Effects of Temperature and Coating Treatment on Gas Exchange of 'Braeburn' Apples

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Abstract

Achieving modified atmosphere (MA) effects on fruit through the use of surface coatings relies upon a suitable degree of internal atmosphere modification, which is strongly dependent upon both respiration rate and skin permeance to gases. In this study, skin porosity, skin permeance, internal partial pressures of oxygen and carbon dioxide, and respiration rate were measured at 0°C, 10°C, 20°C and 30°C in non-coated 'Braeburn' apples. Variation in respiration rate, internal partial pressures of oxygen and carbon dioxide, skin permeance to oxygen and carbon dioxide, and the extent to which all of these gas exchange characteristics affected by temperatures of 0°C, 5°C, 10°C, 15°C, 20°C were characterised in both non-coated and coated 'Braeburn' apples. Coating treatments were 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times either a 2% (w/w) solution of hydroxypropylcellulose (HPC) in distilled water, or a commercial formulation of carnauba wax and shellac coating, achieved by mixing the full strength solutions with distilled water.

There was a 6- or 10-fold difference in respiration rate between fruit kept at 0°C and 20°C, or 0°C and 30°C, whilst the relative permeance to both O_2 and CO_2 differed only a factor of 1.7 or 1.5 in non-coated fruit. The differing effects of temperature upon these two variables were responsible for the depression of internal O_2 and elevation of internal CO_2 associated with increase in temperature from 0°C to 20°C or 30°C. There was no evidence that porosity was dependent on temperature, suggesting that the increasing permeance with higher temperatures may have resulted from increasing permeance of the cuticle. The modification of internal atmosphere composition in carnauba-coated fruit depended upon coating concentration and temperature. The effects of HPC coating on internal atmosphere, especially on

internal CO_2 were less marked than those of temperature.

In non-coated fruit, the magnitude of decline in internal O_2 was slightly greater than the increase in internal CO_2 over the temperature range in the experiment. For apples that were respiring aerobically, this indicates that the fruit skin had a slightly higher permeance to CO_2 than to O_2. Since O_2 diffuses through pores were readily than CO_2, gas exchange of these fruit appeared not to be pore dominated. The suppression of gas exchange by shellac coating was consistent with the coating blocking pores on the fruit surface to an extent that depended on coating concentration. The less pronounced effects of HPC coating in both skin permeance and internal gases were consistent with a coating that loosely covered the fruit surface rather than blocking the pores. Low concentrations of shellac coating achieved low internal O_2 levels at higher temperatures but had only slight effects on internal atmosphere composition at low temperatures. Higher concentrations that achieved MA benefit at low temperatures resulted in fermentation at higher temperatures. Given the natural variability in skin permeance, and the exacerbating effects of coating treatment and temperature, surface coatings appear unlikely to provide a reliable and safe means of achieving modified atmosphere benefits in 'Braeburn' apples.

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Table of Contents

List of Figures

List of symbols and abbreviations

$-a$	=	parameter representing proportional rate of decline in total gas pressure (s^{-1})
A	=	surface area of fruit (m^2)
CA	=	controlled-atmosphere
CO_2	=	carbon dioxide
$D_{j,k}$	=	diffusion constant of j in medium k
Δp_j	=	difference in partial pressure of gas j between internal and external atmospheres (Pa)
Δp^0	=	total initial pressure difference between internal and external atmospheres (Pa)
Δp^{tot}	=	total pressure difference between internal and external atmospheres at time t (Pa).
Δx	=	film thickness (m)
K	=	parameter representing coefficient of the equation.
K_m	=	parameter analagous to a Michaelis-Menten constant (Pa)
M	=	fruit mass (kg)
n	=	absolute amount of gas in a given sample (mol)
O_2	=	oxygen
p^{tot}	=	total pressure in the external atmosphere (Pa)
p_j^i	=	partial pressure of gas j in the internal atmosphere (Pa)
p_j^e	=	partial pressure of gas j in the external atmosphere (Pa)
$p_{CO_2}^i$	=	partial pressure of CO_2 in the internal atmosphere (Pa)
$p_{O_2}^i$	=	partial pressure of O_2 in the internal atmosphere (Pa)
P	=	permeability (mol s^{-1} m m^{-2} Pa^{-1})

P_j	=	permeability to gas j (mol s^{-1} m m^{-2} Pa^{-1})
$P_j^{'}$	=	permeance to gas j (mol s^{-1} m^{-2} Pa^{-1})
$P_j^{'fruit}$	=	skin permeance of fruit to gas j (mol $s^{-1}m^{-2}$ Pa^{-1})
$P_j^{'comb.}$	=	combined permeance of skin and coating to gas j (mol $s^{-1}m^{-2}$ Pa^{-1})
$P_j^{'coat}$	=	permeance of a coating barrier (mol $s^{-1}m^{-2}$ Pa^{-1})
$P_{CO_2}^{'}$	=	permeance to CO_2 (mol $s^{-1}m^{-2}$ Pa^{-1})
$P_{O_2}^{'}$	=	permeance to O_2 (mol $s^{-1}m^{-2}$ Pa^{-1})
$\overline{P}^{skin}$	=	porosity of the fruit skin (mol s^{-1} m^{-2} Pa^{-1})
Q_{10}	=	temperature quotient for respiration
R	=	gas constant (8.3134 m^3 Pa mol^{-1} K^{-1})
R^2	=	square of the correlation coefficient (r), or proportion of the total variability in the y-values that van be accounted for by the independent variable x.
r_j	=	specific rate of transfer of gas j between internal and external atmospheres (mol kg^{-1} s^{-1})
r_{CO_2}	=	specific rate of transfer of CO_2 between internal and external atmospheres (mol $kg^{-1}s^{-1}$)
$r_{O_2}^{T}$	=	respiration rate at T°C (mol kg^{-1} s^{-1})
$r_{O_2}^{max,0}$	=	r_{O_2} at 0°C when oxygen is non-limiting (mol kg^{-1} s^{-1})
$r_{O_2}^{max,T}$	=	inherent maximum r_{O_2} at T°C when oxygen is non-limiting (mol kg^{-1} s^{-1})
RH	=	relative humidity
RQ^{∞}	=	respiratory quotient when O_2 is non-limiting.
$S_{j,k}$	=	solubility coefficient of j in medium k (mol m^{-3} Pa^{-1})
t	=	time (s)
T	=	temperature (°C)

V^a	=	added gas volume before injection (m^3)
V^i	=	volume of internal atmosphere within the fruit (m^3)

Chapter 1 General Introduction

The total value of horticulture exports from New Zealand increased from $18.5 million in 1970 to $1323.8 million in 1997 (Bollard, 1996), with fresh fruit accounting for more than half of this (Horticulture News, Nov. 1997). In the past four years (1995-1998), apples (*Malus domestica* Borkh.) have accounted for about half the value of the total fresh fruit exported from New Zealand.

Controlled atmosphere (CA) storage has been used to extend storage life of apples destined for both export and the local market in New Zealand. CA storage is also applied to the fruit during transportation to distant markets. CA conditions are achieved by decreasing internal O_2 to 1 to 2 % and elevating CO_2 to 0 to 5 %. Modified atmosphere packaging (MAP), which involves maintaining a lower O_2 and higher CO_2 level inside a plastic film packaging than that in air, is used to a lesser extent. The true potential of this technique should be realised when temperature-compensating polymeric films with variable permeability characteristics have been developed (Anon, 1992; Challis and Bevis, 1992). Recently, edible coatings have been increasingly used on fruits to improve cosmetic features, to reduce water loss or to achieve modified atmosphere (MA) benefits (Baldwin et al., 1995; Banks et al., 1993b).

The benefits achieved in CA and MA result from the slowing of physiological processes linked to respiration and ethylene synthesis and action caused by the modified internal atmosphere that develops within the fruit. However, if O_2 levels are too low or CO_2 levels are too high, critical tolerance limits may be reached, beyond which the fruit begin to ferment (Cameron et al., 1995; Yearsley et al.,

1996; Peppelenbos et al., 1998). For this reason it is important to keep fruit above the critical lower O_2 limits (LOLs) but, on the other hand, little benefit is achieved when internal oxygen remains high because there is very little effect on respiration (Banks et al., 1993b). Similarly, CO_2 level should be as high as possible without inducing abnormal metabolism and causing development of disorders. There is therefore an optimum storage atmosphere at which aerobic respiration is at the lowest level which can be achieved without development of anaerobic metabolism, and it occurs just above the LOL (Yearsley et al., 1996). For MAP and use of surface coatings on fruit, exposure to higher than ideal storage temperatures during distribution and retailing may result in fermentation and development of off-flavours because internal O_2 has dropped too low or internal CO_2 has become too high (Cameron et al., 1995; Kader et al., 1989; Banks et al., 1997; Hagenmeier & Shaw, 1992; Mannheim & Soffer 1996).

Internal atmosphere composition of a fruit at a certain external atmosphere composition is determined by its rates of O_2 and CO_2 exchange and skin permeance to these gases, as characterised by the following equation (Fick's First Law of diffusion; Burg and Burg, 1965):

$$\Delta p_j = p_j^i - p_j^e = \frac{r_j}{P_j^{\text{furit}}} \cdot \frac{M}{A} \qquad \textbf{(1.1)}$$

where: A = surface area of fruit (m^2)

Δp_j = difference in partial pressure of gas j between internal and external atmospheres (Pa)

M = fruit mass (kg)

p_j^i = partial pressure of gas j in the internal atmosphere (Pa)

p_j^e = partial pressure of gas j in the external atmosphere (Pa)

P_j^{fruit} = skin permeance to gas j (mol $s^{-1}m^{-2}$ Pa^{-1})

r_j = rate of transfer of gas j between internal and external atmospheres (mol kg^{-1} s^{-1}).

Thus, internal atmosphere composition can be altered by changing skin permeance to gases, rate of gas transfer, or external atmosphere composition (Banks et al., 1993a). At steady state, and given that M and A are effectively constant and uptake of O_2 by respiration and the diffusion of O_2 into the fruit are equal, Δp_{O_2} remains constant and so does $p_{O_2}^i$. When $p_{O_2}^e$ is lowered in CA or MA storage, r_{O_2} continues at the same rate for a short time, Δp_{O_2} is maintained and $p_{O_2}^i$ begins to decline, which inhibits r_{O_2}. This in turn reduces Δp_{O_2}. The cycle of feedback continues until a new steady state is reached. The extent to which $p_{O_2}^i$ is depressed depends upon skin permeance to O_2, i.e., $p_{O_2}^i$ will decrease more for fruit with low skin permeance than those with high permeance.

The relationship of r_{O_2} and $p_{O_2}^i$ can be described by a Michaelis-Menten equation for aerobic respiration (Andrich et al., 1991; Banks et al., 1993a, b; Dadzie, 1992):

$$r_{O_2}^T = r_{O_2}^{max,T}\left[\frac{p_{O_2}^i}{K_m + p_{O_2}^i}\right] \qquad \textbf{(1.2)}$$

where: K_m = Michaelis-Menten constant (Pa)

$r_{O_2}^{max,T}$ = inherent maximum r_{O_2} at T°C when oxygen is non-limiting (mol kg^{-1} s^{-1})

$r_{O_2}^T$ = respiration rate at T°C (mol kg^{-1} s^{-1}).

The rate of CO_2 production at a given temperature ($r^T_{CO_2}$), as another index of respiration, is affected by $p^i_{O_2}$. When $p^i_{O_2}$ declines, $r^T_{CO_2}$ becomes increasingly suppressed until $p^i_{O_2}$ reaches the LOL. Below the LOL, fermentation occurs and $r^T_{CO_2}$ increases dramatically with further decreases in $p^i_{O_2}$.

The relationship between the two respiratory components and $p^i_{O_2}$ was modelled by the following equation by Banks et al.(1993b):

$$r^T_{CO_2} = RQ^{\infty} r^{max,T}_{O_2}\left[\frac{p^i_{O_2}}{K_m + p^i_{O_2}} + \frac{10^{-10}}{K + p^i_{O_2}}\right] \qquad \textbf{(1.3)}$$

where RQ^{∞} is the respiratory quotient when O_2 is unlimiting. K is a coefficient of the equation.

It is well known that temperature has a marked effect on respiration. Dadzie et al. (1993) modelled $r^{max,T}_{O_2}$ as a power function of temperature:

$$r^{max,T}_{O_2} = r^{max,0}_{O_2} Q_{10}^{(0.1T)} \qquad \textbf{(1.4)}$$

where $r^{max,0}_{O_2}$ = r_{O_2} at 0°C when oxygen is non-limiting (mol kg^{-1} s^{-1})

$Q^{0.1T}_{10}$ = temperature quotient for respiration.

As temperature rises, $r^{max,T}_{O_2}$ increases when O_2 is non-limiting (Eq. 1.3), which would cause Δp_{O_2} to increase and $p^i_{O_2}$ to decline to an extent that depends on the skin permeance and its modification by temperature (Eq. 1.1). The decreased $p^i_{O_2}$ in turn limits r_{O_2}. The converse effect occurs with decreasing temperature,

i.e. low temperature suppresses r_{O_2} which increases $p^i_{O_2}$. Changes in $p^i_{O_2}$ and r_{O_2} are both cause and effect in this system.

The effects of skin permeance to gases upon gas exchange characteristics of fruits have been explored from a conceptual perspective (Banks et al., 1993b), but there is only limited information available from experimental work (Banks et al., 1997). In particular, it is not known whether permeance is itself a characteristic that varies substantially with temperature, and this would have profound effects on predictive modelling work made using Eqs. 1-3. It would therefore be of considerable value to establish the relationship between permeance to these gases and temperature.

Gas exchange between the internal and external atmosphere of the fruit occurs in parallel through the pores and cuticle of the skin (Nobel, 1983; Banks et al., 1993b). Permeance of pores to both O_2 and CO_2 should be determined by their respective diffusivities in air and should be similar (Reid et al. 1987): $P'_{CO_2} = 0.87\, P'_{O_2}$, whereas the ratio is quite different for diffusion through pepper cuticle at 20°C: $P'_{CO_2} = 11\ P'_{O_2}$ (Banks unpublished). Thus, the nature of the diffusion barrier in fruit skin would affect the exchange ratio of O_2: CO_2. Depending on whether exchange of both gases occurred exclusively through pores or exclusively through cuticle, this value could range between 0.87 and 11. Given that pores are thought to provide the predominant route for O_2 exchange (Banks et al., 1993b), this explains why researchers have historically assumed a ratio close to 1 (Cameron et al., 1995; Burton, 1982; Burg and Burg, 1965). In contrast, blocking the pores with a surface coating elevates this ratio closer to 3-6, typical of other films (Banks et al., 1993b; Hagenmaier & Shaw, 1992; Cameron et al. 1995).

Temperature effects on film permeance are well known (Cameron et al., 1995). Activation energy (E_a, Joles et al., 1994) is used to describe the relative dependence of permeability of films to gases upon temperature (Doyon et al., 1991). When gas exchange is primarily through holes, then the E_a for permeation would be expected to be less than 5 kJ.mol^{-1} (Cameron et al., 1995). The E_a for diffusion through films is much greater than that for diffusion through holes (Cameron et al. 1994). Thus, generally, packages that use holes or microperforations for gas exchange are particularly vulnerable to increased temperatures because gas diffusion through holes increases little with increasing temperature (Cameron et al., 1995). Assuming that temperature effects on diffusion through fruit cuticle are similar to those on films, then permeance of fruit skins to gases would be expected to be substantially affected by temperature if exchange is dominated by the cuticular route but little affected if it is dominated by exchange through the pores. In addition, Banks et al. (1993b) suggested that the proportion of total gas exchange diffusing through the cuticular route in a fruit would be greater in fruits for which there were few effective pores than for those that were highly porous. Skin porosity provides a measure of the effectiveness of pores on the fruit skin to the passage of gases (Hagenmaier and Baker, 1993). Based on the arguments above, temperature effects on permeance of fruit skins to gases would be likely to be detected in fruits with a low skin porosity, such as 'Braeburn' apples which have a very low skin permeance relative to other cultivars of apples grown in New Zealand (Dadzie, 1992).

The role of coatings as a barrier to gas and water diffusion might be performed in two quite different ways. The coating could form an additional barrier through which gases must permeate, or it could simply plug openings in the peel (Hagenmaier and Baker, 1993). It has been reported that the permeance of coated

fruit is more strongly influenced by the coating's ability to block pores on the fruit surface than by the permeance of the coating *per se* (Banks et al., 1997; Hagenmaier and Baker, 1993; Mannheim and Soffer, 1996), although which mechanism prevails depends on what is the main pathway for gas exchange in the non-coated fruit (Hagenmaier and Baker, 1993). Thus, the final permeance of a coated fruit depends upon a complex set of interactions between the initial skin permeance of the fruit and the types and concentrations of the applied coatings. Once some pores are blocked by a surface coating, a smaller proportion of total gas exchange occurs through the pores and correspondingly a greater proportion occurs through the cuticle. This change might be expected to make the permeance of the fruit more sensitive to the temperature in an analagous way to those fruit that naturally have a low permeance. By measuring the skin permeance on both non-coated and coated fruit at different temperatures, the temperature effect can be separated from that of the coating. However, excessive modification of skin permeance by coating, coupled with elevated respiration at high temperatures may suffocate the fruit and cause them to ferment (Banks et al., 1993b and 1997). Therefore, maintenance of optimum $p^{i}_{O_2}$ and avoiding the risk of fermentation over a range of temperatures in coated fruit relies upon selecting the types and concentrations of coating that will block an appropriate proportion of pores.

The objectives of this study, made upon 'Braeburn' apples, were to characterise the effects of temperature on:

- skin porosity
- permeance to O_2 and CO_2, and the extent of internal atmosphere modification of the fruit treated with different types and concentrations of coating solution.

Chapter 2 Literature Review

2.1 Introduction

In recent years, with the increasing use of edible coatings to extend postharvest shelf-life and maintain quality of fresh products, the emphasis in coating development has switched to the area of controlled gas exchange (Baldwin, 1994). Edible coatings have been used extensively on bulky organs such as apples to modify the internal atmosphere and delay ripening (Banks, 1984a; Banks et al., 1993a and 1997; Baldwin, 1994; Hagenmaier and Baker, 1993). The modified atmosphere effects of coatings on fruits are related to:

- respiration rate of the fruit at a given temperature ($r_{CO_2}^T$, mol $kg^{-1}s^{-1}$), which depends upon temperature (T), physiological state and internal atmosphere composition (Kidd and West, 1925; Dadzie et al., 1996);
- skin permeance of the fruit ($P_j^{'fruit}$, mol $s^{-1}m^{-2}$ Pa^{-1}), which is determined by the structure of the skin and the routes for gas diffusion (Lendzian and Kerstiens, 1991; Banks et al., 1993b);
- the permeance of the coating to gases, which would change with the type and concentration of coating material (McHugh and Krochta, 1994), and be affected by *RH* and temperature (McHugh and Krochta, 1994; Kester and Fennema, 1986);
- the interaction between the fruit skin and the coating, i.e., how tightly the coating adheres to the fruit surface or how many pores are blocked (Banks et al., 1993b).

When a certain kind of coating is applied to a fruit, it may have no effect in delaying ripening at low temperatures, since the low respiration rate causes only

minor modification of the internal atmosphere. However, the increased respiration rate that results at higher temperatures causes a substantial decrease in internal O_2 level and an increase in CO_2 level. Taken to extremes, this modification of the internal atmosphere can incur fermentation of the fruit tissue (Banks et al., 1997; Hagenmaier and Baker, 1993 and 1994; Davis and Hofmann, 1973). Thus, understanding both the physical and physiological issues involved in the use of edible coatings on fruit is very important for achieving optimised results.

2.2 Respiration rate of the fruit (r_{CO_2})

Respiration is a physiological process in which carbohydrates and organic acids are broken down, and CO_2, H_2O and energy are produced (Blanke, 1991). Part of the energy is used in metabolic processes and the remainder is released to the environment as heat. There are two types of respiration: aerobic (O_2 is consumed) and anaerobic (occurs without O_2, generally referred to as fermentation; Fig. 2.1). The respiratory quotient (RQ, the ratio of CO_2 produced to O_2 consumed), can indicate the principal substrate (Wang, 1990). For aerobic respiration, RQ is near 1 for carbohydrate substrates, < 1 for lipids, > 1 for organic acids (1.33 for malic acid). On this basis, values of RQ between 1 to 1.33 are to be expected in apple depending on the metabolic substrate. Much higher values usually indicate fermentation or senescent decay (Blanke, 1991). Postharvest handling practice is aimed at reducing the aerobic respiration to a minimum without fermentation occurring. For a given fruit species, a high respiration rate indicates the rate at which the fruit is deteriorating in both quality and food value and is commonly associated with a short storage life (Phan et al., 1975).

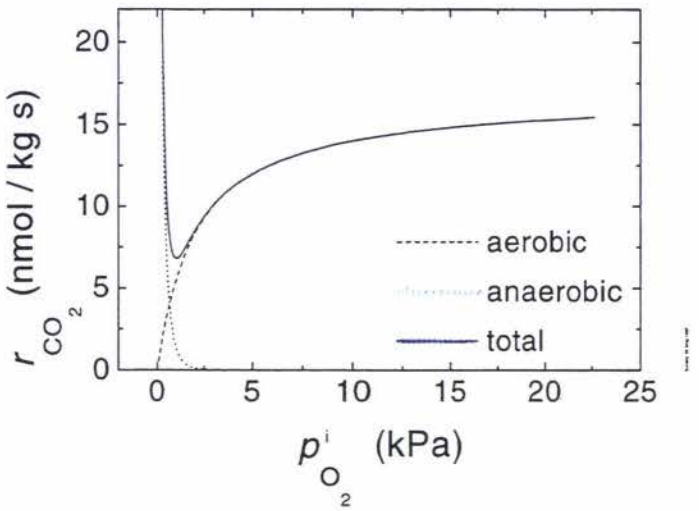

Figure 2.1 Relationship between internal partial pressure of O_2 ($p^i_{O_2}$) and rate of aerobic respiration and fermentation (Dadzie, 1992).

2.2.1 Physiological state

Fruits are classified as 'climacteric' and 'non-climacteric' according to their respiratory and ethylene production profiles during maturation and ripening (Biale and Young, 1981). The dramatic rise in respiration during the ripening of certain fruits, named the respiratory climacteric (Kidd and West, 1925), is a critical phase in fruit ontogeny (Rhodes, 1980). Apples are climacteric fruit, and are normally picked at a physiologically mature but unripe stage. Immediately before harvest, the respiration of the fruit declines to a preclimacteric minimum. At, or shortly after harvest, this is followed by the climacteric rise at the onset of ripening to the climacteric peak. Subsequently, respiration rate declines again in the postclimacteric phase (Watada et al., 1984; Fig. 2.2). The respiration and ethylene production of non-climacteric fruit such as citrus, grapes and strawberry

comparatively stable, undergoing a steady decline after harvest (Biale and Young, 1981).

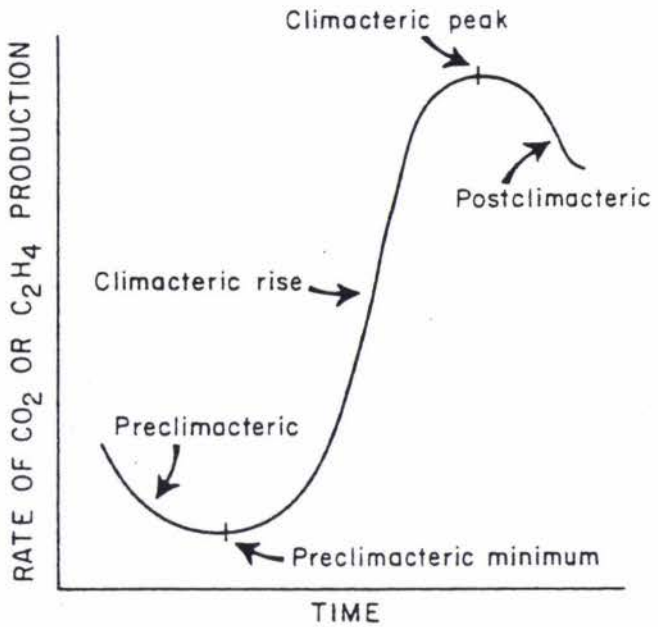

Figure 2.2 Diagram of changes in respiration rate with time before and after harvest (Watada et al., 1984).

During the climacteric, the RQ of apples has been reported to rise from 1.02 to 1.25 at the peak to 1.4-1.62 subsequently, indicating increased use of malic acid (Neal and Hulme, 1958; Hulme and Rhodes, 1971). The occurrence of the climacteric peak indicates the beginning of senescence of the fruit, and signals that the remaining storage life of the fruit is limited. Therefore, lowering respiration rate and postponing the climacteric peak is one of the purposes of postharvest practice for long-term storage of fruit. This can be achieved by

reducing temperature, O_2 availability or by increasing the CO_2 level in the store environment (Fidler and North, 1971; Banks et al., 1993a; Burton, 1982b). Thus, respiration rate of the fruit can be regarded as an indicator of the efficiency of these controls.

2.2.2 Temperature effect on the respiration

Rate of respiration is strongly temperature-dependent (Fig.2.3); this relationship is expressed as the temperature coefficient (Q_{10}), a measure of the relative increase in respiration rate for a 10°C rise in temperature. Between 5 and 25°C the Q_{10} of fruit varies between 1.5 and 2.5 (Blanke, 1991). High values Q_{10} indicate that temperature has a marked effect on respiration.

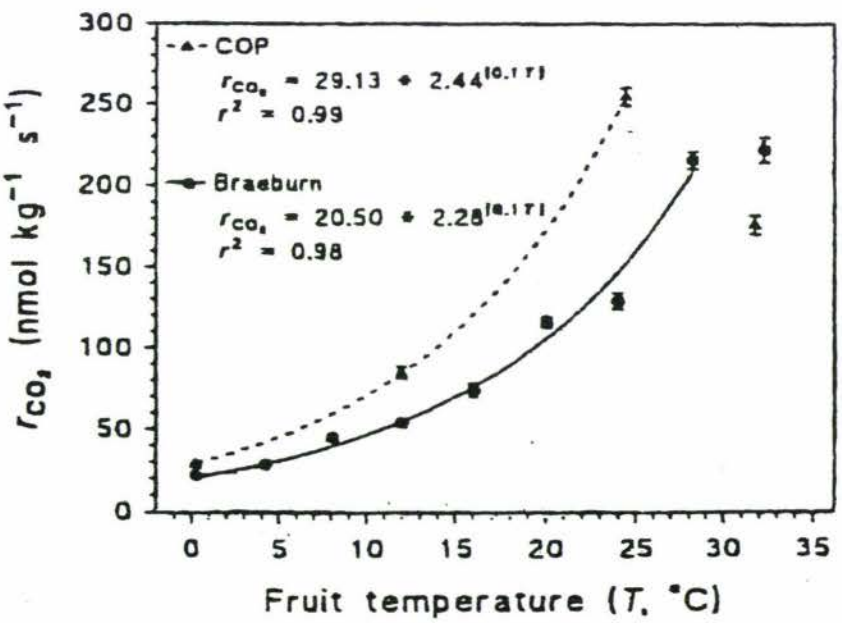

Figure 2.3 Temperature effect on the respiration rate of 'Cox's Orange Pippin' and 'Braeburn' apples (Yearsley et al., 1997).

2.2.3 O_2 and CO_2 effects

Decreased O_2 in the external atmosphere depresses the respiration rate of fruits (Banks et al., 1993a). The relationship between respiration rate and either the internal or external partial pressure of O_2 of crops has been modelled using the Michaelis-Menten equation (Andrich et al., 1991; Banks et al., 1993a,b; Cameron et al., 1995; Dadzie, 1992; Peppelenbos et al., 1993; Solomos 1982, 1985). Above the critical lower O_2 limit, it is thought that respiration rate was suppressed by reduced O_2 level but, without change in RQ (Beaudry et al., 1992; and Banks et al., 1993a,b). Below the LOL, CO_2 production and RQ increase markedly as fermentation increases and aerobic respiration is further depressed.

Reported effects of elevated CO_2 on O_2 uptake are contradictory. Joles et al. (1994) reported that $p^{e}_{CO_2} <$ 17 kPa did not affect respiration for raspberries. Applying more than 20 kPa resulted in only a small reduction in respiration of blueberries (Beaudry, 1993). Elevated CO_2 level also reduce the respiration rate of fresh fruits, but above a level of about 20% or higher, depending on the commodity and the O_2 concentration. (Kader, 1986). It has been reported that elevated CO_2 has no or little effect in reducing respiration rate and O_2 uptake on bananas (Young et al., 1962), and mushrooms (Peppelenbos et al., 1993). Gran (1993) reported that 12 to 15 kPa CO_2 in package headspace increased O_2 uptake compared to packages where CO_2 had been diminished by a CO_2 absorber. Thus, it appears that high levels of CO_2 can either slow or elevate respiration depending on the commodity and the concentration of CO_2 employed (Kidd, 1916; Kerbel et al., 1988; Kubo et al., 1990).

2.3 Skin permeance of the fruit

2.3.1 Law of diffusion

In the absence of cracks, pinholes, or other flaws, the primary mechanism for gas and vapour transfer through a film or coating is by activated diffusion; i.e., the penetrant dissolves in the film matrix at the high concentration side, diffuses through the film driven by a concentration gradient, and evaporates from the other surface (Kester and Fennema, 1986). At steady state, Fick's law of diffusion applies. Fick's law (Eq. 1.1) states that the quantity of penetrant diffusing through unit film area per unit time is proportional to the concentration gradient in the direction of flow. A combination of Fick's first law of diffusion and Henry's law of solubility is used to express permeability (P) of a material to gas j as the product of the diffusion constant of j in medium k ($D_{j,k}$) and the solubility coefficient of j in medium k ($S_{j,k}$; Donhowe and Fennema, 1994; Pascat, 1985):

$$P_j = D_{j,k} \cdot S_{j,k} \qquad \textbf{(2.1)}$$

Permeance is a more useful concept than permeability for postharvest research for estimating the gas exchange properties of a barrier as many barriers are heterogeneous or of unknown thickness (Banks et al., 1995). Permeance ($P_j^{'}$, mol s^{-1} m^{-2} Pa^{-1}) is related to permeability (P_j, mol s^{-1} m m^{-2} Pa^{-1}) for a barrier of thickness Δx (m) by:

$$P_j^{'} = \frac{P_j}{\Delta x} \qquad \textbf{(2.2)}$$

Rearranging Eq. 1.1, skin permeance of a fruit to gas j can be calculated as:

$$P_j^{',fruit} = \frac{r_j}{\Delta p_j} \cdot \frac{M}{A} \qquad \textbf{(2.3)}$$

where: A = surface area of fruit (m^2); M = fruit mass (kg).

Δp_j = difference in partial pressure of gas j between internal and external atmospheres (Pa)

$P_j^{'fruit}$ = skin permeance to gas j (mol $s^{-1}m^{-2}$ Pa^{-1})

r_j = rate of transfer of gas j between internal and external atmospheres (mol kg^{-1} s^{-1})

Eqs. 1.1 and 2.3 are valid only if the gas can diffuse much more easily through the pulp of the organ than through the skin, and the thickness of the skin can be considered to be negligible (Burg and Burg, 1965; Cameron, 1982; Cameron and Yang, 1982).

When the fruit is covered tightly by a coating film, the total permeance to gas j ($P_j^{',comb.}$) comprises the effective permeance of the fruit skin ($P_j^{'fruit}$) and the coating barrier ($P_j^{',coat}$) operating in series (Banks et al., 1993b):

$$\frac{1}{P_j^{'comb.}} = \frac{1}{P_j^{'fruit}} + \frac{1}{P_j^{'coat}} \qquad \textbf{(2.4)}$$

2.3.2 The structure of the skin

A fruit skin normally contains 4 layers of tissue (Bell 1937): a coating of epidermal hairs (absent in mature apples), cuticle, epidermis and hypodermis. The cuticle is the outermost layer of the fruit skin for a mature fruit. Cuticle comprises two groups of materials. One is insoluble polymeric cutin, a diverse group of complex hydrophobic polymers, principally esters of 16- and 18-carbon moncarboxylic acids that have two or three hydroxyl groups (Nobel, 1991, p. 4). Cutin constitutes the framework of the cuticular membrane. The other group includes the soluble cuticular lipids (SCL), which can appear on the surface as epicuticular wax or embedded within the cuticle as intracuticular wax (Holloway 1982).

Mature apples have lenticels that act as gas exchange pores (Burton, 1982a). Two-thirds of the lenticels were distributed over the one-third of the fruit surface nearest the calyx. Most of the open lenticels are in the equatorial portion or at the pedicel end (Tetley, 1930; Clements, 1935). The density of lenticels appears to be cultivar- and maturity-dependent (Tetley, 1930; Clements, 1935). The density of pores on apple has been reported to be 0.018 lenticels per mm^2 (Clements, 1935).

Large cracks in the cuticle have been noted in 'Golden Delicious' apples (Tetley, 1930; Faust and Shear, 1972); These cracks formed a network on the fruit surface. Development of cracks could result from the failure of the cuticle to keep pace with the growth of internal tissues, and is climate-dependent (Faust and Shear, 1972).

2.3.3 Variation in permeance

It is reported that apple skin permeability to O_2 increases with fruit ripening, to reach a maximum near commercial harvesting time (Andrich et al., 1989). Dadzie (1992) found that the skin permeance of freshly harvested New Zealand apples was cultivar-dependent. Among the eight cultivars studied, 'Braeburn' apples had the lowest skin permeance to CO_2 (approximately 0.2 nmol s^{-1} m^{-2} Pa^{-1}), and 'Royal Gala' the highest (0.6 nmol s^{-1} m^{-2} Pa^{-1}). However, variation within a given cultivar was 2-7 fold. Maguire (1998) also reported the similar observations in water vapour permeance of apples. Hence variation, coupled with that in respiration, surface area and mass could potentially account for the different responses of individual fruit to a given CA storage regime (Burton, 1974) and coating treatment (Banks et al., 1993b).

Water vapour permeability of isolated cuticles is reported to be dependent on the water vapour content of the air (Schonherr and Schmidt 1979). This is explained by 2 models in Fig. 2.4. In polar polymers water sorption leads to the formation of water clusters or to continuous water-filled channels, provided the polar groups are sufficiently close to each other. In these membranes water continuity exists across the entire membrane (Schonherr and Schmidt, 1979). Likewise, the gas permeability of hydrophobic polymer films is increased with increased relative humidity (Barrie 1968). This characteristic of the cuticle is supposed similar to permeation of gases in hydrophobic polymer films, showing increased mobility at higher relative humidities.

Schonherr et al. (1979) reported that the water vapour permeance of isolated cuticles from citrus leaves increased 300% for temperatures between 10°C and

30°C. Thus, it seems plausible that the skin permeance of fruits to gases would have a similar response to temperature. If so, the variation of internal O_2 and CO_2 upon increasing temperature would depend upon the extent of relative increases in skin permeance and respiration rate, i.e. $p^i_{O_2}$ would decline and $p^i_{CO_2}$ increase if the extent of respiration rate increased more than that of skin permeance to gases. Fermentation might happen in fruit with very low skin permeance at higher temperatures that may be encountered during transportation and $p^i_{O_2}$ declines below LOL. Unfortunately, the temperature effect on skin permeance has not been reported.

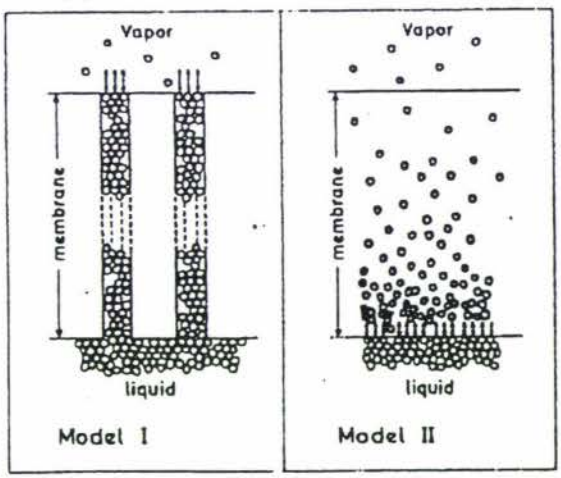

Figure 2.4 Transport models for lipid membranes. Model 1: porous membrane. Model II: Solubility membrane. Liquid vapour interface indicated by double arrows (Schonherr and Schmidt, 1979).

2.3.4 Routes for gas exchange through the skin

The diffusion of a gas through a film or coating is partially determined by structure of the barrier. It has been suggested that the potential routes for gas diffusion through the skin are: (1) cuticle, (2) pores, (3) pedicel and/or floral ends, and (4) cracks and stem scar (Cameron and Yang, 1982; Banks et al., 1993b; Ben-Yehoshua et al., 1985; Faust and Shear, 1972).

Cameron and Yang (1982) estimated 94%, 81% and 67% of C_2H_4, CO_2 and water vapour in tomato fruit occurred through the stem scar. In 'Golden Delicious' apples, 42%, 24% and 2% of total C_2H_4, CO_2 and water vapour transport, respectively occurred through calyx (Cameron, 1982).

Normally, it is thought that diffusion of gases through fruit skins involves parallel transfer through pores and cuticle, in which effective diffusivity and solubility of the gas may differ substantially (Banks et al., 1993b; Ben-Yehoshua et al., 1985; Lendzien and Kirsteins, 1991). The effective diffusion of gases through pores on a fruit surface is proportional to their diffusivities in the gas phase (Nobel, 1983). Thus, the permeance of pores to gases would be expected to be in the order: water vapour > O_2 > CO_2. Assuming the diffusivities of the three gases through cuticle are reasonably similar, the permeance of cuticle to each gas would therefore depend on its solubility in the outer layers (water and waxy materials) of the fruit surface (Banks et al., 1993b). Since water is infinitely self-soluble and CO_2 is far more soluble in water and lipids than O_2 (Mitz, 1979), then the cuticle is differentially permeable to these gases: water vapour >> CO_2 >> O_2 (Banks et al., 1993b).

Fruit skin permeance to gases comprises the combined permeance of pores and cuticle to these gases. From the diffusion characteristics of these gases through pores and cuticle, it is likely that the majority of total water vapour transport occurs preferentially in a liquid aqueous phase in the cuticle (Schonherr, 1976; Schonherr and Schmidt, 1979; Ben-Yehoshua et al., 1985). However, the total fruit skin permeance to CO_2 and O_2 depends on the dominant diffusion routes though the fruit surface. Skin permeance is greater when pore area is high and in this case, P'_{CO_2} and P'_{O_2} are similar. When the skin permeance is low, gas diffusion is dominated by cuticle and $P'_{CO_2} >> P'_{O_2}$. The porosity of the fruit skin can be measured by air flux through whole fruit, a method described by Hagenmaier and Baker (1993). 3 mL gas was injected by a syringe into the fruit through the blossom end, then the syringe was removed and the syringe needle connected by tubing to a manometer to monitor the pressure inside. This method provides a measure of how easily a gas moves through a unit area of the fruit skin in response to a difference in its partial pressures between internal and external atmospheres. This thesis examines use of a similar technique for characterising porosity in 'Braeburn' apples.

2.4 Gas diffusion in fruit flesh

Notable gradients in the flesh can exist when the rate of O_2 uptake exceeds the ability of O_2 to diffuse through the tissue (Solomos, 1987). The magnitude of the O_2 gradients varies between crops and cultivars and depends on respiration rate and on effective O_2 diffusivity in the fruit flesh (Rajapakse et al., 1990). Nobel (1983) reported that the apparent diffusivity of gases in apple flesh is only 10- to 20-fold higher than that of the fruit skin and suggested that considerable

concentration gradients may develop across the flesh of large fruit. Similarly, in 'Golden Delicious', 'Cox's Orange Pippin' and 'Braeburn' apples, significant O_2 gradients existed between surface tissues and the central cavity (Rajapakse et al., 1989 & 1990). Existence of significant CO_2 gradients between centre and surface of peeled apples has also been reported (Solomos, 1987).

Since diffusivities of gases are about 10^4 times greater in the gas phase than in water (Foust et al., 1980), overall tissue porosity and the extent to which intercellular spaces are continuous are crucial to the effective diffusivity of gases in crop tissues (Rajapakse et al., 1990). It is generally assumed that large intercellular space volumes provide an efficient means of aerating fruit tissues (Rajapakse et al., 1990). Experimental evidence indicates that O_2 concentration gradients across flesh tissues of apples are small, due to the large intercellular space volume (15-25%, v/v), and have no physiological significance (Burton, 1982a; Burg and Burg, 1965; Trout et al., 1942). The flesh of dense organs such as immature and climacteric avocado fruit exerts a significant resistance to CO_2 movement, creating a large gas concentration gradient across the flesh tissues (Ben-Yehoshua et al., 1963; Burg and Burg, 1965). Flesh resistance to gas diffusion in potatoes with an intercellular space of 1-2% is also significant (Banks and Kays, 1988).

There is wide variation in tissue porosity between different zones within an individual fruit (Burton, 1974; Soudain and Phan Phuc, 1979), which may cause heterogeneity in internal atmosphere composition within a given fruit. The porosity of tissue from the stem-end and equator of 'Golden Delicious' was found to be greater than those of tissue the calyx-end (Soudain and Phan Phuc, 1979). Furthermore, gradients in CO_2 and O_2 have been reported develop around the vascular bundles and seeds in apple (Brandle, 1968; Henze, 1969a, 1969b). Some

of this variability may partly explain the differing susceptibilities of various tissues to MA-induced disorders in fruit (Dadzie, 1992; Soudain and Phan Phuc, 1979).

Once O_2 moves across the skin, it can diffuse within the flesh tissue in intercellular air channels and/or in the fluid/solid phase of the cellular matrix. Two models have been proposed to explain the diffusion of gas as: a parallel model (diffusion either in air channels or in the fluid/solid phase); a series model (diffusion through air channels and fluid/solid phase in turn; Rajapakse et al., 1990). With the parallel model, it was proposed that even a tissue with large intercellular space volume could develop large O_2 gradients between the tissues beneath the fruit surface and the fruit centre if the gas channels were blocked with cell sap and tissue O_2 demand were high; conversely, a tissue with a small intercellular space could have ample O_2 supply if the intercellular space channels were free of blockage and respiration rate were low (Rajapakse et al., 1990). This may explain changes of gas gradients in avocado flesh during storage, since the resistance of avocado flesh tissues to gas diffusion has been reported to increase with ripening (Ben-Yehoshua et al., 1963). Such a change may result from cell walls and membranes breaking down and cell contents filling some intercellular spaces as plant organs become senescent (Kader et al., 1989). Alternatively, internal tissues may soften and lose cell turgor and the intercellular air space may diminish (Harker and Hallett, 1994). Rajapakse et al. (1990) found flesh firmness and intercellular space volume significantly lower in ripe compared to unripe apple fruit and the gradient in O_2 1.7 times as great.

Rajapakse et al. (1990) indicated that the total O_2 gradient between the external environment and fruit centre depended upon the relative resistance to gas

diffusion offered by both skin and flesh. In 'Braeburn' and 'Cox's Orange Pippin' apples, the gradient across the skin was 89% and 95% of the total; in nectarines, O_2 gradients across the flesh were significant and slightly higher than those across the skin. Thus, for any given external O_2 level, the O_2 level in the centre of an apple would be likely to be lower than that at the surface. Since the respiration rate and skin and flesh permeance change during storage, Wollin et al. (1985) suggested it may be necessary to continuously change the external atmospheric composition in long-term CA/MA storage to compensate for these changes.

2.5 Edible coatings

Since edible coatings were first used in the twelfth century (Hardenberg, 1967), many materials have been tried for potential application on various foods. The application has been developed to reduce transpiration losses (Hagenmeier and Shaw, 1992), improve cosmetic features and to achieve modified atmosphere benefits (Banks et al., 1997; Baldwin, 1994; Hagenmaier and Baker, 1995; Mannheim and Soffer, 1996).

2.5.1 Types of coating

Edible coatings are generally made from one or more of four major types of materials: lipids, resins, polysaccharides, and proteins (Baldwin et al., 1995).

2.5.1.1 Lipids and resins

Lipid-based coatings are made from waxes and oils, such as paraffin wax or oil, beeswax, carnauba wax, candelilla wax, mineral oil, vegetable oil, acetylated monoglycerides, stearic acid, lauric acid, or sucrose esters of fatty acids (Baldwin et al., 1995). Resins such as shellac, wood rosin, coumarone-indene resin are a group of acidic substances that are usually secreted by special plant cells into long resin ducts or canals in response to injury or infection in many trees and shrubs (Hernandez, 1994). Lipids are generally effective barriers to moisture and cutins are more permeable to water vapour than lipids (Hagenmaier and Shaw, 1990; Baldwin et al., 1995). Lipids and resins with low gas-permeability characteristics (Hagenmaier and Shaw, 1992), are added to food coatings to reduce gas exchange, and impart hydrophobicity (to reduce water loss) and gloss (Baldwin, 1994; Baldwin et al., 1997; Hernandez, 1994). However, some lipid and most resin coatings can cause fermentation at higher storage temperatures (Hagenmaier and Shaw, 1990), depending upon the amount deposited on the fruit surface (Banks et al., 1997).

The permeability of lipid components of coatings to gases depends on their polarity (Baldwin et al., 1997). In general, coating polymers with polar groups (i.e. ester and hydroxyl groups) tends to result in lower permeability to O_2 (Hagenmaier and Shaw, 1991). In contrast, the permeability of lipid films to water vapour increases with increasing polarity, unsaturation and branching of the lipids (Baldwin et al., 1997; Hernandez, 1994). Thus, coatings with shellac and other polar resins have lower permeability to gases (O_2, CO_2 and C_2H_4) than films prepared with waxes (Baldwin, 1994), and waxes are normally more resistant to

moisture transport than all the other components in edible film formulations (Hernandez, 1994).

2.5.1.2 Polysaccharides

Coatings made of polysaccharides (cellulose, pectin, starch, alginates, chitosan, carrageenan, gums) are good gas barriers, but their hydrophilic nature makes them poor barriers to water vapour (Kester and Fennema, 1986; Swenson et al., 1953). This group of coatings includes cellulose derivatives such as methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), hydroxypropylcellulose (HPC) and carboxymethylcellulose (CMC; Nisperos-Carriedo, 1994).

MC, HPMC, and HPC are nonionic, water-soluble ethers with good film-forming properties. They are capable of yielding tough and flexible transparent films owing to the linear structure of the polymer backbone (Krumel and Lindsay, 1976). The solutions are stable at pH 2-11 (Nisperos-Carriedo, 1994).

CMC, an anionic cellulose ether, can form strong, oil-resistant films; the solutions are stable at pH 7-9 (Nisperos-Carriedo, 1994). Two commercially available coatings based on CMC and sucrose esters are Semperfresh and TAL Pro-long. These coatings have been shown to extend the shelf-life and preserved important flavour components of some fresh commodities (Banks, 1984a & 1985; Drake et al., 1987; Bayindirli et al., 1995; Lau and Meheriuk, 1994; Sumnu and Bayindirli, 1994 & 1995). The basic function of CMC in edible fruits is to bind water or impart viscosity to the aqueous phase thereby stabilising the other ingredients or preventing syneresis, i.e. the loss of water from colloids.

2.5.1.3 Proteins

Protein-based coatings (casein, gelatin, soy, zein, egg albumen) are good film-formers, but have poor water vapour resistance (Gennadios and Weller, 1990; Gontard et al., 1996). Protein films are excellent O_2 and CO_2 barriers at low *RH*, but not in high humidity environments because of protein films' susceptibility to moisture absorption and swelling (Gontard et al., 1996). Thus, the use of coating made of proteins has not been popular in the past (Gennadios et al., 1994; McHugh and Krochta, 1994).

2.5.1.4 Composite and bilayer coatings

In composite or bilayer coatings, two or more materials from the above groups are combined or layered to improve gas exchange, adherence, and water vapour permeability properties (Baldwin et al., 1995).

Voids are developed when edible film emulsions are cast on the product (Ukai et al., 1976). The permeability of the film to water vapour and gases is determined by both the presence of voids and the ratio of hydrophilic to hydrophobic materials (Hernandez, 1994), though diffusion of gases is less affected than water vapour by the film's hydrophobicity (Baldwin et al., 1995). The ability of a hydrophobic substance to retard moisture transfer depends on the homogeneity of its final repartition in the supporting matrix and/or on the surface (Martin-Polo et al., 1992).

Incorporating lipids into low-methoxyl pectinate films can improve resistance to water vapour permeation (Schultz et al., 1949). Hagenmaier and Shaw (1990)

reported the poor water vapour barrier properties of HPMC-based coatings can be improved by increasing the chain length and concentration of the fatty acid in the coating. Kamper and Fennema (1984a, b) developed an HPMC-fatty acid bilayer film by combining HPMC and a blend of palmitic and stearic acids. The film provided vapour-barrier properties at *RH* values up to 90%.

Lowings and Cutts (1982) proposed coating fresh fruits and vegetables with a semi-permeable composite film comprising the sodium salt of CMC and sucrose fatty acid esters. The coating was more resistant to O_2 diffusion than to CO_2, thereby allowing a reduction in the internal O_2 without an equivalent increase in CO_2 level.

Coatings can serve as carriers of ingredients that perform a specific function such as to influence mechanical, protective, sensory, or nutritional properties, but which is separate from general coating performance (barrier properties, etc.; Baldwin et al., 1995; Kester and Fennema, 1986). Examples of this approach include: adding plasticizers to impart flexibility to a polymer film; a small amount of an appropriate wetting agent to facilitate uniform spreading; antioxidants and antimicrobial agents to prevent microbial growth or oxidation (Kester and Fennema, 1986).

2.5.2 Internal atmosphere of coated fruit

Surface coatings mainly exert their effects on skin permeance to gases by blocking a greater or lesser proportion of the pores on the fruit surface (Banks et al., 1993b & 1997; Mannheim and Soffer, 1996). Thus, the interaction of coatings

with fruit surface will depend on the coating types. Temperature and *RH* conditions can affect coating properties and performance including affecting its permeance to gases (Baldwin et al., 1995).

2.5.2.1 Type of coating

Owing to the variation in the skin permeance and respiration among fruit, the extent of modification of internal O_2 and CO_2 by a given coating treatment can be quite different. Different types of coating material and different concentrations of the same coating can exaggerate this variability. Banks et al. (1997) used a plot of $p^i_{CO_2}$ versus $p^i_{O_2}$ in coated fruit to identify the crop's internal lower O_2 limit (LOL), and indicated that this lay just below the optimum internal O_2 level for modified atmosphere effects. They applied polyethylene, CMC and shellac coatings on 'Royal Gala' apples kept at 20°C. Shellac-treated fruit had lower $p^i_{O_2}$ and higher $p^i_{CO_2}$ than those treated with CMC or polyethylene. On 'Granny Smith' apples treated with a 1%, 2%, 3% or 4% CMC solution, depression of $p^i_{O_2}$ increased with increased concentration up to 2% CMC, in contrast, $p^i_{CO_2}$ increased progressively with CMC concentration.

2.5.2.2 Pore blockage

Banks et al. (1997) used a model to predict the extent of $p^i_{O_2}$ depression resulting from the percentage of pore blockage. Higher modifications of internal atmosphere would be expected to occur in fruit with low skin permeance and high respiration rate, and with the use of coatings with low permeance. In expermental work, large fruit-to-fruit variability with some coating treatments indicated that uniformity of response may be as important as average response in selection of

coatings (Banks et al., 1997). In another study, coatings used on fruits and vegetables had permeabilities to CO_2 2-8 times greater than that to O_2, and were 40 to 20000 times more permeable to water vapour than to O_2 (Hagenmeier and Shaw, 1992). Thus, increasing the blockage of pores in the fruit skin with a coating film results in $P'_{H_2O} >> P'_{CO_2} > P'_{O_2}$ (Ben-Yehoshua et al., 1985). Covering the pores of the skin provides limited reduction in water loss, since extensive diffusion of water occurs through the cuticle and the coating film (Banks, 1984b; Banks et al., 1993b), or through the small cracks of the coating films (Ben-Yehoshua et al., 1985).

2.5.2.3 Relative humidity (RH)

The permeability of more hydrophilic coatings to gases may increase with increase in *RH*, which causes a significant increase in the solubilisation of water in the coating film (Rico-Pena and Torres, 1990; McHugh and Krochta, 1994) and increased solubility of gases, especially CO_2. Hagenmaier and Shaw reported the *RH*-dependence of water vapour permeance of several polyethylene waxes (1991) and shellac and resin films (1992). Substantial increases in P'_{O_2} and P'_{CO_2} with increased *RH* were observed on wheat gluten edible coatings (Gontard et al., 1996). At *RH* > 50%, P'_{O_2} and P'_{CO_2} increased exponentially with increased *RH*. However, at high *RH*, P'_{CO_2} increased more than P'_{O_2} since the free water of the film becomes the main medium for the transport of these gases through the coating and the solubility of CO_2 is higher than that of O_2.

Increasing *RH* can increase the permeability of isolated cuticles (see 2.3.3) and coating films. However, in order to minimise the water loss of fruit, the *RH* inside

the storage environment is normally kept very high. The extent of impact of the *RH* on skin permeance to gases of fruit per se and on fruit treated with coating materials is not known.

2.5.2.4 Temperature

Increasing temperature increases film permeability due to its impact on diffusivity and solubility of the permeant gas in the coating material (Kester and Fennema, 1986). The temperature-dependence of the gas and vapour permeability of edible films often obeys the Arrhenius relationship, and migration of gases through polymeric films generally exhibits activation energies (E_a) of 12 to 63 kJ mol^{-1} (Donhowe and Fennema, 1994).

Temperature-dependence of permeance has been observed in many coating films. Hagenmaier and Shaw (1991) reported shellac films have an E_a for O_2 from 53 kJ mol^{-1} (shellac cast from ethanol) to 65 kJ mol^{-1} (for water-soluble shellac) at 55% *RH*. For O_2 (at 0% *RH*), beeswax had an E_a of 48 kJ mol^{-1}, and microcrystalline had an E_a of 51 kJ mol^{-1}. Both waxes had E_a of about 29 kJ mol^{-1} for water vapour (at 100% *RH*).

In an MA package, steady-state package partial pressures of O_2 and CO_2 are achieved when fruit O_2 uptake and CO_2 production rates are equal to the rates of O_2 and CO_2 flux through the film (Beaudry et al., 1992; Cameron et al., 1989). However, fruit in MA packages are often subject to quite high temperatures, at which a decrease of O_2 levels in package occurs because respiration tends to increase more than permeation through the film (Kader et al., 1989). Thus, if an

MA packaging system is optimised at low temperature and the fruit are subsequently exposed to much higher temperatures, their elevated respiration rates at high temperature may then lead them to become anaerobic (Dazie et al., 1993). This emphasises the need to design such systems for the maximum temperature to which they are subsequently going to be exposed (Dazie et al., 1993; Beaudry et al., 1992). With data on blueberry fruit, Cameron et al. (1994) predicted that a film with an activation energy of approximately 60 $kJ.mol^{-1}$ would maintain close-to-optimum O_2 inside the package across the range of temperatures between 0 to 25°C.

Cameron et al. (1993) introduced the concept of sense-and-respond technology. They proposed that some component of the package would sense a signal, such as an increase in temperature, and initiate a marked increase in permeability to compensate for the change. A system for increasing permeability in response to increasing temperature was proposed by Patterson and Cameron (1992). The system was based on opening holes originally blocked by solid hydrocarbons with melting points between 10 to 30°C. Once the melting point was exceeded, permeability increased dramatically as the hydrocarbons melted and were wicked from the hole(s). Cameron et al. (1995) also developed a system that could sense and respond to fermentation of the packaged product. However, handling the active portion of the package before packaging could be a problem (Cameron et al., 1995) and more practical issues need to be considered.

Coated fruits face the same problems as MA packages: each coated fruit acts like an MA package. Maintaining an optimum $p^{i}_{O_2}$ over a range of temperature for coated fruit depends on the modification of fruit skin permeance by the coating film, i.e. by blocking a greater or lesser proportion of the pores on the fruit surface

(Banks et al., 1993b; Banks et al., 1997; Hagenmaier and Baker, 1993). Small modification of fruit internal atmosphere may be the result of an inadequate cover of pores on the skin or the low respiration rate at low temperature. The elevated respiration at higher temperature, coupled with variation in permeance of coated fruit would cause large variance on the internal gas composition, which in turn would bring different levels of MA benefit to the fruit. Therefore, optimising the use of coatings on fruits at different temperatures requires knowledge of their effects on internal gas composition that result from temperature-driven changes in coated skin permeance and fruit respiration. This thesis examines such changes in 'Braeburn' apples.

Chapter 3 Materials and Methods

3.1 Experiment 1

The experiment had a nested design at each of the 5 temperatures, 6 concentrations of each 2 coating materials were applied.

Mid-season harvested 'Braeburn' apples (*Malus domestica* Borkh.; count 100; mean mass 0.186 kg) were obtained from a Wanganui orchard and stored in air at 0°C until needed (8-16 weeks). Samples of 120 apples were selected at random for each of the following temperatures: 0°, 5°, 10°, 15°, and 20°C, equilibrated at 20°C for 24 h, then canulated for internal atmosphere sampling as described by Banks (1983; Fig. 3.1A and B), and left for another 24 h to allow the sealant to dry completely.

Initial measurements of fruit mass (kg), respiration rate (r_{CO_2}, mol kg^{-1} s^{-1}), internal O_2 and CO_2 partial pressure ($p^i_{O_2}$ and $p^i_{CO_2}$ (Pa)) were made at 20°C. After equilibrating the fruit to the treatment temperature for 48 h, the measurements were repeated. Groups of 10 randomly selected fruit were then allocated to the following coating treatments:

(1) dilutions of hydroxypropylcellulose (HPC) in distilled water at 0, 0.2, 0.4, 0.6, 0.8, 1.0 times a 2% HPC solution. Wetting agent ("Pulse"; 0.1% w/v; Monsanto, New Zealand) was added to each of the HPC solutions to lessen the surface tension and ensure even wetting of the fruit surface.

(2) dilutions of a carnauba wax and shellac coating ('Apple Glaze', Castle Chemicals, Australia) in distilled water at 0.2, 0.4, 0.6, 0.8, or 1.0 times commercial formulation.

Fruit were dipped for 1 s in each of the solutions, then allowed to dry on a rack. After a further equilibration in high relative humidity (*RH*, 93-98%) for 48 h, final measurements were taken. Data on gas composition, volume and time were converted to final format using formulae presented by Banks et al. (1995).

Figure 3.1A Canulated fruit for internal atmosphere sampling and porosity measurement.

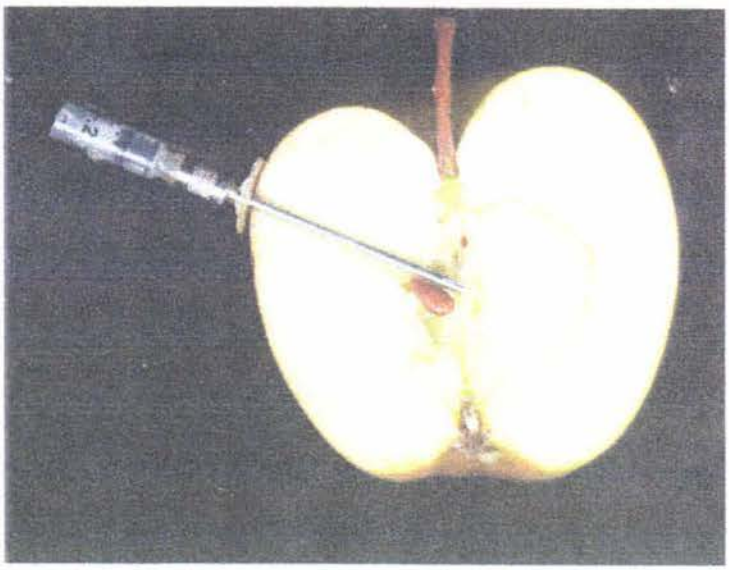

Figure 3.1B Transverse section of a canulated fruit for internal atmosphere sampling and porosity measurement

3.1.1 Gas measurements and analysis

Internal CO_2 and O_2 partial pressures ($p^i_{O_2}$ and $p^i_{CO_2}$) were estimated from 100 μL aliquots of internal atmosphere sampled non-destructively using a hypodermic syringe inserted through the septa in the cannulae (Banks 1983). Gas sample composition was determined using an O_2 electrode (Citicell C/S type, City Technology Ltd., London, UK) in series with a miniature infra-red CO_2 transducer (Analytical Development Company, Hoddesdon, UK), with O_2-free N_2 as carrier gas (flow rate 580 $mm^3\ s^{-1}$, Yearsley et al., 1996)

3.1.2 Respiration rate

Respiration rate (r_{CO_2}) was estimated by measuring the change in CO_2 partial pressure in 1mL samples sampled from 580 mL opaque containers in which each

fruit was sealed for 30 min (for treatments 15 and 20°C) or for 60 min (for treatments between 0 and 10°C). Samples were analysed using an O_2 electrode (Citicell C/S type, City Technology Ltd., London, UK) in series with a miniature infra-red CO_2 transducer (Analytical Development Company, Hoddesdon, UK), with O_2-free N_2 as carrier gas (flow rate 580 $mm^3\ s^{-1}$, Yearsley et al., 1996)

3.1.3 Skin permeance to gases

Values for permeance of the fruit's skin to CO_2 and O_2 (P'_{O_2}, P'_{CO_2}) were calculated using Eq. 2.3.

Fruit surface area was estimated from fruit mass using the following regression equation (Clayton et al., 1995):

$$A = 0.0581 \cdot M^{0.685} \qquad \textbf{(3.2)}$$

where: A = fruit surface area (m^2); and M = fruit mass (kg).

Data were subjected to analysis of variance (ANOVA) and linear, polynomial and non-linear regressions, using the Statistical Analysis System (SAS, 1990).

3.2 Experiment 2

Mid-season 'Braeburn' apples (*Malus domestica* Borkh.; count 100; mean mass 0.173 kg) were canulated to enable characterisation of internal atmosphere composition (Banks, 1983) and determination of porosity.

Groups of 10 randomly selected fruit were equilibrated 48 h to one of the 4 temperatures 0, 10, 20 and 30°C in a high *RH* environment achieved by enclosing the fruit in a perforated polyethylene tent. Data required for calculating r_{CO_2} (mol kg^{-1} s^{-1}), porosity (mol s^{-1} m^{-1} Pa^{-1}) and $p^i_{O_2}$ and $p^i_{CO_2}$ (Pa) were collected. At the end of each set of measurements at a given temperature, fruit were equilibrated for 48 h to another of the 3 temperatures and another set of measurements was made. Each group of fruit was measured at 4 temperatures. Gas and respiration measurements and gas analyses were made using the same techniques as those described in Experiment 1.

The method described here for cannulated apples (see 3.1, Figs. 3.1 A & B) was developed from a method used by Hagenmaier and Shaw (1992) to characterise porosity in oranges. Pressure changes with time after injecting 5mL gas into the cavity of apple were used to calculate the porosity of skin.

Rate of decline in total pressure within the fruit that occurred after injecting 5 mL air into the cavity through the cannula was characterised using a manometer (610-03 digital electronic manometer, Li-Cor, Inc., Nebraska, USA), connected to a data logger (ADE-16 high resolution data logger, *pico* Technology Limited) and a computer (Fig. 3.2).

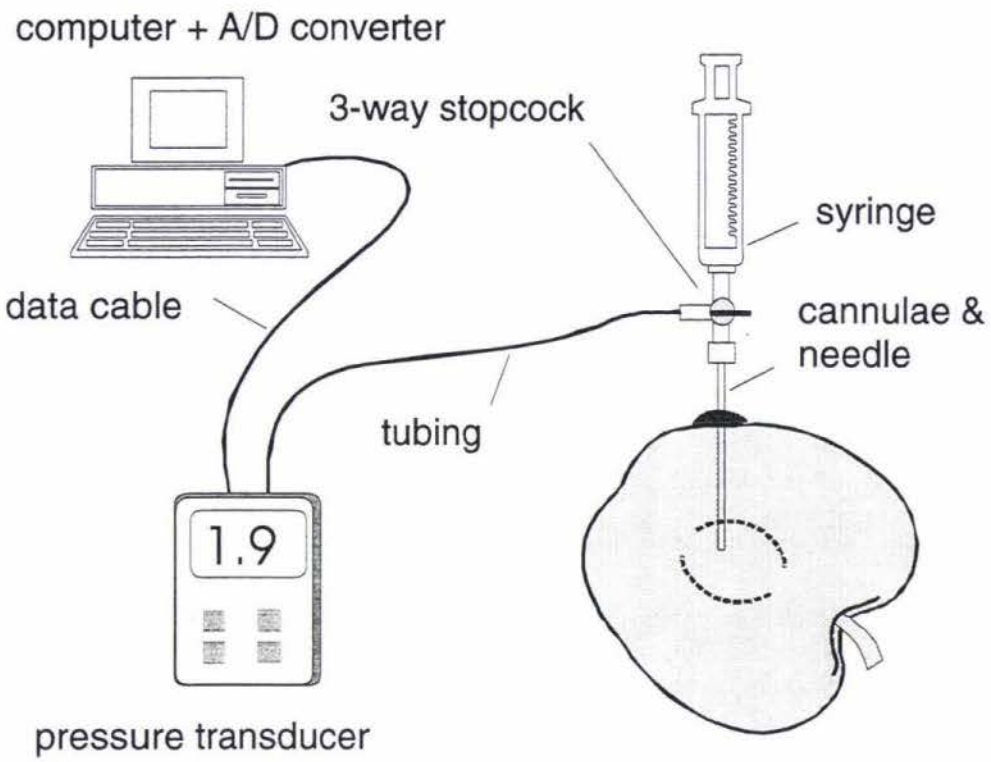

Figure 3.2 System for measuring porosity of cannulated 'Braeburn' apples

The amount of gas added to the system can be calculated from the universal gas law:

$$n = \frac{p^{tot} \cdot V^{a}}{R \cdot (T + 273.15)} \qquad \textbf{(3.3)}$$

where: n = absolute amount of gas in a given sample (mol)

p^{tot} = total pressure in the external atmosphere (Pa)

R = gas constant (8.3134 m^3 Pa mol^{-1} K^{-1})

T = temperature (°C)

V^a = added gas volume at atmospheric pressure before injection (m^3).

The proportion of the added gas that was subsequently released through the fruit skin per unit time can be expressed as:

$$\frac{p^{tot} \cdot V^{a}}{R \cdot (T + 273.15)} \times \frac{\frac{d\Delta p^{tot}}{dt}}{\Delta p^{0}} \qquad \textbf{(3.4)}$$

where: Δp^{0} = total initial pressure difference between internal and external atmospheres (Pa)

Δp^{tot} = total pressure difference between internal and external atmospheres at time t (Pa).

Porosity of the skin ($\overline{P}^{skin}$, mol s^{-1} m^{-2} Pa^{-1}) can then be calculated as:

$$\overline{P}^{skin} = \frac{\frac{p^{tot} \cdot V^{a}}{R \cdot (T + 273.15)} \times \frac{\frac{d\Delta p^{tot}}{dt}}{\Delta p^{0}}}{A \cdot \Delta p^{tot}} \qquad \textbf{(3.5)}$$

where: A = surface area of the fruit (m^2);

Assuming that changes in Δp^{tot} with time could be described by an exponential equation:

$$\Delta p^{tot} = \Delta p^{0} \cdot e^{-at} \qquad \textbf{(3.6)}$$

where $-a$ = proportional rate of decline in total gas pressure (s^{-1}).

Rate of change in Δp^{tot} would be given by:

$$\frac{d\Delta p^{tot}}{dt} = -a \cdot \Delta p^{0} \cdot e^{-at} \tag{3.7}$$

Substituting Eqs. 3.6 and 3.7 into Eq. 3.5, $\overline{P}^{skin}$ is given by:

$$\overline{P}^{skin} = \frac{\dfrac{p^{tot} \cdot V^{a}}{R \cdot (T + 273.15)} \times \dfrac{-a \cdot \Delta p^{0} \cdot e^{-at}}{\Delta p^{0}}}{A \cdot \Delta p^{0} \cdot e^{-at}}$$

$$= \frac{-a \cdot p^{tot} \cdot V^{a}}{A \cdot R \cdot (T + 273.15) \cdot \Delta p^{0}} \tag{3.8}$$

Values of a for each fruit were obtained by non-linear regression of Δp^{tot} against t using SAS. Values of Δp^{0} were calculated by extrapolation of the fitted curve back to the time of injection. These were used to estimate volume of internal atmosphere (V^{i}, m^3) within the fruit. Estimate of V^{i} ranged between 16 and 44 mL, with an average value of 32 mL or 17 % of fruit volume.

Chapter 4 Results

4.1 Porosity changes

Before injecting air into the fruit, internal and external pressures were equal (Figure 4.1). The injection of gas made internal pressure increase abruptly to a peak that occurred almost as soon as injection was complete. Subsequently, pressure initially declined rapidly. The rapid decline gave way to a slow decline within a few seconds as the internal pressure returned gradually to the normal state.

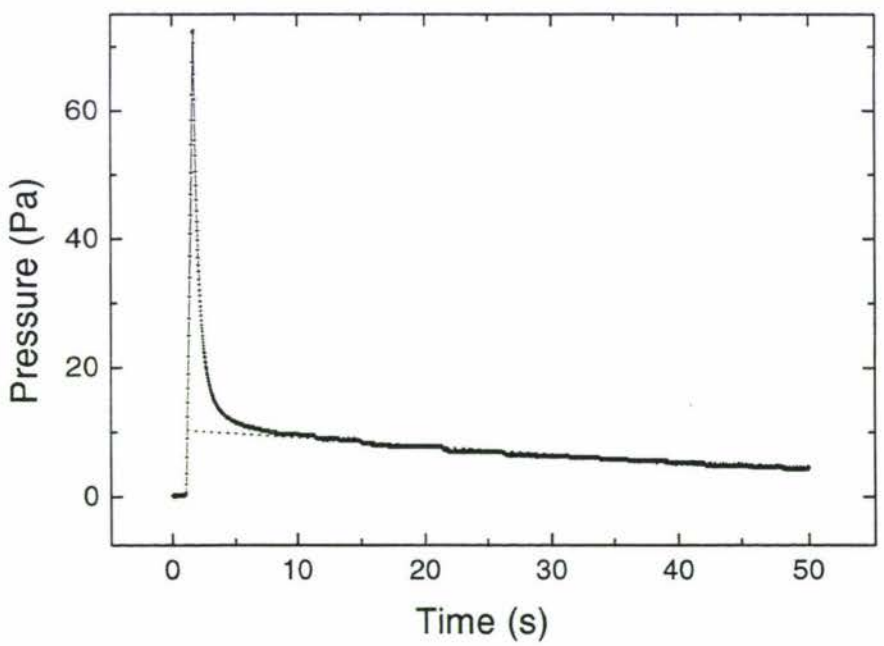

Figure 4.1 A typical plot of pressure changes with time after injecting 5 mL of air into a 'Braeburn' apple.

Linear regressions fitted to data beyond 8 s gave slopes that ranged between 8 to 50 Pa s^{-1}. Back-extrapolation to the time of injection of these lines gave initial intercepts ranging between 11 and 24 Pa.

Porosity values calculated using Eq. 3.8 ranged between 7 and 50 (pmol s^{-1} m^{-2} Pa^{-1}, Fig. 4.2), with an overall average of 18 ± 0.86 pmol s^{-1} m^{-2} Pa^{-1} (df = 129). Permeance values to O_2, calculated using Eq. 2.3 ranged between 60 and 320 pmol s^{-1} m^{-2} Pa^{-1}, with an overall average of 183 ± 5 pmol s^{-1} m^{-2} Pa^{-1} (df = 126). There were no clear relationship between porosity and permeance (Fig. 4.3), nor between porosity and internal atmosphere composition (Fig. 4.3). Neither was there a clear relationship between porosity values and temperature (Figs 4.4 A-D). In contrast, internal atmosphere composition, respiration rate and permeance were all consistently and markedly affected by temperature (Figs. 4.6, 4.10, 4.14 & 4.16).

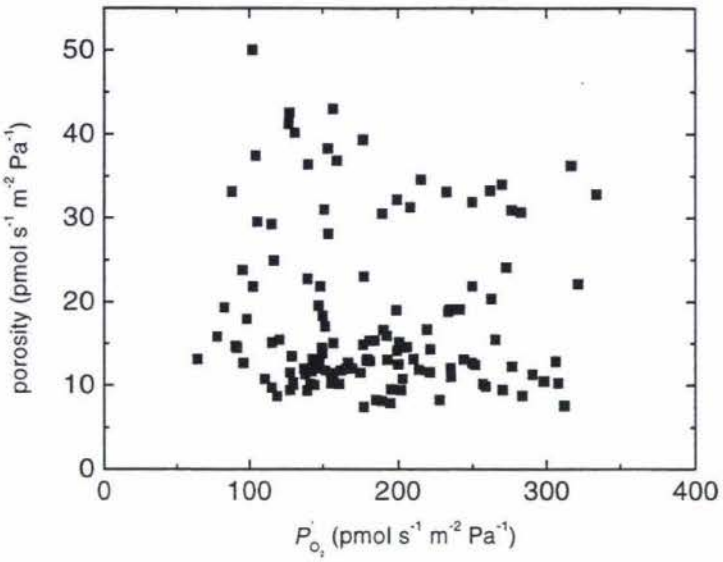

Figure 4.2 Relationship between porosity and skin permeance to O_2 of 'Braeburn' apples.

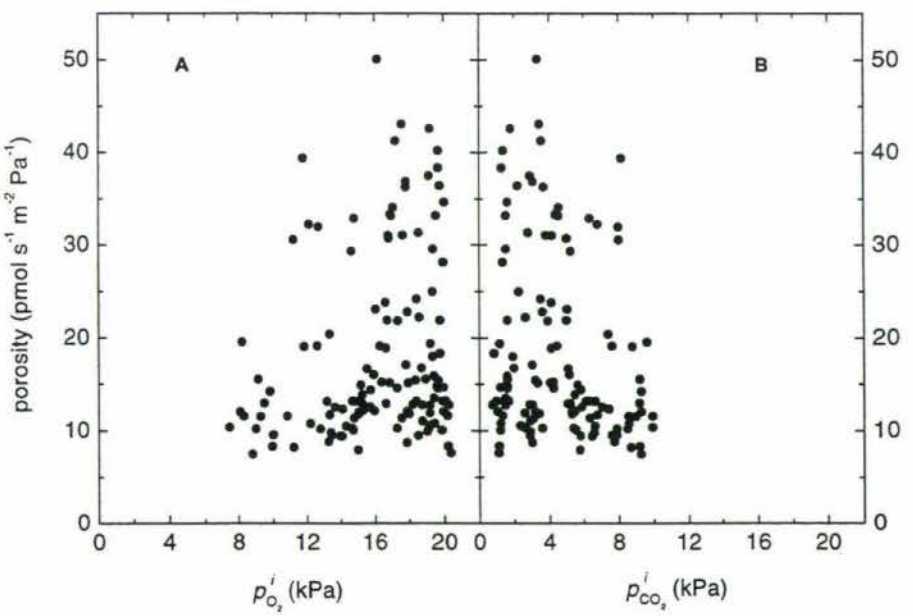

Figure 4.3 Variation in porosity and internal O_2 and CO_2 of 'Braeburn' apples.

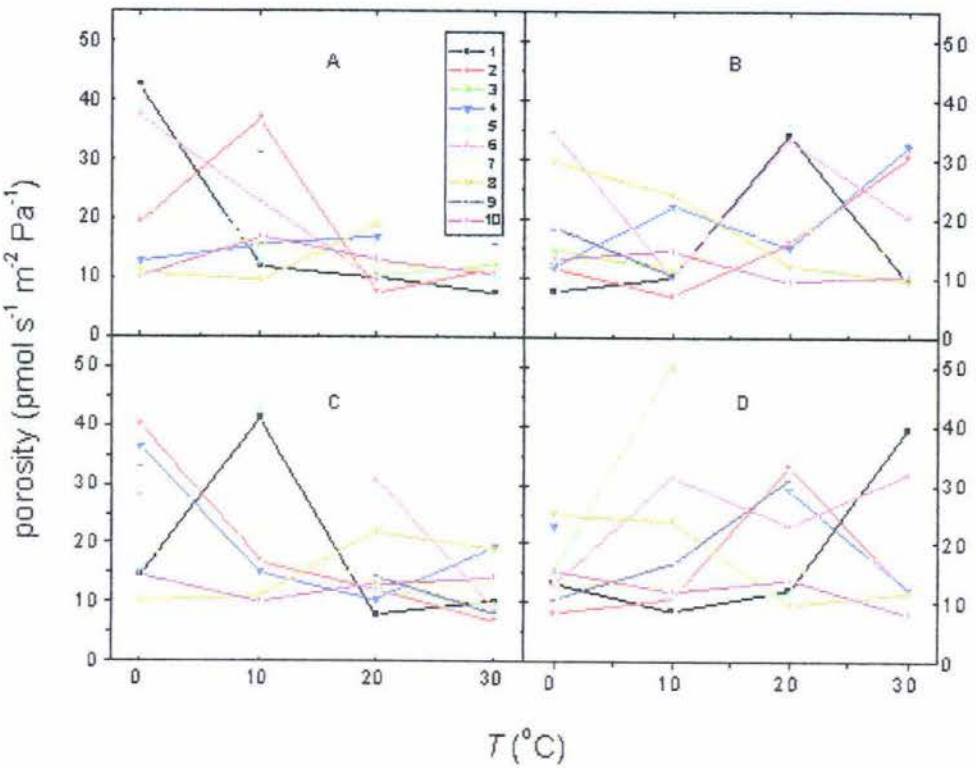

Figure 4.4 Variation in porosity of individual 'Braeburn' apple fruit with temperature between 0 and 30°C. Each panel (A, B, C or D) presents data from 10 fruit.

4.2 Temperature effect on respiration rate

4.2.1 Non-coated fruit

There was a quadratic increase in r_{CO_2} with increasing temperature (Figs. 4.5 & 4.6), a relationship which was a better fit to the data than those obtained with either a Q_{10} or an Arrhenius function (data not shown). Values for r_{CO_2} increased about 6 fold from 19.1 nmol kg^{-1} s^{-1} to 119.2 nmol kg^{-1} s^{-1} as temperature increased from 0° to 20°C. Across the entire range of temperatures, this was equivalent to a Q_{10} of about 2.4 and an effective activation energy of about 55.3 kJ mol^{-1}. Values for r_{CO_2} increased about 10 fold from 18 nmol kg^{-1} s^{-1} to 179 nmol kg^{-1} s^{-1} as temperature increased from 0° to 30°C, this was equivalent to a Q_{10} of about 2.14.

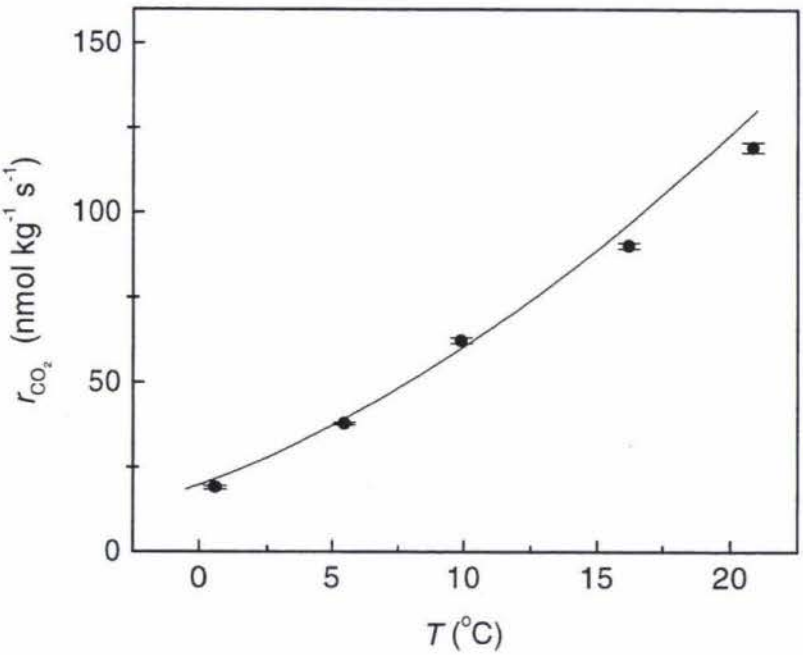

Figure 4.5 Respiration rate of 'Braeburn' apples held at between 0 and 20°C.

Solid line was fitted by quadratic regression:

$r_{CO_2} = (19.9 \pm 0.87) + (2.98 \pm 0.138) \cdot T + (0.109 \pm 0.0045) \cdot T^2$;

$R^2 = 0.98$.

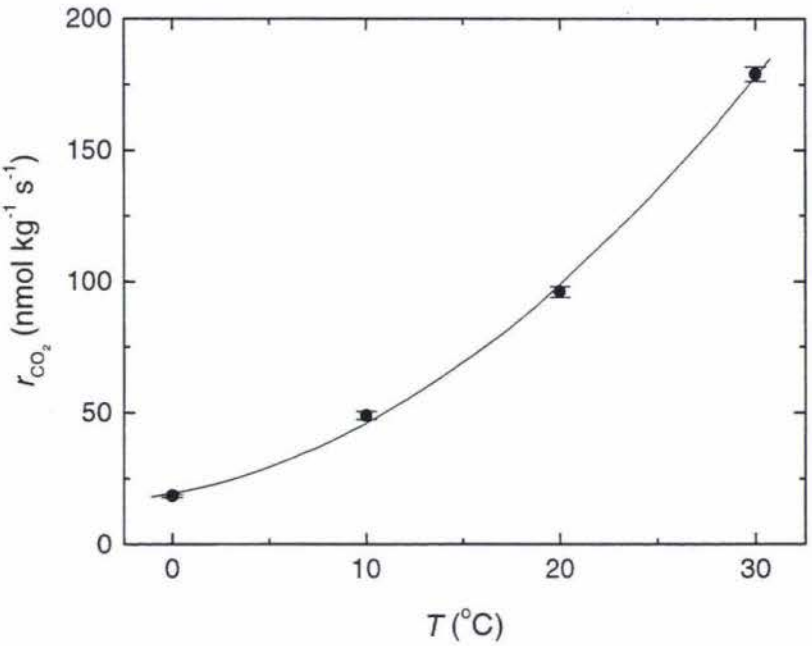

Figure 4.6 Respiration rate of 'Braeburn' apples held at between 0 and 30°C.

Solid line was fitted by quadratic regression:

$r_{CO_2} = (19.32 \pm 4.24) + (1.35 \pm 0.68) \cdot T + (0.131 \pm 0.02) \cdot T^2$;

$R^2 = 0.99$.

4.2.2 Coated fruit

Respiration rate increased in a curvilinear fashion by up to 7.9 times as temperature was increased from 0 to 20°C for both coatings (Figs. 4.7A & B). In general, respiration was suppressed to some extent by coating at all temperatures. However, at low temperatures, the suppression was very small, with no differences for HPC coated fruit at 0, 5 and 10°C, or for carnauba coated fruit at 0 and 5°C. Fruit treated with carnauba coating had lower respiration rates than fruit treated with HPC coating. At 20°C, respiration of fruit treated with 0.8 and 1 times full strength carnauba coating solution was higher than that of 0.4 and 0.6 times, close to that of 0.2 treatment.

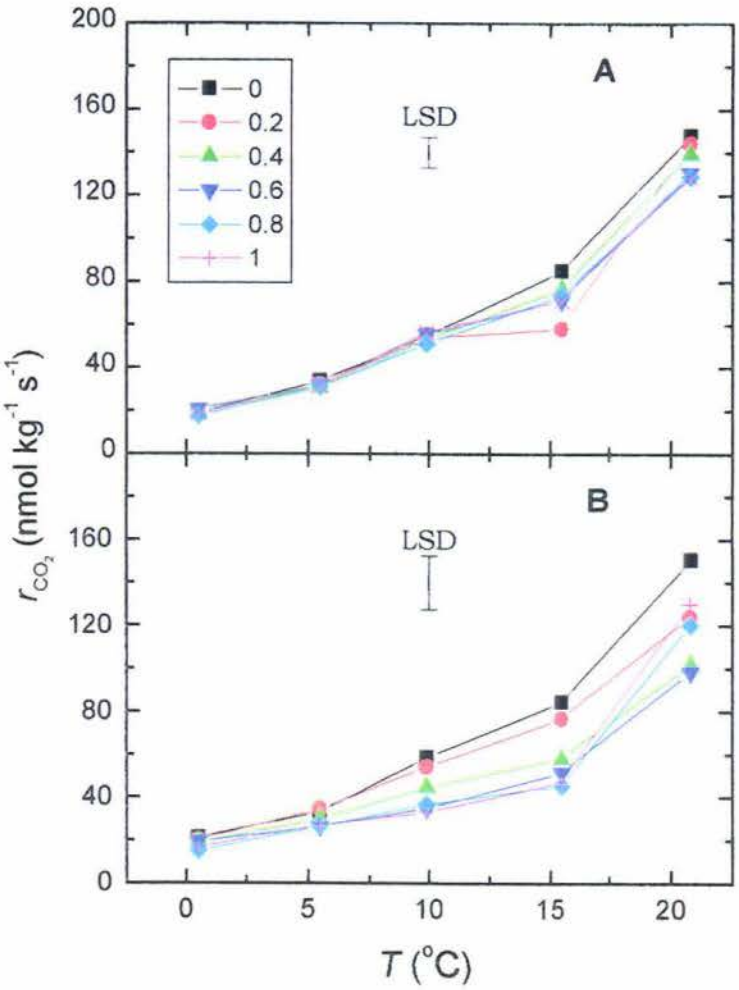

Figure 4.7 Variation in respiration rate (r_{CO_2}, mol kg^{-1} s^{-1}) of 'Braeburn' apples associated with temperature and A) HPC surface coatings at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times 2% HPC solution, and B) carnauba wax at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times commercial formulation.

4.3 Temperature effect on skin permeance

4.3.1 Non-coated fruit

There was a curvilinear relationship between temperature and the average absolute estimates of P'_{O_2} and P'_{CO_2} (Figs. 4.8A and B) from experiment 1 data that reflected initial variation in permeance for fruit in the samples at different temperatures (data not shown). Use of $rel\,P'_{O_2}$ and $rel\,P'_{CO_2}$ in regression analysis, which corrected for this initial variation by dividing individual fruit's permeance values at a given temperature by the initial values obtained for the same fruit at 20°C, indicated that permeance to both gases was positively, linearly related to temperature (Figs. 4.8C and D), reaching values 1.7 fold as great at 20°C as at 0°C. Plots of data for individual fruit show that P'_{CO_2} and P'_{O_2} were strongly correlated at every temperature (Fig. 4.9), with the slope relating P'_{CO_2} to P'_{O_2} similar at all temperatures, though values for the intercepts for P'_{CO_2} roughly increased 1.5 times between 0° and 20°C.

There was a positive linear relationship between temperature and the average absolute values of P'_{O_2} and P'_{CO_2} (Figs. 4.10A and B) from Experiment 2 data. P'_{O_2} and P'_{CO_2} increased about 1.5 and 1.7 fold between 0° and 30°C.

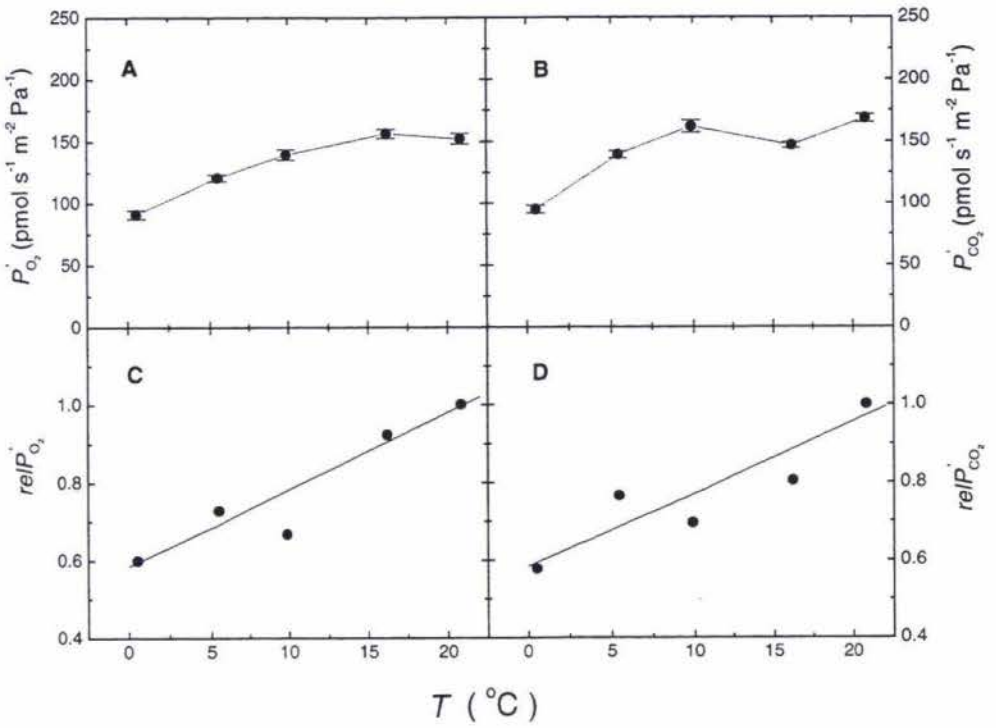

Figure 4.8 Changes in skin permeance to A), O_2; and B), CO_2; and relative permeance to C), O_2; and D), CO_2 of 'Braeburn' apples held at between 0 and 20°C.

Solid lines were fitted by regression:

C: $relP'_{O_2} = (0.584 \pm 0.0424) + (0.0198 \pm 0.00235) \cdot T$; $R^2 = 0.93$.

D: $relP'_{CO_2} = (0.583 \pm 0.0441) + (0.0187 \pm 0.00245) \cdot T$; $R^2 = 0.92$.

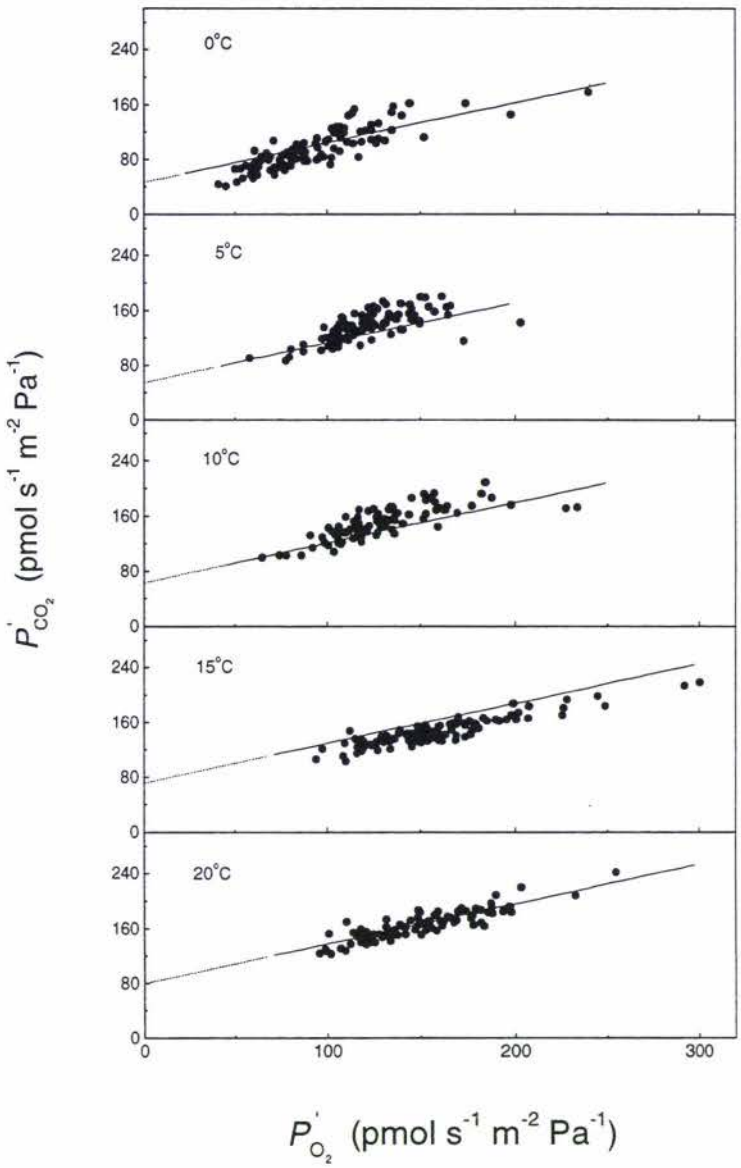

Figure 4.9 Predicted relationships between P'_{CO_2} and P'_{O_2} of 'Braeburn' apples held at between 0 and 20°C.

Solid lines were fitted by regression using Equation:

$P'_{CO_2} = (46.6 \pm 2.01) + (1.67 \pm 0.083) \cdot T + (581 \pm 17.2) \cdot P'_{O_2}$;

R^2 =0.87.

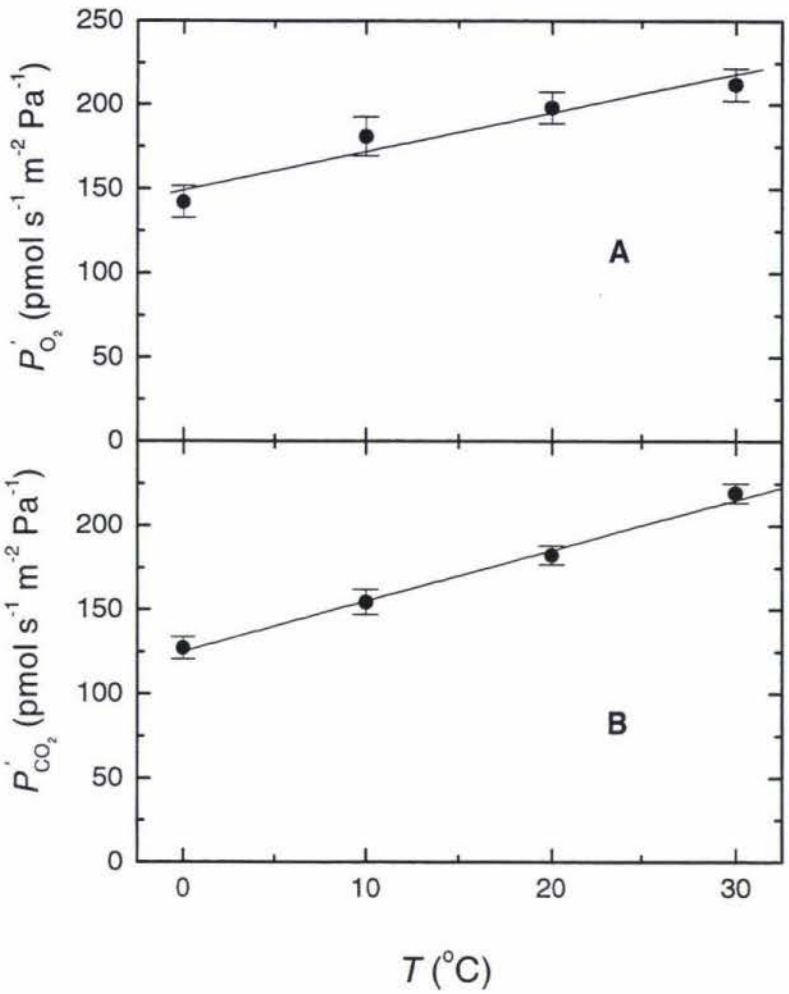

Figure 4.10 Changes in skin permeance to A), O_2; and B), CO_2 of 'Braeburn' apples held at between 0 and 30°C.

Solid lines were fitted by linear regression:

A: $P'_{O_2} = (149.4 \pm 7.9) + (2.26 \pm 0.42) \cdot T$; $R^2 = 0.93$.

B: $P'_{CO_2} = (125 \pm 3) + (3 \pm 0.16) \cdot T$; $R^2 = 0.99$.

4.3.2 Coated fruit

For all concentrations of applied coating, permeance to O_2 was increased as temperature was increased from 0 to 20°C (Figs. 4.11A & B). For HPC coating, P'_{O_2} in control fruit increased about 1.5 times between 0 to 20°C, while P'_{O_2} in other treatments doubled except treatment with 0.2% solution, which apparently increased nearly 8 fold. P'_{O_2} in control fruit of carnauba coating increased about 0.8 times between 0 and 20°C, P'_{O_2} in other treatments of carnauba coating had a slight increase.

For all concentrations of coating applied, permeance to CO_2 was also increased with increased temperature between 0 and 20°C (Figs. 4.12A & B). Control fruit had the highest value for both coatings at each temperature, the permeance was depressed more by carnauba coating than by coating with HPC.

Permeance to both gases was suppressed by both coating treatments and, to an upper limit, proportional to the increased concentrations of coating. The effect of the suppression of skin permeance by increased concentration of coating HPC was not significant, and concentrations of carnauba coating over 0.6 times commercial formulation exerted no further effect. For a given level of coating concentration, permeance to O_2 was generally depressed more than that to CO_2.

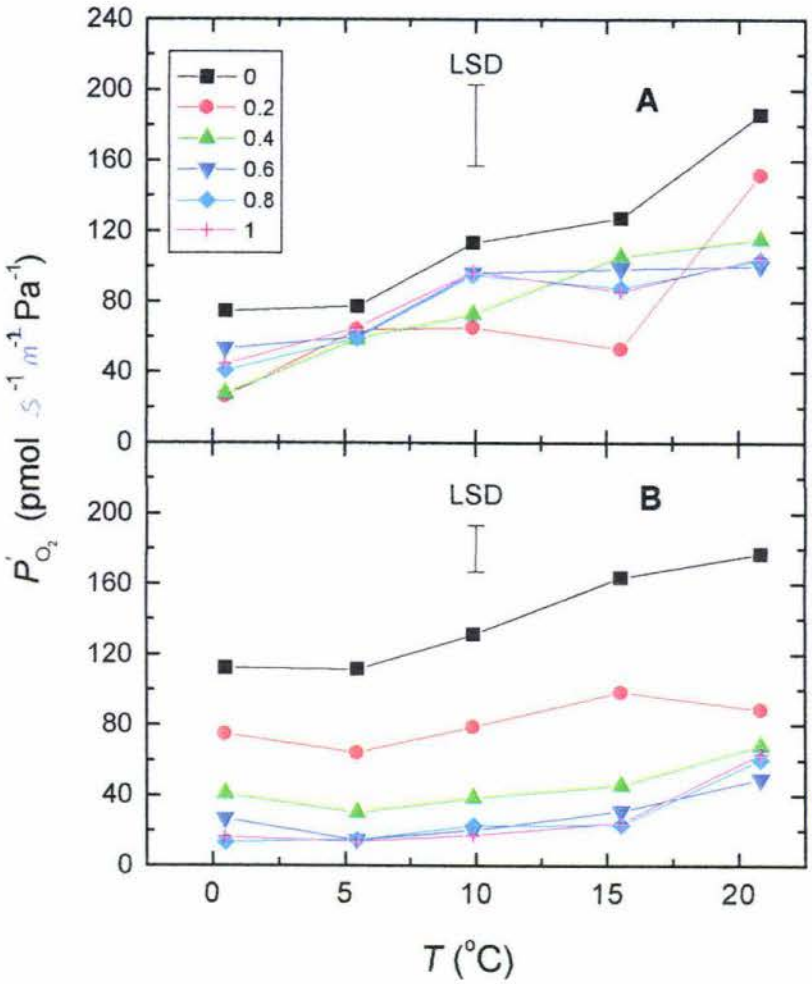

Figure 4.11 Variation in skin permeance to O_2 (P'_{O_2}, mol s^{-1} m^{-2} Pa^{-1}) of 'Braeburn' apples associated with temperature A) HPC surface coatings at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times 2% HPC solution, and B) carnauba wax at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times commercial formulation.

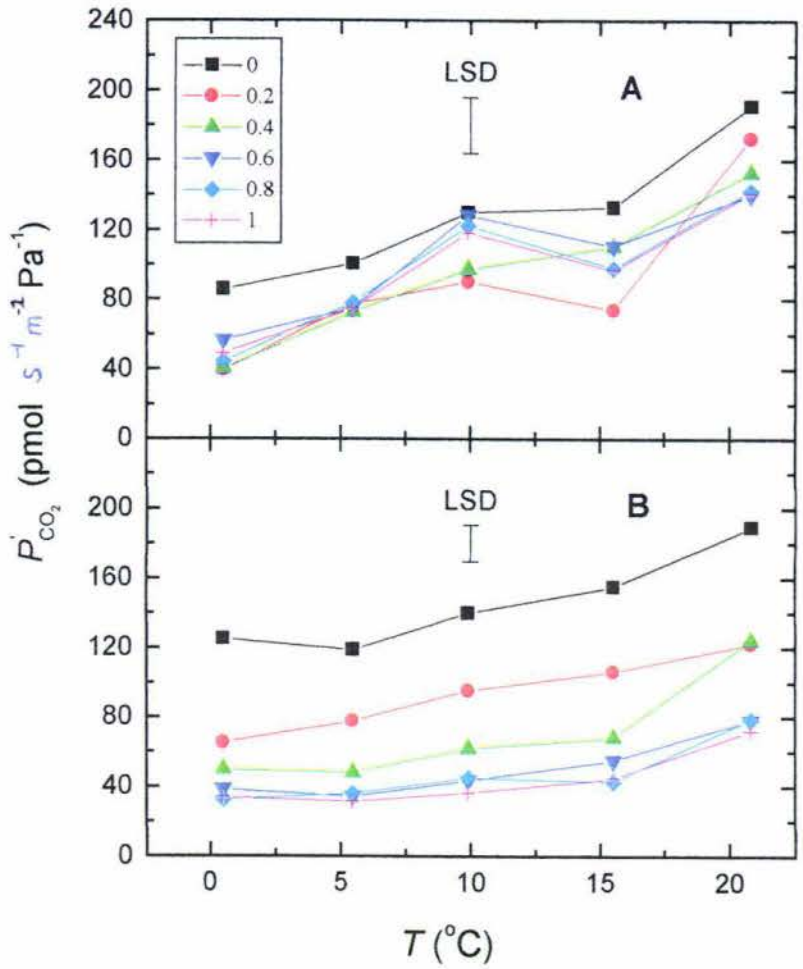

Figure 4.12 Variation in skin permeance to CO_2 (P'_{CO_2}, mol s^{-1} m^{-2} Pa^{-1}) of 'Braeburn' apples associated with temperature A) HPC surface coatings at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times 2% HPC solution, and B) carnauba wax at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times commercial formulation.

4.4 Temperature effects on internal gas composition

4.4.1 Non-coated fruit

On average, $p^i_{O_2}$ declined progressively with increasing temperature between 0°C and 20°C (Fig. 4.13A), whilst $p^i_{CO_2}$ increased concomitantly (Fig. 4.13B). There were no significant polynomial deviations from the fitted linear regressions in either case. The absolute slope of $p^i_{O_2}$ depression with respect to temperature was 12% greater than that for increase in $p^i_{CO_2}$. The changes of average $p^i_{O_2}$ and $p^i_{CO_2}$ with increasing temperature between 0°C and 30°C had similar trends (Fig. 4.14). However, the slope of $p^i_{O_2}$ depression was somewhat greater than that for increase in $p^i_{CO_2}$.

Values for $p^i_{O_2}$ and $p^i_{CO_2}$ were about 19 kPa and 2 kPa at 0°C. At 20°C, $p^i_{O_2}$ and $p^i_{CO_2}$ were around 12 kPa and 8 kPa. The sum of $p^i_{O_2}$ and $p^i_{CO_2}$ was 21 kPa at 0°C and 20 kPa at 20°C. There was a negatively linear relationship between $p^i_{O_2}$ and $p^i_{CO_2}$ (Fig. 4.15) and the data lay on a consistent fitted line at each temperature. The slope of the line became flatter at higher temperatures. At 0°C, $p^i_{CO_2}$ was uniformly low at 1-3 kPa, and $p^i_{O_2}$ was high at 18 - 20 kPa. At higher temperatures, the spread in values for both variables was greater, though that for $p^i_{O_2}$ was greater than that for $p^i_{CO_2}$. For fruit with highest $p^i_{O_2}$ at each temperature, the sum of $p^i_{O_2}$ and $p^i_{CO_2}$ was consistently c. 21 kPa. At the other extreme, the sum of $p^i_{O_2}$ and $p^i_{CO_2}$ was consistently less than 21 kPa for fruit with low $p^i_{O_2}$ values.

At low temperatures, the trend of $p^i_{O_2}$ upon $P^{'}_{O_2}$ was flat (Fig. 4.16). As temperature increased between 0°C and 30°C, the positive trend became steeper, whilst the negative trend of $p^i_{CO_2}$ upon $P^{'}_{O_2}$ became steeper too.

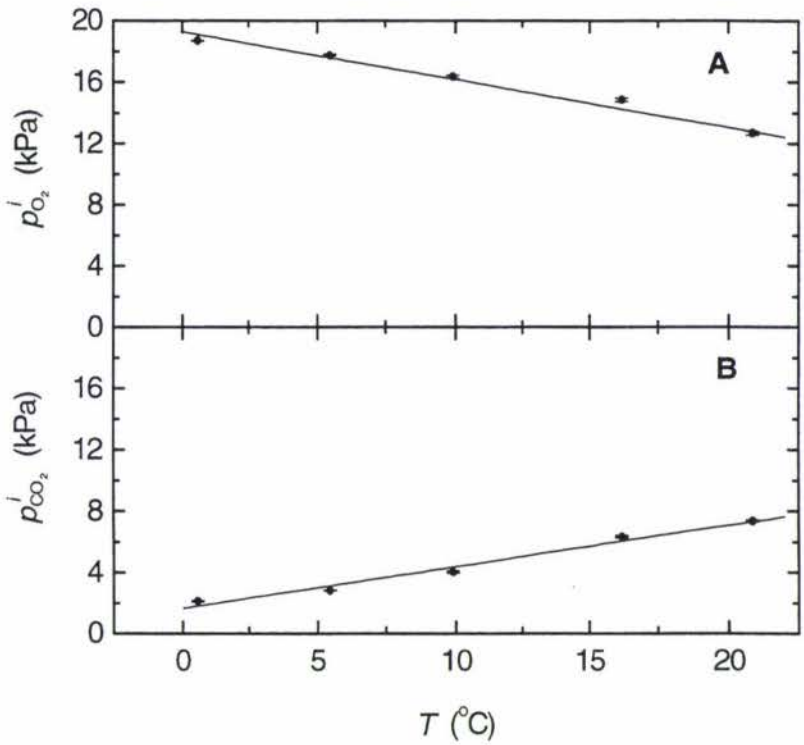

Figure 4.13 Variation in A, internal O_2 ($p^i_{O_2}$, Pa); and B, internal CO_2 partial pressures ($p^i_{CO_2}$, Pa) of 'Braeburn' apples held at between 0 and 20°C.

Solid lines were fitted by linear regression:

A: $p^i_{O_2} = (19.28 \pm 0.272) - (0.31 \pm 0.147) \cdot T$; $R^2 = 0.99$

B: $p^i_{CO_2} = (1.65 \pm 0.202) - (0.272 \pm 0.0109) \cdot T$; $R^2 = 0.99$

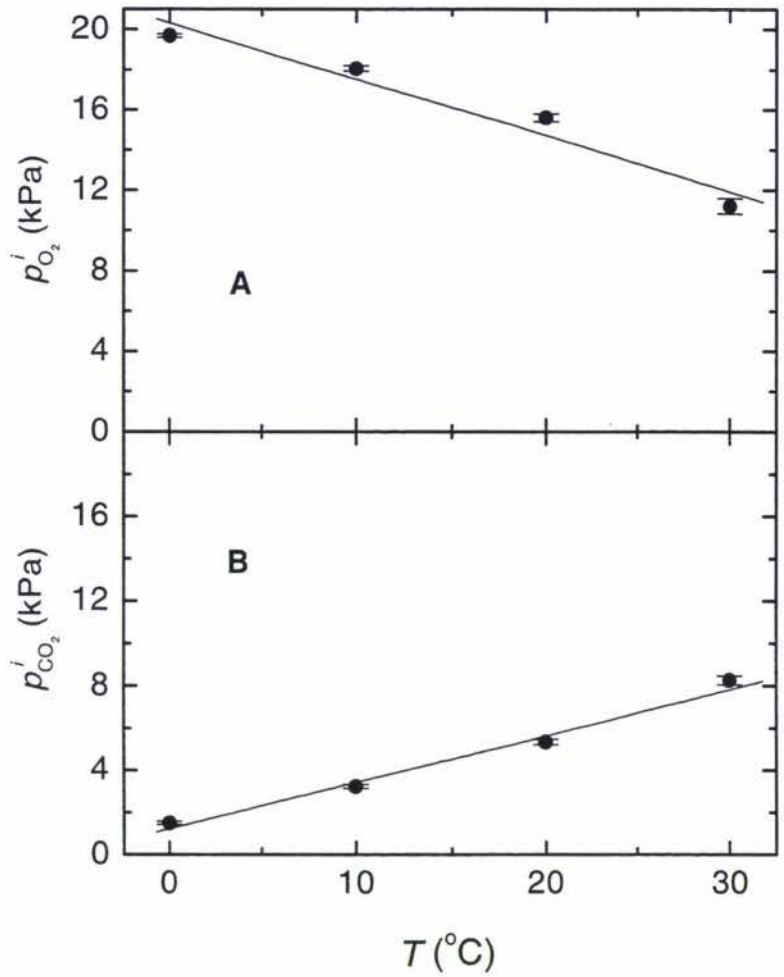

Figure 4.14 Variation in A, internal O_2 ($p^i_{O_2}$, Pa); and B, internal CO_2 partial pressures ($p^i_{CO_2}$, Pa) of 'Braeburn' apples held at between 0 and 30°C.

Solid lines were fitted by linear regression:

A: $p^i_{O_2} = (20.3 \pm 0.83) - (0.28 \pm 0.04) \cdot T$; $R^2 = 0.95$

B: $p^i_{CO_2} = (1.21 \pm 0.35) - (0.22 \pm 0.019) \cdot T$; $R^2 = 0.99$

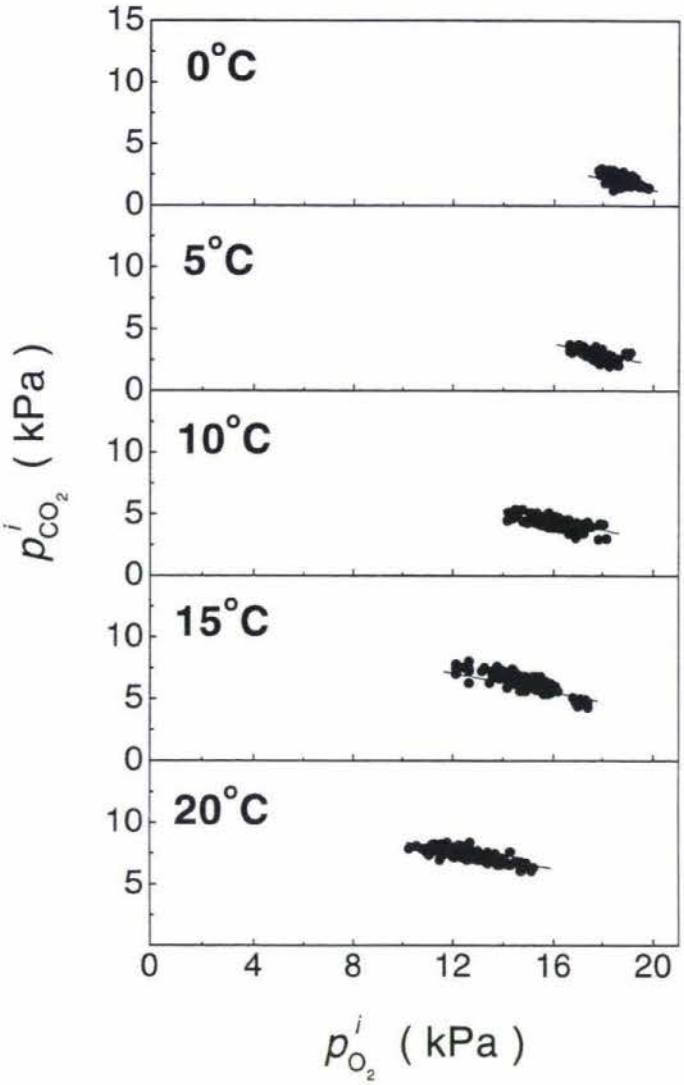

Figure 4.15 Relationships between internal O_2 and CO_2 partial pressures in 'Braeburn' apples held at between 0 and 20°C.

Solid lines were fitted by regression using Equation:

$$p^i_{CO_2} = (10.14 \pm 0.380) + (0.096 \pm 0.0124) \cdot T$$
$$- (0.448 \pm 0.0209) \cdot p^i_{O_2} + (0.00375 \pm 0.000667) \cdot T \cdot p^i_{O_2}$$

R^2=0.87.

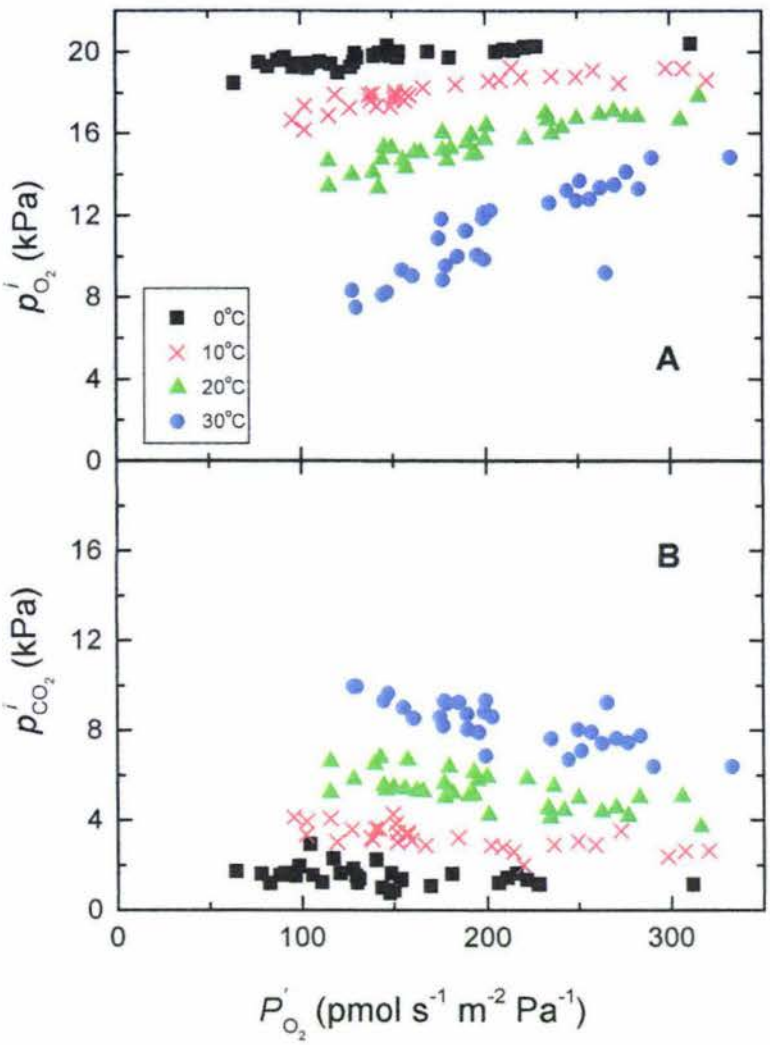

Figure 4.16 Relationships between and $P^{'}_{O_2}$ with A, internal O_2 ($p^{i}_{O_2}$, Pa); and B, internal CO_2 partial pressures ($p^{i}_{CO_2}$, Pa) of 'Braeburn' apples held at between 0 and 30°C.

4.4.2 Coated fruit

Internal oxygen was depressed by both types of coating treatment. However, the levels of $p^i_{O_2}$ in the different HPC treatments at each temperature were very close, and the average value of $p^i_{O_2}$ at 20°C was about 8 kPa (Fig. 4.17A). $p^i_{O_2}$ was gradually reduced by increased concentration of carnauba treatment with higher temperatures (Fig. 4.17B), with a low value of $p^i_{O_2}$ less than 1 kPa. At 0 and 5°C, $p^i_{O_2}$ was substantially reduced by higher concentration treatments (0.6, 0.8 and 1%) of carnauba coating. Fruit were close to being anaerobic for these three coating treatments at temperatures over 5°C.

Internal CO_2 partial pressures were greater at higher temperatures in all coating treatments (Figs 4.18A & B). Effects with coating HPC were small and, in many cases, not significant. The highest $p^i_{CO_2}$ was no more than 10 kPa. In fruit treated with carnauba coating, $p^i_{CO_2}$ was progressively increased at both higher coating concentrations and higher temperatures. At the highest temperature and coating concentration, internal CO_2 reached 18 kPa.

For a given level of treatment for both coatings, the extent of $p^i_{O_2}$ reduced was greater than that of $p^i_{CO_2}$ increased. Average values for $p^i_{O_2}$ treated with both coatings were spread more widely than $p^i_{CO_2}$ at each temperature.

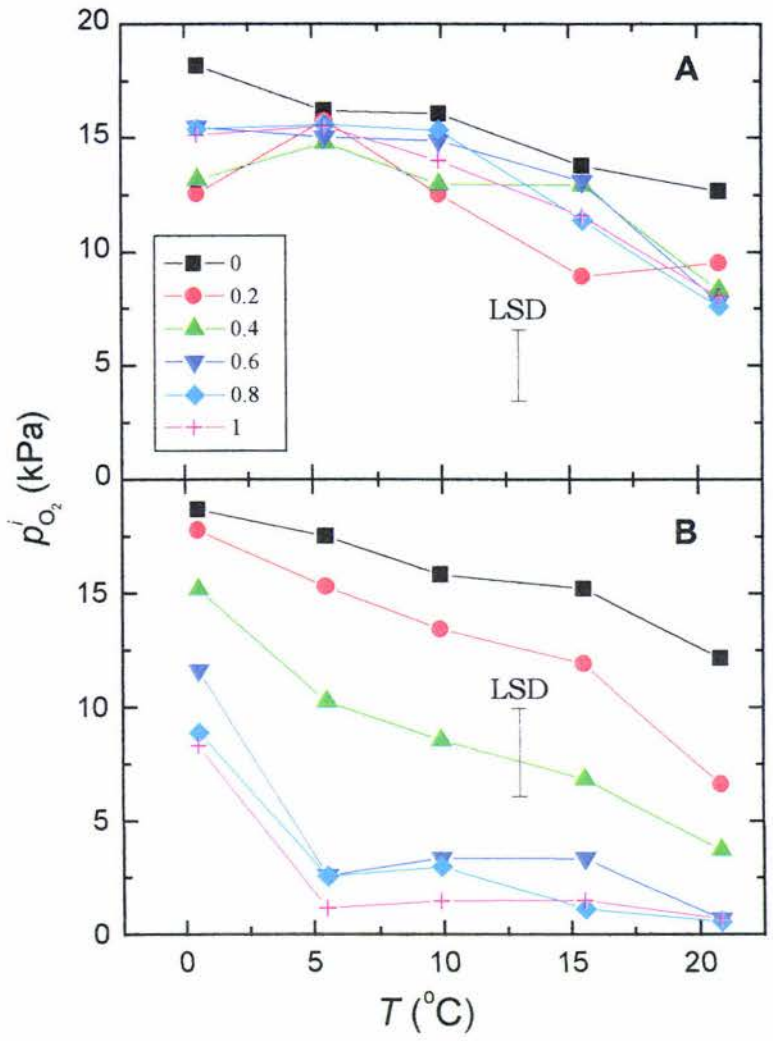

Figure 4.17 Variation in internal O_2 partial pressure ($p^i_{O_2}$, Pa) of 'Braeburn' apples associated with temperature A) HPC surface coatings at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times 2% HPC solution, and B) carnauba wax at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times commercial formulation.

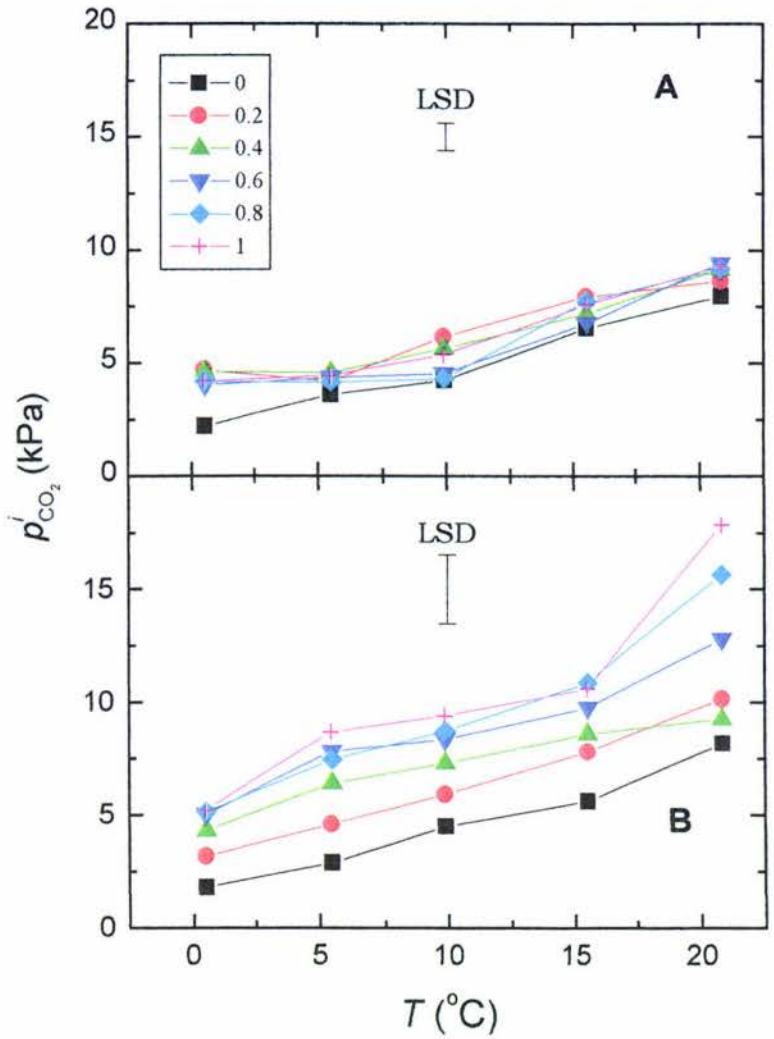

Figure 4.18 Variation in internal CO_2 partial pressure ($p^i_{CO_2}$, Pa) of 'Braeburn' apples associated with temperature A) HPC surface coatings at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times 2% HPC solution, and B) carnauba wax at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times commercial formulation.

4.5 Respiration and internal CO_2 vs internal O_2

Above about 1-2 kPa $p^i_{O_2}$, CO_2 production showed a positive relationship with $p^i_{O_2}$ (Fig 4.19). At these O_2 levels, the slope relating CO_2 production to internal O_2 was quite flat at low temperatures (0, 5 and 15°C) but, at higher temperatures, the slope became increasingly steep. Below 1-2 kPa O_2, CO_2 production increased abruptly, to an extent that was greater at higher temperatures. Average values for internal CO_2 increased as internal O_2 was decreased by the application of coatings for fruit held at all temperatures (Fig. 4.17 and 4.18). The higher values of internal O_2 shifted from about 19 kPa at 0°C to 14 kPa at 20°C. An upswing in the slope relating internal CO_2 to O_2 at low levels of internal O_2 became clear at higher temperatures.

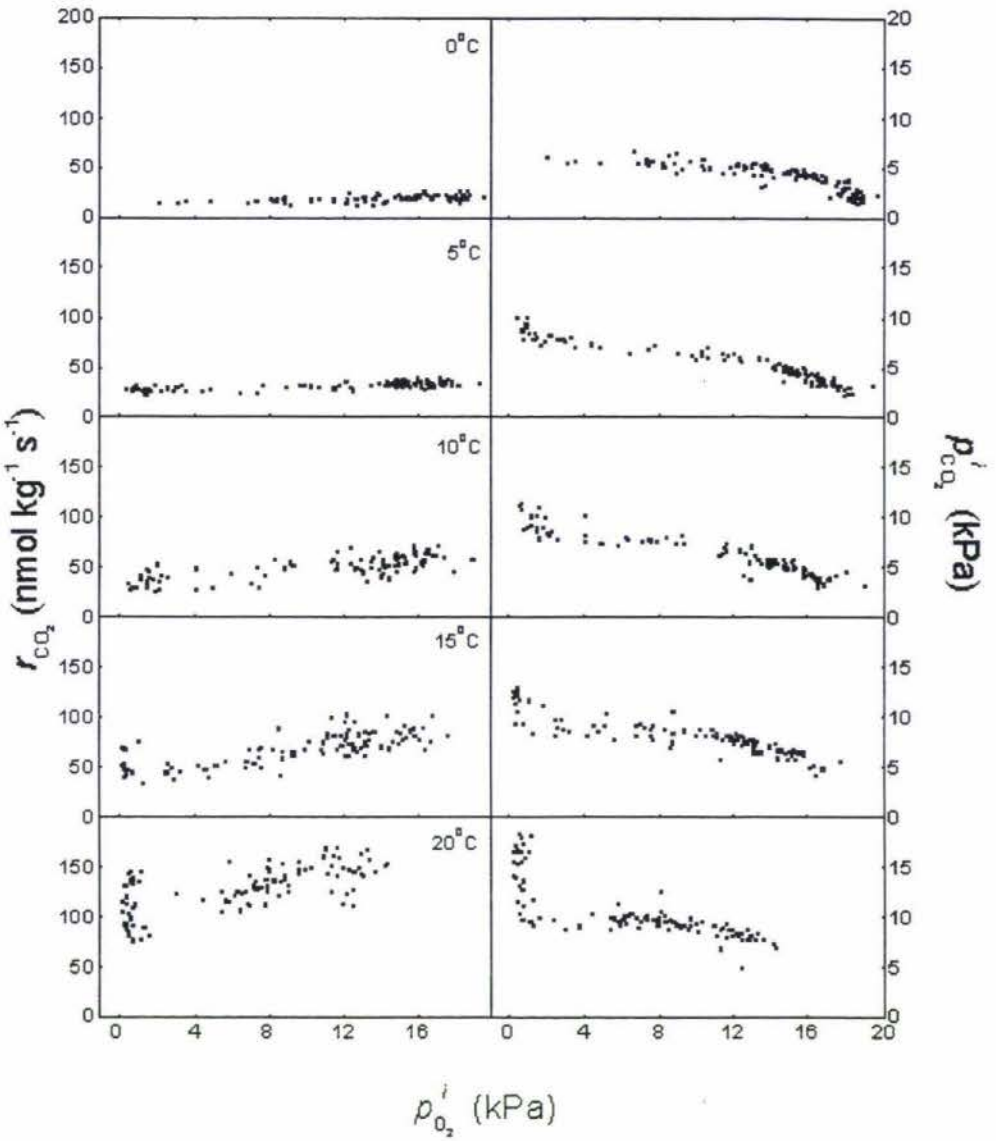

Figure 4.19 Variation in respiration rate (r_{CO_2}, mol kg^{-1} s^{-1}), internal CO_2 partial pressure ($p^i_{CO_2}$, Pa) of 'Braeburn' apples associated with temperature between 0 to 20°C with HPC surface coatings at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times 2% HPC solution, and carnauba wax at 0, 0.2, 0.4, 0.6, 0.8 and 1.0 times commercial formulation.

Chapter 5 Discussion

The effects of temperature and coating on respiration rate, skin permeance and their inter-relationships in determining internal atmospheres are summarised diagrammatically in figure 5.1.

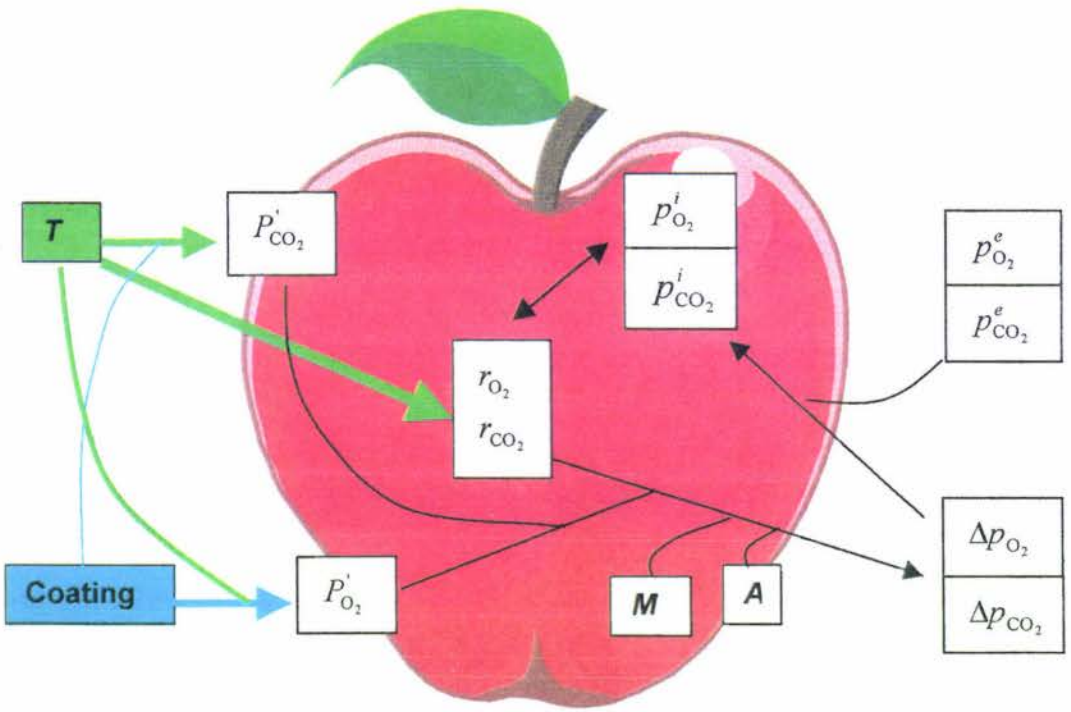

Figure 5.1 Schematic diagram for the effects of temperature and surface coaitngs on gas exchange and internal O_2 and CO_2. Arrow thickness is proportional to the magnitude of effect on permeance.

5.1 Porosity

Although effort was made to achieve uniform rates of injection for porosity measurements, there was inevitably some variation. The maximum pressure after injection of air would have depended on the speed of injection. A slow injection resulted in a low maximum pressure since some of the injected air escaped into the intercelluar spaces before the completion of injection. The gas injected into the cavity moved towards to the skin through the flesh. Thus, a rapid decline of pressure indicated a lesser resistance of the intercelluar spaces to gas movement. The curve after the quick decline represents a transfer of the route of air movement from the intercelluar spaces to the pores in the skin. The slope of the subsequent approximately straight line was a reflection of the slow movement of air through the skin, which might be explained by the Model I in Fig. 2.4. Fruit with larger amounts of pores would have had a steeper slope as air was able to escape more readily from the fruit.

The consistent effects of temperature on respiration rate (Fig. 4.6), skin permeance (Fig. 4.10) and internal partial pressures of O_2 and CO_2 (Figs. 4.14 & 4.16) at the different temperatures were very similar to those obtained in Experiment 1 at temperatures between 0 to 20°C. The porosity values of individual fruit were highly variable between temperatures (Fig. 4.4), which might have masked a real relationship between porosity with permeance and temperature. The variability might have arisen as a result of leakage through the septum or glue around the canulae, and variation in the speed of injecting gas. This indicates that some further perfection of the technique may be required before it could be assumed that the porosity of fruit was being accurately characterised. This might be achieved by improving the uniformity with which air

was injected into the fruit, paying particular attention to the prevention of blockage of the needle/canula used to make the injection.

5.2 Respiration

The curvilinear relationship identified between r_{CO_2} and temperature on non-coated (Figs. 4.5 & 4.6) and coated fruit (Fig. 4.7) was consistent with previously published reports on the effects of temperature on respiration rate (Ryall & Pentzer 1982; Johnson & Ertan 1983; Dadzie, 1992; Cameron et al., 1994). The quadratic model presented on non-coated fruit lacks the apparent mechanistic basis of the Arrhenius model used previously (Cameron et al. 1994) but provided a better fit to the data in this case. The estimated activation energy and Q_{10} values obtained with the alternative models (55 kJ mol^{-1}, 2.4 and 2.12, respectively) were somewhat less than previously published values for blueberries (Q_{10} = 3.2) but were slightly higher or lower than those for 'Cox's Orange Pippin' apples (Q_{10} = 2.2; Dadzie, 1992) and 'Braeburn' apples (Q_{10} = 2.28; Yearsley et al., 1997), but one of the values was identical to that of 'Cox's Orange Pippin' apples (Q_{10} = 2.44) used by Yearsley et al. (1997). Variation in these values indicates differences in the temperature sensitivity of respiration in these crops. These could relate to a wide range of inherent and environmental variables that affect the physiological state of the fruit at the time of measurement.

Depression of respiration with coating treatments was generally consistent with the proposition that respiration was limited by internal O_2 (Figs. 4.7 and 4.19) in a relationship similar to that described by other workers (Cameron et al. 1994; Dadzie et al. 1996; Peppelenbos et al. 1996). Respiration was suppressed more by higher concentrations of carnauba coating at higher temperatures, which is

correlated with the lower internal O_2 levels (Fig. 4.17B). However, at very low levels of internal O_2, rate of CO_2 production increased indicating that these fruit had started to ferment. The strength of upswing in both CO_2 production and internal CO_2 at very low internal O_2 became much stronger for fruit held at higher temperatures (Fig. 4.19), indicating that the tendency to ferment was greater at the higher temperatures, perhaps as a result of greater energy demand of the fruit tissues at the higher temperatures.

5.3 Permeance

On non-coated fruits, the slope of the relationship between P'_{CO_2} and P'_{O_2} was similar at every temperature (~0.6), which is somewhat lower than would be expected (0.87) on a theoretical basis if P'_{O_2} were pore dominated (Banks et al. 1997) and the relative ease of diffusion through the pores conformed to Graham's Law. Thus, for a fixed increment in P'_{O_2} associated with greater porosity of the skin there would be a somewhat smaller increment in P'_{CO_2} than would be predicted on theoretical grounds. The slope remained unchanged with change in temperature, which is consistent with the low activation energy for diffusion through pores (Cameron et al. 1994). However, there was as great an increase in P'_{O_2} as that in P'_{CO_2}, particularly for fruit with lower permeance values (Fig. 4.9) as temperature was increased from 0° to 20°C. This indicates that a significant proportion of total O_2 transfer occurs through the cuticle and is therefore more responsive to temperature than would be expected if the process was pore dominated. Likewise, the marked effect of temperature on the intercepts of plots of P'_{CO_2} against P'_{O_2} (Fig. 4.9), indicated a pronounced temperature dependence in permeance of the cuticle to CO_2, considerably greater than that for pores but less

than that for plastic films such as low density polyethylene (Cameron et al. 1994). In this study the data indicate that the simple model of skin permeance suggested by Banks et al. (1997), in which cuticular permeance to O_2 is negligible whereas that to CO_2 contributes a significant portion to P'_{CO_2}, may be an oversimplification in the case of 'Braeburn' apples. The substantial increase in lowest values for P'_{O_2} with temperature (Fig. 4.9) suggests that the cuticular route contribute substantially to O_2, as well as CO_2, exchange. The large variation in permeance indicates that individual fruit have widely differing numbers of effective lenticels on their surfaces. Such variation could be critically important in the relative sensitivities of individual fruit to modified atmosphere-induced disorders; 'Braeburn' apples are known to be particularly prone to such disorders (Elgar et al. 1997). The apparent jump in P'_{O_2} for coated fruit at high temperatures seems likely to have been artificial. This probably arose because a proportion of these fruit were fermenting (Fig. 4.19) and may not have been at steady state.

Based on the discussion above on the gas exchange routes, it is understandable that the depressions of permeance to O_2 by coating treatments were greater than those to CO_2 permeance (Figs. 4.11 and 4.12). This is in agreement with the proposal by Banks (1984b) and Ben-Yehoshua et al. (1985) that coatings affect permeance to gases that move predominantly through pores to a greater extent than those that move to a significant extent through the cuticle. The wider spread of P'_{O_2} values than those for P'_{CO_2} was also evidence of the differing rates of exchange for the two gases. The incremental suppression of permeance by higher concentrations of carnauba treatment suggests that the coating was adhering closely to the fruit surface. A higher proportion of pores would have been blocked by a higher concentrations of coating solution, though the extent of suppression achieved by the 0.6% coating left little scope for further reduction with the higher

carnauba coating concentrations. In contrast, HPC may act as a loosely adhering coating, with gas exchange through the coating film occurring in a similar way through a MA packaging film, as proposed in the model published by Banks et al. (1993b). The modification of skin permeance by coating with HPC may act by increasing the barrier properties of the coating rather than by blocking more pores. Thus, the continuity is much more important than the thickness of the coating film to gas exchange, which would have reduced the concentration dependence of permeance. The continuity of HPC coating on the fruit surface may be critically dependent upon formulation of the applied coating mixture.

5.4 Internal gases

The progressively more severe modification of internal atmosphere composition that developed at the higher temperatures (Figs. 4.13 - 4.16) was a reflection of the modest increase in permeance to each gas relative to the much greater increase in respiration rate. Through Eq.1.1, this effect can also be seen to have been responsible for the increasing spread of $p^i_{O_2}$ values developed at the higher temperatures (Fig. 4.15). The differential effects of temperature on permeance of the cuticle to gases resulted in a somewhat steeper slope of the relationship for O_2 than for CO2 (Figs. 4.13 & 4.14). For fruit with the most permeable skins (those with highest $p^i_{O_2}$ values at a given temperature), the sum of the two gas partial pressures was 21 kPa or slightly greater. These were the fruit in which gas exchange was pore dominated, values of P'_{O_2} exceeded those of P'_{CO_2}, and Δp_{CO_2} was greater than Δp_{O_2} because diffusivity of CO_2 through the gas phase is lower than that of O_2. In contrast, those fruit with less permeable skins had more of the total gas exchange occurring through the cuticle and as a result their value for

P'_{CO_2} exceeded that of P'_{O_2} (Banks et al. 1997). This effect was responsible for the flattening of slopes relating $p^i_{CO_2}$ and $p^i_{O_2}$ at lower values of $p^i_{O_2}$ and higher values of temperature (Fig. 4.15), the sum of $p^i_{CO_2}$ and $p^i_{O_2}$ becoming less than 21 kPa, and the differing slopes in the relationships presented in Figs. 4.13 to 4.15.

The extent of depression of internal O_2 became progressively greater at higher concentrations of carnauba treatment, an effect that was consistent with the change of respiration and P'_{O_2}. This effect was magnified by the higher temperatures which caused a higher increase of respiration than that of P'_{O_2}. The depression reached a maximum as fruit approached anaerobiosis. LOL for 'Braeburn' apples is changed with temperature (Yeasley et al., 1997). LOL is slightly higher at higher temperatures, thus fruit are likely reach LOL more readily for a given coating treatment at higher temperatures as a result of the higher rate of respiration and because the LOL is itself higher at high temperatures. Elevations of internal CO_2 were generally consistent with reductions in internal O_2 (Figs. 4.17 - 4.19). For fruit that were respiring aerobically and in which the respiratory quotient was approximately constant at a value of perhaps about one, internal O_2 was depressed more than elevation of internal CO_2 since coating would have modified skin permeance, reducing exchange through the pores on the fruit surface. The effect would also have caused a larger variation on the internal O_2 than internal CO_2 values. Thus, the extent of the depression of internal O_2 was generally higher than the elevation of internal CO_2 except in fruit treated with high concentration of coating coupled with high temperatures which resulted in the internal O_2 lower than LOL and fermentation occurred in these fruit. The RQ of the fermented fruit would have been greater than unity since $p^i_{CO_2}$ increased dramatically with suppression of internal O_2 close to zero. The low internal O_2 levels at which the upswing in both

CO_2 production and internal CO_2 started might be regraded as the LOL for these fruit and at 20°C, the LOL appeared to be about 1 kPa. The optimum internal O_2 to be targetted using coatings should be slightly higher than the LOL, say 3-4 kPa. Similar results have recently been reported in 'Granny Smith' apples treated with carboxymethylcellulose surface coatings (Banks et al., 1997).

Gradients are formed when the rate of O_2 uptake exceeds the ability of O_2 to diffuse through the tissue (Solomos, 1987). Flesh gradients in internal atmosphere composition may mean that temperature effects on permeance could have been underestimated. However, in the work by Rajapakse et al. (1990), such gradients accounted for only 11% of the total difference between core and external atmosphere composition on 'Braeburn' apples. Such an effect would be small relative to the very large variation in absolute permeance, which spanned almost an entire order of magnitude at a given temperature, indicating that the effects characterised here on non-coated fruit are likely to be close to actual changes.

Applied coatings on the surface of fruit augumented the variability in skin permeance and internal atmosphere composition, presumably due to the unpredictable percentage of pore blockage achieved by coating. The variability in internal atmosphere compostion was exacerbated by the increased temperature, which caused a large elevation of respiration with only a relatively small increase in skin permeance. Thus, application of coatings for their modified atmosphere benefits would be a risky undertaking unless uniform degrees of internal atmosphere modification can be developed. None of the coating treatment used in this study could porvide an optimum internal O_2 levels over the entire temperature range of 0 to 20°C.

5.5 Conclusions

Respiration rate was quadratically increased with increasing temperature between 0 to 20 or 30°C on non-coated fruit, whilst the skin permeance increased much less. Increases in respiration rate with both surface coating treatments at elevated temperatures between 0 and 20°C were greater than analagous increases in the fruit's skin permeance to gases. There was no relationship between porosity and temperature, though this posibility has not been ruled out by this work because of variability in porosity estimates of individual fruit. Carnauba coating was more effective than HPC in decreasing skin permeance at each temperature. The extent of suppression of skin permeance was proportional to the concentration of carnauba coating solutions. This led to a progressive decline in O_2, and an increase in CO_2 levels in both the non-coated and coated fruit's internal atmosphere at higher temperatures.

Evidence presented here casts doubt in the proposition route for O_2 diffusion through the skin of control fruit is pore dominated. Rather the diffusion of both O_2 and CO_2 appears to occur through the cuticle to an extent, which must affected by integrity of the cuticle and temperature at which fruit are kept. The effect of carnauba coating in reducing gas exchange seems likely to occur through the blocking of pores. In contrast, the effects of HPC were consistent with those material held only loosely to the fruit surface. Both carnauba coating treatment and temperature had marked effects on internal gases, while the effect exerted by HPC treatment was considerably less dramatic. Low concentrations of carnauba coating achieved low internal O_2 levels at higher temperatures had only slight modification effects at low temperatures. Higher concentrations that achieved MA

benefit at low temperatures resulted in fermentation at higher temperatures. Given the natural variability in skin permeance, and the exacerbating effects of coating treatment and temperature, surface coatings appear unlikely to provide a reliable and safe means of achieving modified atmosphere benefits in 'Braeburn' apples.

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