from respiratory model with values for a, b, and c as given in Table 5.



V_{max} (mmol·kg⁻¹·h⁻¹)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
5
10
15
Temperature (°C)

Figure 17. Effect of temperature on for K_T as determined from respiratory model with values for m and n as given in Table 5.

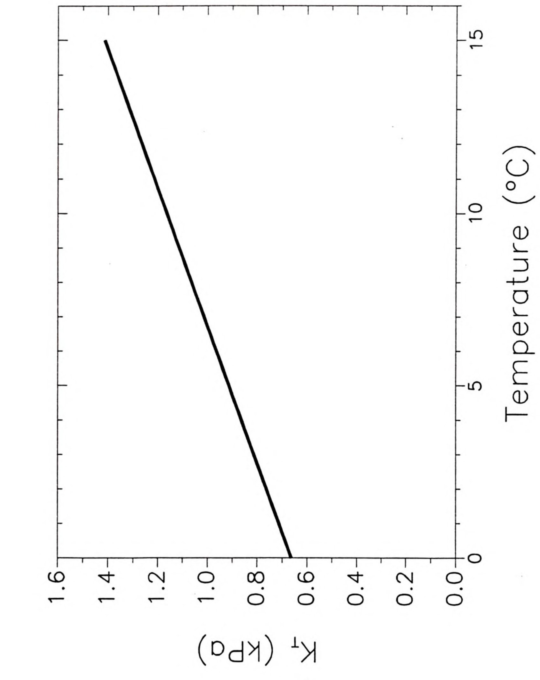

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
K_T (kPa)
0
5
10
15
Temperature (°C)

Figure 18. Effect of temperature on the rate of O_2 uptake over a range of O_2 partial pressure for apple slices. Data were obtained from the fitted O_2 partial pressure model (equation 18).

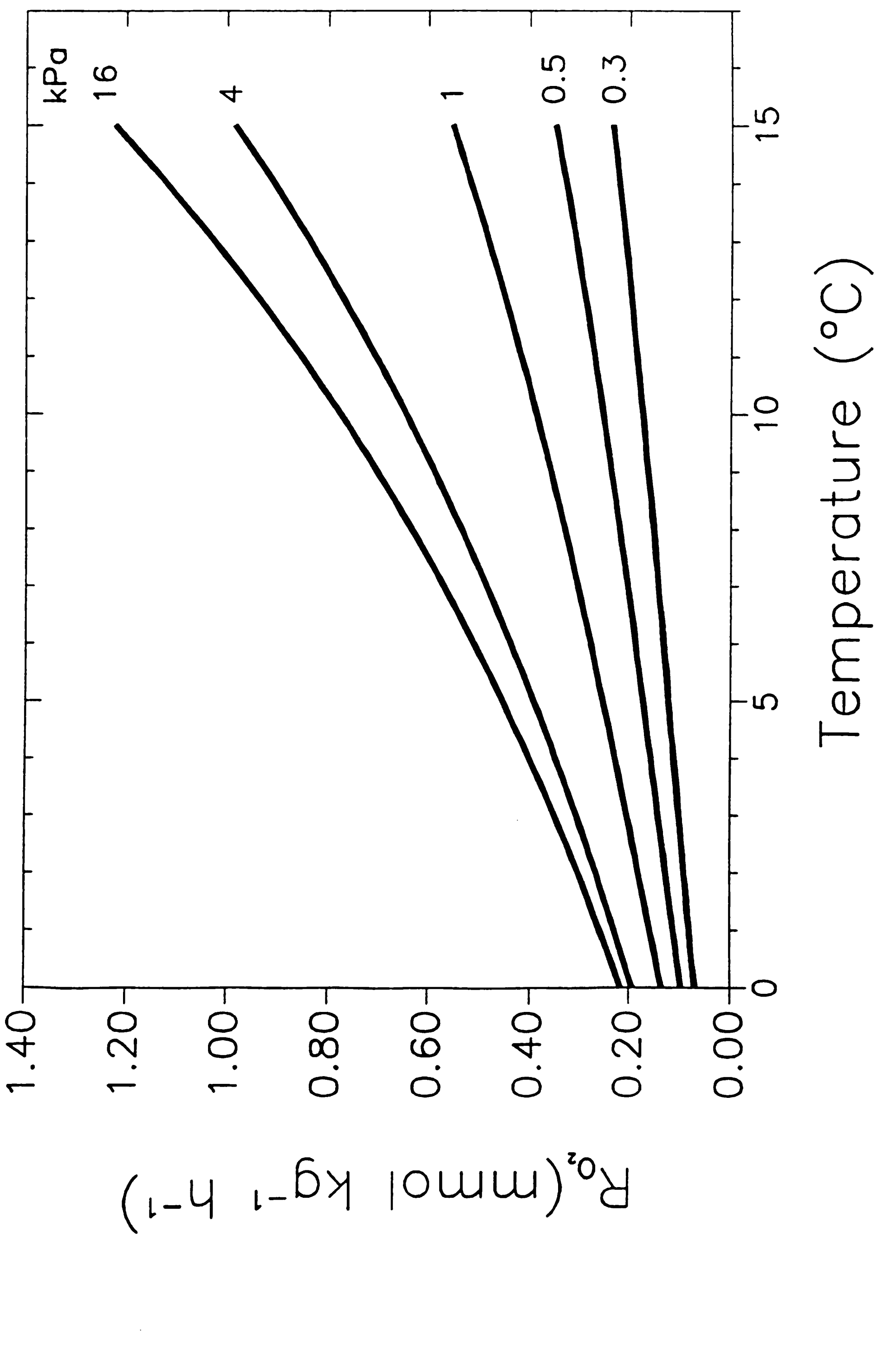
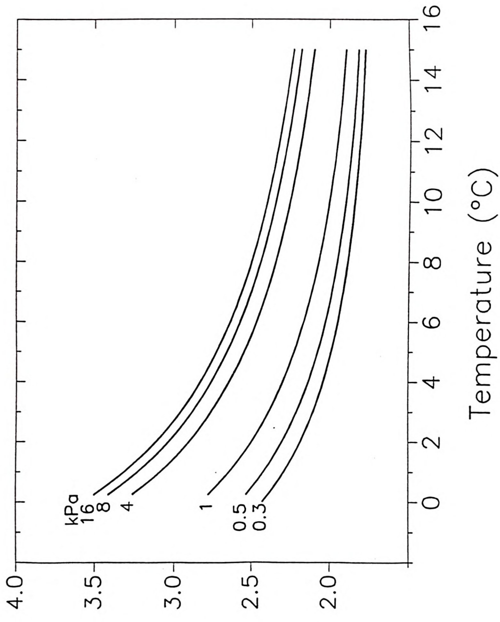

kPa
16
4
1
0.5
0.3
Temperature (°C)
0
5
10
15
R_{O_2}(mmol kg⁻¹ h⁻¹)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00

Figure 19. Effect of temperature and O_2 partial pressure on Q_{10} (the rate of O_2 uptake at temperature T+10C devided by rate of O_2 uptake at temperature TC) of apple slices in the sealed LDPE packages. Data were obtained from the fitted O_2 partial pressure model.



Q_{10}
4.0
3.5
3.0
2.5
2.0
kPa
16
8
4
1
0.5
0.3
0
2
4
6
8
10
12
14
16
Temperature (°C)

Figure 20. Predicted O_2 partial pressure changes in MA packages of sliced apple based on initial optimization to 0.6 kPa at 0C for films with various values for activation energy. Predicted O_2 partial pressure inside the package were generated using Equation 18 with appropriate substitutions from Equation 14. Film permeability was assumed to respond temperature as in Figure 8.

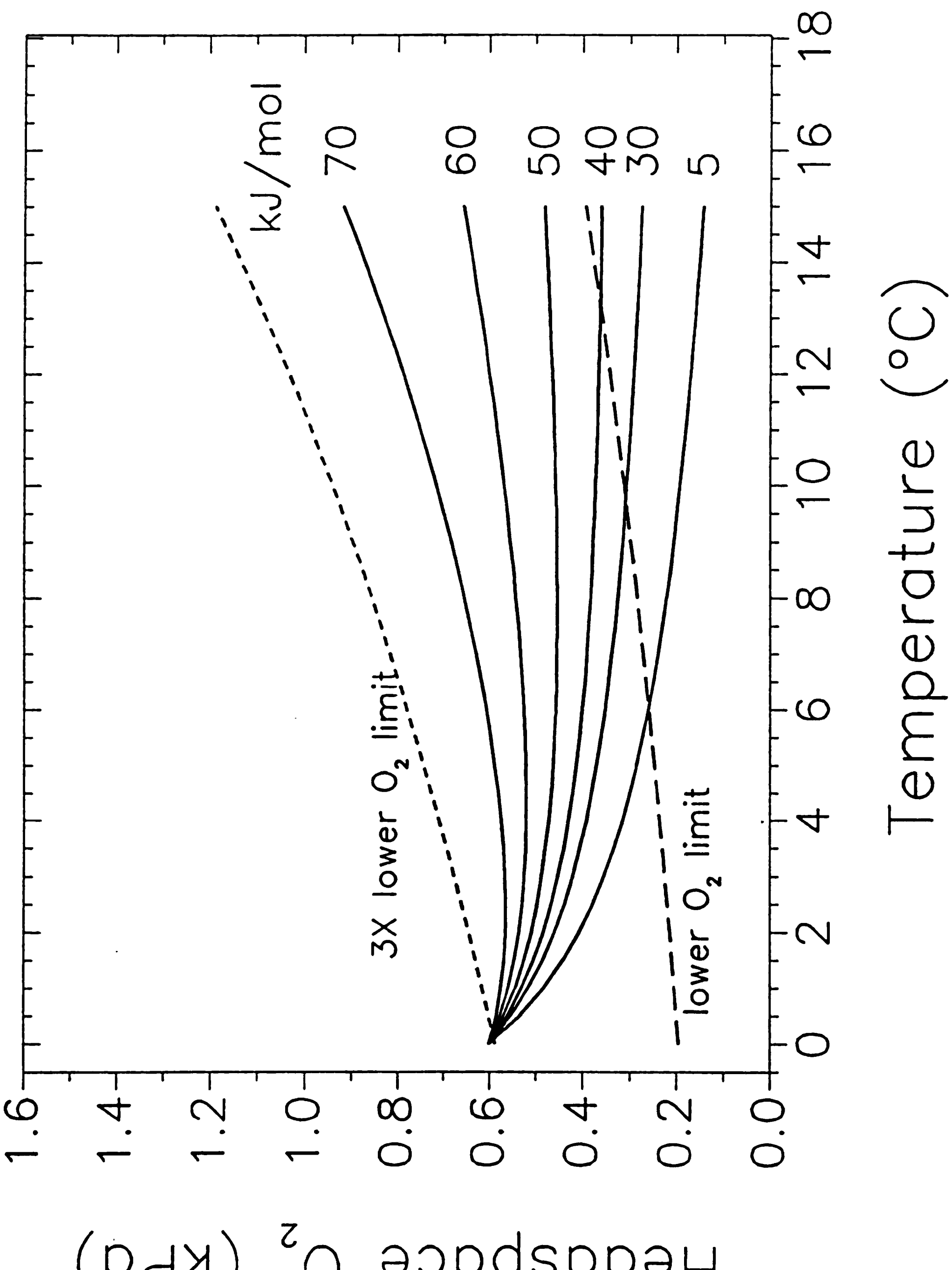
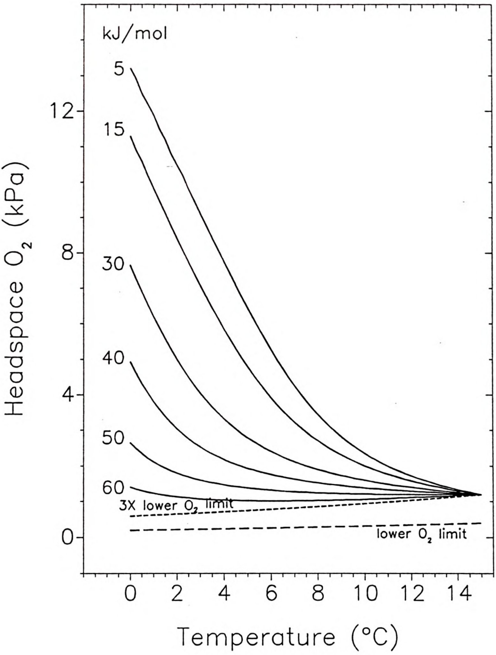

Headspace O_2 (kPa)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Temperature (°C)
0
2
4
6
8
10
12
14
16
18
kJ/mol
70
60
50
40
30
5
3X lower O_2 limit
lower O_2 limit

Figure 21. Predicted O_2 partial pressure changes in MA packages of sliced apple based on initial optimization to 1.2 kPa at 15C for films with different values for activation energy. Predicted O_2 partial pressure were generated using Equation 18 with appropriate substitutions from equation 14. Film permeability was assumed to respond temperature as in Figure 8.



kJ/mol
5
15
30
40
50
60
3X lower O2 limit
lower O2 limit
Headspace O2 (kPa)
Temperature (°C)
0
4
8
12
0
2
4
6
8
10
12
14

Figure 22. Effect of temperature on predicted O_2 partial pressure for packages of apple slices composed of LDPE having a range of thicknesses. Predictions were generated using equation 18 with appropriate substitutions from equation 14. 3-fold lower O_2 limit line was represents an exponential equation Lower O_2 limit= $0.587e^{0.047T}$ fitted to lower O_2 limit estimates Table 4.

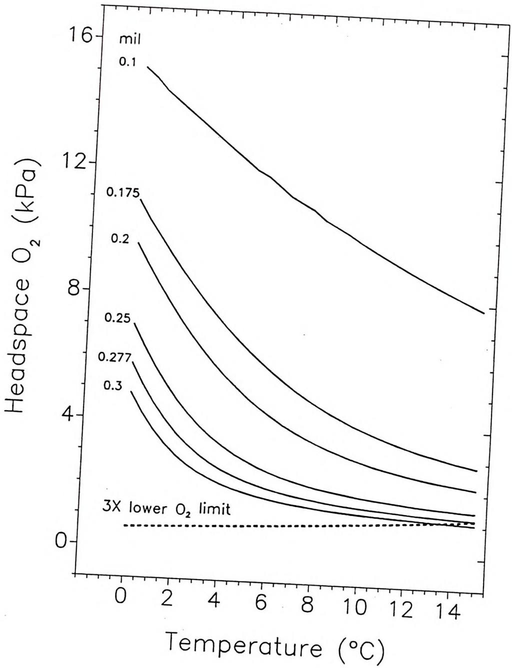
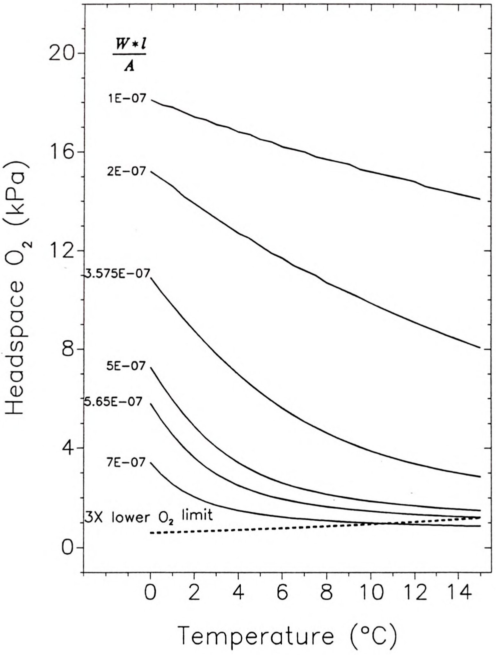
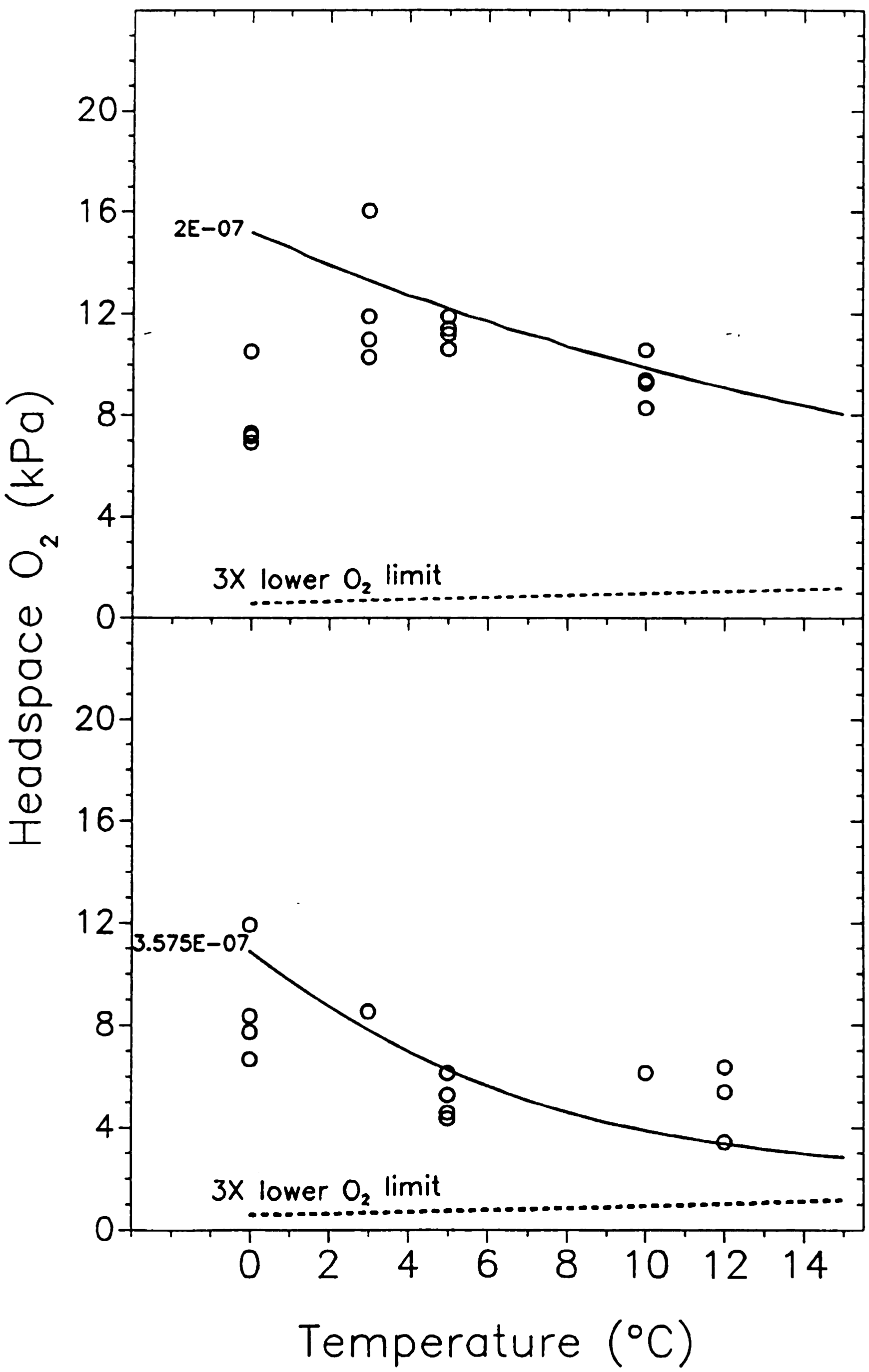

Headspace O2 (kPa)
16
12
8
4
0
mil
0.1
0.175
0.2
0.25
0.277
0.3
3X lower O2 limit
0
2
4
6
8
10
12
14
Temperature (°C)

Figure 23. Effect of temperature on predicted O_2 partial pressure for packages of apple slices composed of LDPE, posessing various ratios of W*l*/A of LDPE packages of apple slices. Predictions were generated using equation 18 with appropriate substitutions from equation 14. 3-fold lower O_2 limit line represents by an exponential equation on Lower O_2 limit= $0.587e^{0.047T}$ fitted to lower O_2 estimates Table 4.



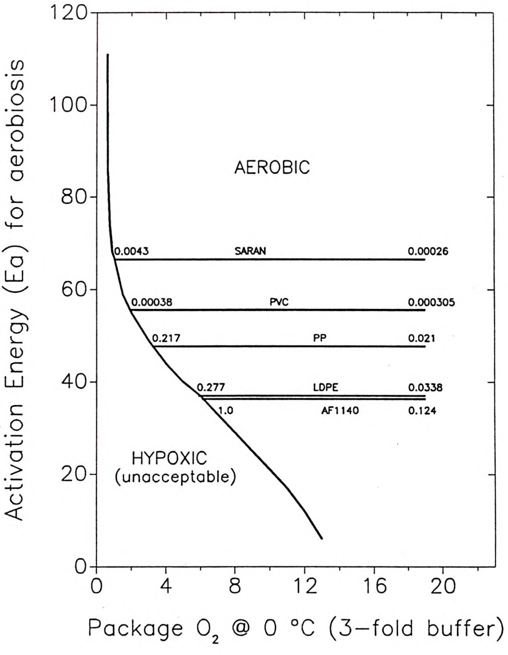
Headspace O_2 (kPa)
Temperature (°C)
$\frac{W*l}{A}$
1E−07
2E−07
3.575E−07
5E−07
5.65E−07
7E−07
3X lower O_2 limit
0
4
8
12
16
20
0
2
4
6
8
10
12
14

Figure 24. Validation of the model by designing packages target headspace O_2 from 3.575E-07 and 2E-07 W*l*/A ratios in Figures 23. 3-fold lower O_2 limit line represents by an exponential equation on Lower O_2 limit = $0.587e^{0.047T}$.



Headspace O_2 (kPa)
2E-07
3X lower O_2 limit
3.575E-07
3X lower O_2 limit
Temperature (°C)

Figure 25. Effect of ranges of thicknesses of various films on O_2 partial pressure in the package at 0C. Thicknesses noted will provide aerobic conditions throughout the temperature range shown. Curves were generated from the fitted O_2 partial pressure model Equation 18 with substitution of different Ep^{O_2}, package surface area 120 cm^2 and fruit weight 0.1 kg. Lines parallel x-axis represent the range of thickness of each film that can be used in aerobic range.



120
100
80
60
40
20
0
0
4
8
12
16
20
Activation Energy (Ea) for aerobiosis
Package O2 @ 0 °C (3-fold buffer)
AEROBIC
HYPOXIC
(unacceptable)
0.0043
SARAN
0.00026
0.00038
PVC
0.000305
0.217
PP
0.021
0.277
LDPE
0.0338
1.0
AF1140
0.124

CONCLUSION

Browning of sliced apple could not be retarded with Controlled-atmosphere made of the O_2 and CO_2 combinations tested (0.1 or 20% O_2 with 0.03, 5, 10, 15, or 20% CO_2). Thus, no optimum gas concentrations could be identified. Alternative methods for controlling browning may be achieved with packaged apple slices by such method as spraying seaweed-based edible coating. Modified-atmosphere packaging was used as a tool for obtaining respiratory data needed to calculated permeability characteristics of packaging films that will achieve and maintain target gas levels in the package headspace at 0, 5, 10, and 15C for cultivar NY'674'. The lower O_2 limits were found to increase with increasing temperature. A lower O_2 limit was determined to be three-fold higher than the O_2 limit at RQ breakpoint throughout the temperature range. This 3 fold buffer was calculated to be a low risk O_2 minimum, having only a 1 in 1,000,000 change of undergoing fermentation. A mathematical model was developed to characterize the interaction of fruit R_{O_2}, $p_i^{O_2}$ and P_{O_2} film permeability. V_{max} increased exponentially with increasing temperature. K_T increased linearly with increasing temperature. The $p_i^{O_2}$ model was used for predicting the effect of P_{O_2}, $Ea^{P_{O_2}}$, temperature, film type and film thickness on $p_i^{O_2}$ of any package system. This model can be further used to demonstrate in the minimum ratio of Wl/A that can achieve and maintain aerobic condition throughout the temperature range. Once the ratio has been set, packages can be designed for any weight of fruit, thickness of the film and size of the package. A film with high P_{O_2} approximately 1E-08 mmol·cm^{-2}·h^{-1}·kPa^{-1} (10 times higher than common LDPE) is recommended to be used with apple slices. Decay is also needed to be controlled in the MAP of apple slices. This model can be further to predict release rate requirements for antifungal compounds such as 2 nonanone, based on film recommendation generated by the present p_{O_2} model.

APPENDIX A

Table 1: Analysis of Variance Procedure for 'L', 'a', and 'b' values

Dependent Variable: L-value

Source	DF	Sum of Squares	Mean Square	F-value	P
Model	69	426.493	6.18	3.41	0.0001
Error	210	380.398	1.81		
Corrected Total	279	806.892			

Dependent Variable: a-value

Source	DF	Sum of Squares	Mean Square	F-value	P
Model	69	0.272	0.0039	3.41	0.0001
Error	210	0.242	0.0011		
Corrected Total	279	0.514			

Dependent Variable: b-value

Source	DF	Sum of Squares	Mean Square	F-value	P
Model	69	412.10	5.972	2.09	0.0001
Error	210	599.172	2.853		
Corrected Total	279	1011.27			

Table 2: Analysis of Variance Procedure; the effects of each treatment and between treatments to 'L', 'a', and 'b' values.

Dependent Variable: L-value

Source	DF	Sum of Squares	Mean Square	F-value	P
O_2	1	2.4219	2.4219	1.34	0.2489
CO_2	4	59.923	14.981	8.27	0.0001
date	6	123.84	20.641	11.39	0.0001
O_2*date	6	57.79	9.633	5.32	0.0001
CO_2*date	24	88.21	3.675	2.03	0.0044
O_2*CO_2	4	10.37	2.593	1.43	0.2247
O_2*CO_2*date	24	83.92	3.496	1.93	0.0076

Dependent Variable: a-value

Source	DF	Sum of Squares	Mean Square	F-value	P
O_2	1	0.00154	0.00154	1.34	0.2489
CO_2	4	0.03819	0.00955	8.27	0.0001
date	6	0.07895	0.01315	11.39	0.0001
O_2*date	6	0.03684	0.00614	5.32	0.0001
CO_2*date	24	0.05623	0.00234	2.03	0.0044
O_2*CO_2	4	0.00661	0.00165	1.43	0.2247
O_2*CO_2*date	24	0.05349	0.00223	1.93	0.0076

Dependent Variable: b-value

Source	DF	Sum of Squares	Mean Square	F-value	P
O_2	1	49.97	47.97	16.81	0.0001
CO_2	4	58.78	14.69	5.15	0.0006
date	6	76.38	12.73	4.46	0.0003
O_2*date	6	9.96	1.65	0.58	0.7448
CO_2*date	24	89.80	3.74	1.31	0.1587
O_2*CO_2	4	54.70	13.67	4.79	0.0010
O_2*CO_2*date	24	74.51	3.10	1.09	0.3594

Table 3: Analysis of Variance Procedure for CO_2 injury.

Dependent Variable: CO_2 injury

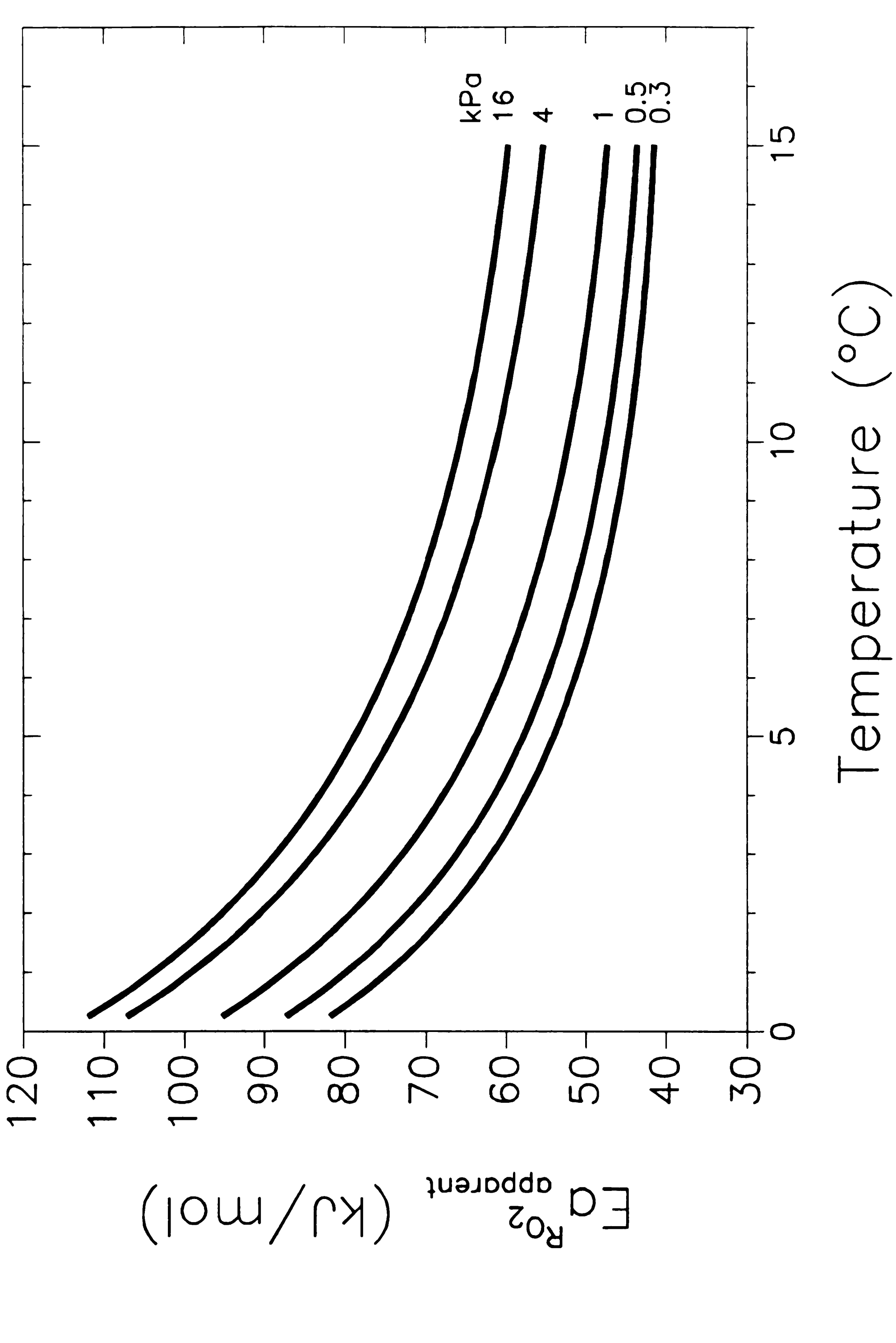
Source	DF	Sum of Squares	Mean Square	F-value	P
Model	9	16.525	1.836	3.87	0.0024
Error	30	14.25	0.475		
Corrected Total	39	30.775			

Dependent Variable: CO_2 injury

Source	DF	Sum of Squares	Mean Square	F-value	P
O_2	1	0.625	0.625	1.32	0.2600
CO_2	4	15.40	3.85	8.11	0.0001
O_2 and CO_2	4	0.5	0.125	0.26	0.8993

APPENDIX B

Figure 1. Calculated apparent activation energy ($Ea^{R_{O_2}}$) for sliced apple fruit respiration as affected by temperature and O_2 partial pressure. Calculated values for $Ea^{R_{O_2}}$ obtained by stepwise numerical integration of the relationship between ln(O_2 uptake) and 1/Temperature in K at O_2 partial pressure 0.3, 0.5, 1, 4, and 16 kPa.



$Ea^{RO_2}_{apparent}$ (kJ/mol)
120
110
100
90
80
70
60
50
40
30
0
5
10
15
Temperature (°C)
kPa
16
4
1
0.5
0.3

APPENDIX C

Affinity 1140

Dow Company Texas

Density = 0.895

melt index = 1.6

$Ea^{P_{O_2}}$ = 36.34 kJ/mol

$Ea^{P_{CO_2}}$ = 32.36 kJ/mol

$P_{O_2} = 0.254 \exp(-4371/T)$

$P_{CO_2} = 0.25 \exp(-3923/T)$

$P_{CO_2}/P_{O_2} = 4.3$