The effect of temperature on gas relations in MA packages for capsicums (Capsicum annuum L., cv. Tasty): an integrated approach

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Abstract

A range of gas conditions was generated by packing individual capsicums (green ‘Tasty’ bell peppers, Capsicum annuum L.) in packages with different areas of permeable low-density polyethylene film (0.0006–0.48 m²) at four different temperatures (0, 12, 20 and 30°C). Steady-state O₂ and CO₂ partial pressures in the package were used to calculate rates of O₂ uptake and CO₂ production. The results were analysed applying a mechanistic model approach. The applied film resulted in temperature stable gas conditions inside the packages, as the temperature dependence of the permeability of the film was close to the temperature dependence of capsicum respiration. Capsicums showed a slight degree of fermentation in packages with a small film area. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Bell peppers; Capsicum annuum; Fermentation; Gas exchange; MA packaging; Modelling; Respiration; Temperature

1. Introduction

The accumulation of CO₂ and depletion of O₂ to beneficial levels by the application of modified atmosphere packaging (MA packaging) is steadily becoming more important as a treatment to prolong the storage life of perishable commodities (Beaudry and Lakakul, 1995; Christie et al., 1995; Lerdthanangkul and Krochta, 1996; Merts, 1996).

MA packaging can be difficult to implement commercially because of the range of variation in produce respiration rates and the inevitable temperature changes throughout the postharvest chain. Produce held in MA packages may undergo fermentation and generate off-flavours.
if temperature increases (Kader et al., 1989; Cameron et al., 1995). MA packaging has been shown to prolong shelf life of green capsicums (*Capsicum annuum* L.) (Bussel and Kenigsberger, 1975; Hughes et al., 1981; Meir et al., 1995; Lerdthanangkul and Krochta, 1996), but little has been published on the possibilities and limitations of MA packaging for bell peppers.

Gas permeation rate through the film, product respiration, and CO₂ and O₂ levels within the MA package change dynamically with time and temperature. MA packaging models have been developed, that describe the O₂ and CO₂ levels in polymeric film packages as affected by film permeability, temperature and the rate of gas exchange of the stored product (Beaudry et al., 1992; Cameron et al., 1994; Merts, 1996; Hertog et al., 1997a, 1998). The general applicability of such predictive models strongly depends on the completeness of information on how, at different temperatures, gas exchange depends on the fruit’s internal atmosphere (Banks et al., 1994) and on how this, in its turn, depends on the gas conditions inside the package.

Although the effect of O₂ on fruit respiration rate is consistent in its general appearance and can be successfully described applying Michaelis–Menten kinetics (Chevillotte, 1973; Cameron et al., 1994; Dadzie et al., 1996) the effect of CO₂ is more difficult to generalise due to the less consistent responses reported. For capsicum, the possible effect of CO₂ on respiration has not yet been reported.

Green capsicums have been reported to respond very favorably to seal-packaging techniques (Ben-Yehoshua et al., 1995). Since they do not exhibit marked ripening and climacteric processes (Ben-Yehoshua et al., 1995) they are expected to respond to MA packaging in a stable and predictable way.

In this study, we have characterised the effect of temperature on film permeability, respiration rate and atmosphere compositions inside the package and inside the cavity of the packed capsicums. We have used these data to develop a model that describes the complex system of MA packed capsicums.

### 2. Materials and methods

#### 2.1. Film permeability

The permeability of a 60 μm thick low-density polyethylene (LDPE) film (Transpak, Auckland, New Zealand) at 0, 5, 10, 15, 20, 25, 30 and 35°C (±0.5°C) was determined using a continuous flow system (Merts, 1996) with the film mounted in a small PVC permeability cell. Eight samples from the outlet stream were analysed for each of three replicate runs.

At steady state, the outflow of O₂ and CO₂ should equal their diffusion through the film resulting in:

\[
F_{\text{out}} \cdot c_{i_{\text{out}}} \cdot \frac{P_{\text{atm}}}{R \cdot T} = P_{i_{\text{film}}} \cdot \frac{A_{\text{film}}}{\Delta X_{\text{film}}} \cdot (c_{i_{\text{in}}} - c_{i_{\text{out}}}) \cdot P_{\text{atm}}
\]

were \(F_{\text{out}}\) represents rate of outflow (m³·s⁻¹), \(c_{i_{\text{out}}}\) concentration of gas i (either O₂ or CO₂) in the outlet stream (m³·m⁻³), \(P_{\text{atm}}\) atmospheric pressure (Pa), \(R\) the universal gas constant (8.314 J·mol⁻¹·K⁻¹), \(T\) temperature of the air (K), \(P_{i_{\text{film}}}\) permeability of the film to gas i (mol·s⁻¹·m⁻¹·Pa⁻¹), \(A_{\text{film}}\) exposed area of the film (m²), \(\Delta X_{\text{film}}\) thickness of the film (m) and \(c_{i_{\text{in}}}\) concentration of gas i in the inlet stream (m³·m⁻³). Solving for \(P_{i_{\text{film}}}\) results in:

\[
P_{i_{\text{film}}} = \frac{F_{\text{out}} \cdot c_{i_{\text{out}}} \cdot \Delta X_{\text{film}}}{A_{\text{film}} \cdot (c_{i_{\text{in}}} - c_{i_{\text{out}}}) \cdot R \cdot T}
\]

which was used for calculating film permeability to O₂ and CO₂.

#### 2.2. Packaging experiment

One hundred and twenty freshly harvested, mature, greenhouse grown green bell peppers (*Capsicum annuum* L., cv. Tasty) of uniform size were obtained directly from a local grower in Palmerston North, New Zealand.

The initial respiration rate of each individual fruit at 20°C was determined by sealing them in a 1.1-l container for 1.5 h, producing an increase in CO₂ of up to about 0.5 kPa. Before sealing into packages, cannulae (14 gauge stainless steel needles, cut down to 2-cm length) were inserted...
through the fruit wall into the cavity of the fruit. The connection between cannula and skin was sealed gas-tight using epoxy adhesive (5 min cure; Areldite®, Ciba–Geigy, Auckland, New Zealand). Once the cannulae were attached, fruit were equilibrated for 24 h overnight and steady state internal gas conditions at 20°C in air were determined by sampling 100 µl from the fruit cavities through the cannulae.

The fruit were randomly divided into four groups of 30, one lot for each of the four temperatures (0, 12, 20 and 30°C). Each fruit was individually packed. Within each temperature treatment, 15 packages had soda lime added to remove all CO₂, while the remaining 15 packages had no soda lime added to allow accumulation of CO₂. Within each soda lime treatment the 15 packages all had different areas of permeable film exposed (0.806, 0.0018, 0.005, 0.015, 0.025, 0.034, 0.044, 0.054, 0.068, 0.088, 0.096, 0.108, 0.196, 0.240 or 0.486 m²). The remaining package area consisted of impermeable plasticised foil.

The cannulae on the fruit were connected to sampling ports on the outer surface of the packages using flexible tubing (internal diameter: 0.5 mm, length: 7 cm). Through these, internal atmospheres of the capsicum cavities could be monitored. Another sampling port was added to each package for sampling the O₂ and CO₂ levels in the package. Silicone sealant (Window and Glass silicone, acid cured, Selleys Chemical Company Ltd., Auckland, NZ) was used to seal all connections on the surface of each package. Mesh was added in each package between fruit and film to ensure the complete area of the package film being available for gas exchange. To promote rapid equilibration package volumes were reduced by reducing the headspace. At steady state, 100 ml samples were taken to determine the gas conditions inside the cavity and inside the bag. Given that, at steady state, gas exchange equals the diffusion through the film, O₂ consumption (\( r_{O_2} \), mol·kg\(^{-1}\)·s\(^{-1}\)) and CO₂ production (\( r_{CO_2} \), mol·kg\(^{-1}\)·s\(^{-1}\)) could be calculated as:

\[
r_{O_2} = P_{O_2} \cdot \frac{A_{film}}{\Delta X_{film}} \cdot (p_{O_2}^{atm} - p_{O_2}^{pkg})/M
\]

\[
r_{CO_2} = P_{CO_2} \cdot \frac{A_{film}}{\Delta X_{film}} \cdot (p_{CO_2}^{atm} - p_{CO_2}^{pkg})/M
\]

where: \( M \) is fruit mass (kg), \( p_{O_2}^{pkg} \) and \( p_{O_2}^{atm} \) the oxygen partial pressures (Pa) and \( p_{CO_2}^{pkg} \) and \( p_{CO_2}^{atm} \) is the CO₂ partial pressures (Pa) in the package and in the surrounding atmosphere.

2.3. Additional respiration measurements

A second batch of freshly harvested, mature, greenhouse-grown green bell peppers (Capsicum annuum L., cv. Tasty) was obtained from the same local grower in Palmerston North, New Zealand.

Respiration rates of 30 individual fruit were determined at 20°C by measuring the accumulation of CO₂. Subsequently, they were divided into three groups of ten fruit each, for measurements at either 0, 12 or 30°C. The respiration rate of each fruit was again measured individually. The times for which each fruit was sealed in the 1.1-l jar were 4.5, 2.5, 1.5 and 0.5 h at 0, 12, 20 and 30°C, respectively.

2.4. Gas analysis

All gas samples were analysed using an O₂ electrode (Citicell C/S type, City Technology Ltd., London, UK) in series with a miniature infra-red CO₂ transducer (Analytical Development Company, Hoddesdon, UK), with O₂-free N₂ as carrier gas (flow rate 35 ml·min\(^{-1}\)). Output signals were analysed using HP integrators (Hewlett Packard, model 3396A). Commercially prepared standards were used for calibration of the gas analysers. Ambient pressure data were collected with a pressure transducer (Barigo Electronic Altimeter, Barigo Barometerfabrik GmbH, D-7730 Villingen Schwenningen).

2.5. Data analysis

All data collected were expressed according to the units proposed by Banks et al. (1995). The data were analysed statistically with the iterative non-linear regression routine of Statistical Analysis System (SAS, 1992). The data on film permeability were analysed using the temperature dependence according Arrhenius’ law from Eq.
The data from the packaging experiment were analysed together in one run, simultaneously using temperature, film area, $p_{\text{air}}$ and $p_{\text{CO}_2}^\text{film}$ as independent variables and $r_{\text{O}_2}$, $r_{\text{CO}_2}$, $p_{\text{O}_2}^\text{cav}$ and $p_{\text{CO}_2}^\text{cav}$ as dependent variables using the model formulation from Eqs. (14), (15), (8) and (9) with the temperature dependence according to Arrhenius' law (Eq. (10)) applied to $r_{\text{O}_2}^\text{max}$, $r_{\text{CO}_2}^\text{max}$, $P_{\text{O}_2}^\text{film}$ and $P_{\text{CO}_2}^\text{film}$ (multi-response, multivariate, non-linear regression analysis). The data on temperature dependence of the additional respiration measurements were analysed using the temperature dependence according to Arrhenius' law (Eq. (10)). The reference temperature for Arrhenius’ law was in all cases fixed at 15°C (288.15 K). The non-linear equations were applied directly, without transformation to data or equations.

3. Model development

3.1. Gas exchange

The $O_2$ uptake of the packed fruit was modelled as a function of $p_{\text{O}_2}^\text{cav}$ applying Michaelis–Menten kinetics as introduced by Chevillotte (1973):

$$r_{\text{O}_2} = \frac{r_{\text{O}_2}^\text{max} \cdot p_{\text{O}_2}^\text{cav}}{(K_{\text{O}_2} + p_{\text{O}_2}^\text{cav})}$$  \hspace{1cm} (5)

where $r_{\text{O}_2}^\text{max}$ is the maximum $O_2$ consumption rate (mol·kg$^{-1}$·s$^{-1}$) unconstrained by $O_2$ availability, $K_{\text{O}_2}$ is the Michaelis constant for $O_2$ consumption (Pa) and $p_{\text{O}_2}^\text{cav}$ is the $O_2$ partial pressure (Pa) in the cavity of the capsicum.

The $CO_2$ production of the fruit was modelled as described by Peppelenbos et al. (1996), taking into account $CO_2$ coming from both oxidative and fermentative processes:

$$r_{\text{CO}_2} = RQ_{\text{ox}} \cdot r_{\text{O}_2} + \frac{r_{\text{CO}_2}^\text{max} \cdot p_{\text{CO}_2}^\text{cav}}{K_{\text{CO}_2} + p_{\text{CO}_2}^\text{cav}}$$  \hspace{1cm} (6)

where $RQ_{\text{ox}}$ represents the respiration quotient (ratio of $CO_2$ production to $O_2$ consumption) for oxidative respiration, $r_{\text{CO}_2}^\text{max}$ is the maximum fermentative $CO_2$ production rate (mol·kg$^{-1}$·s$^{-1}$) and $K_{\text{CO}_2}(0)$ is the Michaelis constant for the inhibition of this fermentative $CO_2$ production by $O_2$ (Pa).

As the Michaelis–Menten approach is a simplified representation of a more complex biochemical and physiological process including several diffusion steps, the constants $K_{\text{O}_2}$ and $K_{\text{O}_2}(0)$ are in fact apparent $K_{\text{ms}}$ instead of pure Michaelis constants.

3.2. Package conditions

At steady state, the rate of $O_2$ diffusion through the packing film equals the rate of $O_2$ diffusion into the fruit, which equals the rate of $O_2$ consumption due to respiration, resulting in:

$$\frac{p_{\text{O}_2}^\text{max} \cdot p_{\text{O}_2}^\text{cav}}{K_{\text{O}_2} + p_{\text{O}_2}^\text{cav}} \cdot M = \frac{P_{\text{O}_2}^\text{film} \cdot \Delta X_{\text{film}}}{(p_{\text{O}_2}^\text{atm} - p_{\text{O}_2}^\text{pkg})}$$

with $P_{\text{fruit}}$ the fruit permeance for $O_2$ (mol·s$^{-1}$·m$^{-2}$·Pa$^{-1}$) and $A_{\text{fruit}}$, the diffusion area (m$^2$). Using these relationships, $p_{\text{O}_2}^\text{cav}$ can be expressed as a function of $p_{\text{O}_2}^\text{atm}$:

$$p_{\text{O}_2}^\text{cav} = \frac{1}{2} \cdot a + \frac{1}{2} \cdot a^2 + 4 \cdot K_{\text{O}_2} \cdot p_{\text{O}_2}^\text{atm}$$  \hspace{1cm} (8)

with: $a = p_{\text{O}_2}^\text{atm} - K_{\text{O}_2}$

$$- r_{\text{O}_2}^\text{max} \cdot M \cdot \left( \frac{1}{P_{\text{O}_2}^\text{film} \cdot A_{\text{film}}} \right)$$

$$+ \frac{\Delta X_{\text{film}}}{P_{\text{O}_2}^\text{film} \cdot A_{\text{film}}}$$

A comparable approach is taken to express $p_{\text{CO}_2}^\text{cav}$ as a function of $p_{\text{CO}_2}^\text{atm}$ and $p_{\text{CO}_2}^\text{cav}$ at steady state, resulting in:

$$p_{\text{CO}_2}^\text{cav} = p_{\text{CO}_2}^\text{atm}$$

$$+ \left( RQ_{\text{ox}} \cdot r_{\text{O}_2} + M \cdot r_{\text{CO}_2}^\text{max} \cdot K_{\text{CO}_2}(0) + p_{\text{CO}_2}^\text{cav} \right)$$

$$\cdot \left( \frac{1}{P_{\text{CO}_2}^\text{film} \cdot A_{\text{film}}} + \frac{\Delta X_{\text{film}}}{P_{\text{CO}_2}^\text{film} \cdot A_{\text{film}}} \right)$$  \hspace{1cm} (9)

with $P_{\text{fruit}}$ the fruit permeance for $CO_2$ (mol·s$^{-1}$·m$^{-2}$·Pa$^{-1}$).

Equivalent approaches were applied by Dadzie et al. (1996) describing internal atmospheres of unpacked apples, Banks et al. (1993) describing internal atmospheres in waxed apples, and...
3.3. Temperature dependence

Temperature influences the system through both its effects on gas exchange and film permeability. In both cases the effect of temperature can be described according to Arrhenius’ law:

\[ k = k_{\text{ref}} \cdot e^{\frac{E_a}{R} \left( \frac{1}{T \text{ref}} - \frac{1}{T} \right)} \]  

(10)

where the energy of activation \( E_a \) (J·mol\(^{-1}\)) expresses the dependence of a given rate \( k \) (exact unit depends on the rate) on temperature \( T \) (K). The parameter \( k_{\text{ref}} \) (exact unit depends on the rate) is the rate at an arbitrarily chosen reference temperature \( T_{\text{ref}} \) (K). In accordance with Hertog et al. (1998) it was assumed that the temperature effect on respiration can be accurately described by solely applying the Arrhenius equation to the parameters \( r_{\text{O}_2}^{\text{max}} \) and \( r_{\text{CO}_2}^{\text{max}} \), assuming \( K_{\text{O}_2} \) and \( K_{\text{O}_2,0} \) being relatively temperature independent.

For packaging films it is also generally accepted to express permeability as a function of temperature according to Arrhenius’ law (Beaudry et al., 1992; Exama et al., 1993; Cameron et al., 1994). The permeability of the fruit was considered reasonably temperature independent as, with capsicums, most of the diffusion takes place in air through gaps underneath the stem plate into the central cavity (De Vries et al., 1996; personal communications N.H. Banks and J.P. Bower).

3.4. Fruit-to-fruit variation

As all the experimental work was done on individually packed fruit, large variations were expected due to fruit-to-fruit variation in both gas exchange and fruit permeability. Mechanistic models enable discrimination between those parameters likely to vary between individual fruit and those that would likely be constant for all fruit. Variation in experimental data has previously been handled by relating it to specific parameters in models that include cultivar, batch and individual fruit effects (Hertog et al., 1997b; Tijskens et al., 1997; Hertog et al., 1999).

Fruit permeance \( P_{O_2}^{\text{fruit}} \) would probably vary substantially between fruit. In addition to this, the diffusion area \( A_{\text{fruit}} \) would vary between the fruit. As these features are quite hard to measure directly, the initial measurements in air at 20°C made before packing, were used to determine the combination of these two parameters for each of the individual fruit. This was done by analogy to Eqs. (3) and (4) assuming a steady state between respiration and diffusion resulting in:

\[ P_{O_2}^{\text{fruit}} \cdot A_{\text{fruit}} = \frac{r_{\text{O}_2}}{P_{\text{O}_2}^{\text{ox}} - P_{\text{O}_2}^{\text{atm}}} \]  

(11)

\[ P_{\text{CO}_2}^{\text{fruit}} \cdot A_{\text{fruit}} = \frac{r_{\text{CO}_2}^{\text{max}} \cdot M}{P_{\text{CO}_2}^{\text{atm}} - P_{\text{CO}_2}^{\text{ox}}} \]  

(12)

The meaning of the parameters from Eqs. (5) and (6) describing respiration, provides useful insight into the likely sources of variation in fruit gas exchange. The Michaelis constants \( K_{\text{O}_2} \) and \( K_{\text{O}_2,0} \) are based on enzymatic reaction rate constants while the maximum rates \( r_{\text{O}_2}^{\text{max}} \) and \( r_{\text{CO}_2}^{\text{max}} \) are also related to the amount of enzymes present (Hertog et al., 1998). Assuming that pure rate constants are intrinsic attributes of enzymes, and at the same time realising that the amount of enzyme present would vary between fruit, supports the conclusion that differences between individual capsicums would most likely result from differences in \( r_{\text{O}_2}^{\text{max}} \) and \( r_{\text{CO}_2}^{\text{max}} \). The rate constants \( K_{\text{O}_2} \) and \( K_{\text{O}_2,0} \) can be safely assumed constant for a given capsicum cultivar. Based on this reasoning, the relative respiration of the individual fruit \( r_{\text{O}_2}^{\text{fruit}} \) was determined relative to the mean respiration \( r_{\text{O}_2} \), using the initial measurements in air at 20°C before packing as:

\[ r_{\text{O}_2}^{\text{fruit}} = \frac{r_{\text{O}_2}}{r_{\text{O}_2}} \]  

(13)

This relative respiration was subsequently introduced into the formulation of gas exchange (Eqs. (5) and (6)), to take into account the variation between fruit, resulting in:

\[ r_{\text{O}_2} = \frac{r_{\text{O}_2}^{\text{fruit}} \cdot r_{\text{O}_2}^{\text{max}} \cdot P_{\text{O}_2}^{\text{ox}}}{(K_{\text{O}_2} + P_{\text{O}_2}^{\text{atm}})} \]  

(14)

\[ r_{\text{CO}_2} = RQ_{\text{ox}} \cdot r_{\text{O}_2} + \frac{r_{\text{O}_2}^{\text{fruit}} \cdot r_{\text{CO}_2}^{\text{max}}}{1 + \frac{P_{\text{CO}_2}^{\text{atm}}}{K_{\text{O}_2,0}}} \]  

(15)
4. Results and discussion

4.1. Film permeability

The permeability of the LDPE film used in the packaging experiment to O$_2$ and CO$_2$ increased exponentially with increasing temperature (Fig. 1). The estimates for activation energy ($E_{a_{O_2}}$, $E_{a_{CO_2}}$) and permeability at reference temperature ($P_{O_2}^{film}$, $P_{CO_2}^{film}$) for O$_2$ and CO$_2$ are given in Table 1. The two activation energies appeared to be very similar. The parameter values were consistent with data reported earlier by Donhowe and Fennema (1994) and Exama et al. (1993), although the permeability at the reference temperature was about three times higher than reported by Beaudry et al. (1992).

4.2. Packaging experiment

The time needed to achieve steady-state conditions in the packages was longer at lower storage temperatures. For the packages with the smallest areas of permeable film, steady state O$_2$ and CO$_2$ partial pressures were reached after 11, 14, 27 and 32 days at 30, 20, 12 and 0°C, respectively. This seems fairly long, but is in agreement with what is expected based on the film permeability, the respiration rate of bell peppers and the dimensions of the packages.

At steady state, the measurements in the packaging experiment showed an almost one-to-one relationship between the gas conditions in the pack ($p_{O_2}^{pkg}$ and $p_{CO_2}^{pkg}$) and in the cavity of the fruit ($p_{O_2}^{cav}$ and $p_{CO_2}^{cav}$; data not shown). This was due to the relatively large permeance of the fruit’s stem plate that, on average, was 0.014 nmol·s$^{-1}$·Pa$^{-1}$ for both O$_2$ and CO$_2$, comparable to the permeance of a 0.25 m$^2$ LDPE bag at 20°C.

As a consequence of the one-to-one relationship between the gas conditions in the pack and in the cavity of the fruit, plots of other gas variables as a function of composition of the cavity atmosphere were a virtual copy of those in terms of composition of the package atmosphere. As the set of experimental data on package atmospheres was the most complete, all results are shown in terms of package atmosphere composition.

The soda lime treatment was applied to elucidate the possible effect of CO$_2$ on gas exchange. However, there was no evidence that the CO$_2$ levels up to 25 kPa that occurred in the experiments had any effect on the gas exchange of the capsicums (data not shown). As a result, only the straightforward model formulation for gas exchange without CO$_2$ inhibition was applied.

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Table 1

Parameter estimates and their standard errors (S.E.) resulting from the non-linear regression analysis of the data on the effect of temperature on permeation of O$_2$ and CO$_2$ through the LDPE film used in this study

<table>
<thead>
<tr>
<th>Gas (i)</th>
<th>$P_{i, ref}^{film}$ (S.E.)$^b$</th>
<th>$E_{a_{i}}^{film}$ (S.E.)$^c$</th>
<th>$R_{adj}^2$</th>
<th>n$^d$</th>
<th>n$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>1.46 (4.6)</td>
<td>30450 (7.3)</td>
<td>97.1</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>4.25 (3.4)</td>
<td>31751 (5.0)</td>
<td>98.5</td>
<td>46</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The standard errors (S.E.) are expressed as a percentage, relative to the estimated values.

$^b$ $P_{i, ref}^{film}$ is the permeability ($10^{-15}$ mol·s$^{-1}$·m·m$^{-2}$·Pa$^{-1}$) of the film to gas i at reference temperature $T_{ref}$ ($=15^\circ$C).

$^c$ $E_{a_{i}}^{film}$ is the energy of activation (J·mol$^{-1}$) of the permeability $P_{i}^{film}$.

$^d$ $R_{adj}^2$ is the percentage variance accounted for.

$^e$ n is the number of observations.
Both O₂ uptake and CO₂ production decreased in response to decreasing temperature and decreasing steady state $p_{O_2}^{kg}$ (Fig. 2). Increasing temperature from 0 to 30°C resulted in a threefold increase in respiration. This was due to the temperature effect on $r_{O_2}^{max}$ and $r_{CO_2}^{max}$ as there was no evidence for a change in $K_{mO_2}$ with increasing temperature. From Fig. 2, there is no clear indication that capsicum exhibits substantial fermentation at low O₂ levels as there was no visible Pasteur effect. However, looking at the RQ for the different temperatures (Fig. 3) shows an increase in RQ at O₂ levels below 2 kPa revealing a substantial fermentation relative to the aerobic respiration.

The different O₂ and CO₂ levels measured in the package atmospheres, resulted from the different film areas applied coupled with the natural variation in the gas exchange characteristics of the packed fruit (Fig. 4). Large areas resulted in almost atmospheric conditions inside the packages. By reducing the film area, O₂ levels dropped towards 0 kPa while CO₂ levels first increased to about 5–7 kPa. This accumulating CO₂ mainly originated from oxidative respiration. At the extremely small packaging areas (0.0018 and 0.806 m²), CO₂ levels increased even more (up to 20–25 kPa) due to the slight fermentation present. Although the absolute fermentation is low (as indicated by Fig. 2), the fermentation indicated by the shift in RQ (Fig. 3) was enough to generate high CO₂ levels when the product was packed with small permeable film areas. Film areas larger than 0.075 m² result in O₂ levels above 10 kPa, not effectively inhibiting the gas exchange of packed capsicums (Fig. 2).

The multi-response, multivariate, non-linear regression analysis of the packaging data resulted in the parameter estimates as shown in Table 2 and the fitted lines from Figs. 2 and 4. During the iterative process of non-linear regression the parameters on fermentation were not clearly defined due to lack of data on fermentation. As the packs with the smallest film areas were defin-
Fig. 4. Steady-state gas conditions (A–D: $p_{O_2}^{pkg}$; E–H: $p_{CO_2}^{pkg}$) inside MA packages of individually packed capsicums using different film areas. Packs were held at temperatures ranging from 0 to 30°C. Symbols are measured values. Lines were plotted according the model fitted using the parameter values from Table 2.

In spite of the clear temperature effect on film permeability (Fig. 1) and gas exchange (Fig. 2), the gas conditions inside the package (Fig. 4) were almost insensitive to temperature between 0 and 30°C. This is explained by the fact that the energy of activation for capsicum respiration (Table 2) was very close to the energies of activation for film permeabilities to the respiratory gases (Table 1). As a result, capsicums packed in the LDPE film tested in these experiments would be stable and reliable in terms of gas conditions, irrespective of any temperature changes. This situation is in marked contrast to that described for blueberries (Beaudry et al., 1992; Cameron et al., 1994) in which package atmosphere composition was highly sensitive to temperature as a result of the very different energies of activation for respiration and film permeability.

One can argue whether the temperature-independent atmosphere inside the package is important in its own right. The aim of MAP is to retain quality. With constant gas conditions at increasing temperatures, respiration rate and the rate of quality decay will still increase due to the increasing temperature. What we really need is a package design that counteracts this temperature effect by generating lower O$_2$ and higher CO$_2$ levels with higher temperatures, further reducing respiration rate and the rate of respiration-related quality breakdown processes, without driving the product anaerobic. However, if the package conditions are already close to the fermentation threshold (Yearsley et al., 1997) there is no space to further decrease O$_2$ levels. In fact, you would need to provide a greater margin for error at higher temperatures. Depending on the temperature dependence of the fermentation threshold (Yearsley et al., 1997), O$_2$ levels should increase with increasing temperature to prevent fermentation (Beaudry et al. 1992).

4.3. Additional respiration measurements

Respiration measurements at different temperatures in air on a second lot of green capsicums showed quite a different response to temperature (Fig. 5) from the fruits used in the packaging experiment. This was reflected in the activation energy $E_A$, which was estimated at 61180 ± 2948 J·mol$^{-1}$, twice the value found for the fruit used in the packaging experiment (Table 2). Assuming the same $RQ$ (Table 2), $r_{O_2,ref}$ was estimated at 0.098 ± 0.005 µmol·kg$^{-1}$·s$^{-1}$. This was less than the value previously found (Table 2).
Table 2
Parameter estimates and their standard errors (S.E.) resulting from the non-linear regression analysis of respiration and cavity atmosphere data coming from the packaging experiment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate (S.E.)</th>
<th>Parameter</th>
<th>Estimate (S.E.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters describing respiration:</td>
<td></td>
<td>Parameters describing fermentation:</td>
<td></td>
</tr>
<tr>
<td>$r_{O_2,ref}^{max}$</td>
<td>0.145 (3.7)</td>
<td>$RQ_{ox}$</td>
<td>0.88 (1.8)</td>
</tr>
<tr>
<td>$Ea_{O_2}$</td>
<td>30947 (2.6)</td>
<td>$r_{CO_2,ref}^{max}$</td>
<td>0.0067 (7.5)</td>
</tr>
<tr>
<td>$Km_{O_2}$</td>
<td>3.4 (14)</td>
<td>$Ea_{CO_2}$</td>
<td>39869 (15)</td>
</tr>
<tr>
<td>$Km_{O_2(f)}$</td>
<td></td>
<td>$Km_{CO_2(f)}$</td>
<td>0.1 (--)</td>
</tr>
<tr>
<td>$R^2_{adj}$</td>
<td>96.1</td>
<td>$n$</td>
<td>840</td>
</tr>
</tbody>
</table>

* The standard errors (S.E.) are expressed as a percentage, relative to the estimated values.

| $r_{O_2,ref}^{max}$ | the maximum $O_2$ consumption rate ($\mu$mol kg$^{-1}$ s$^{-1}$) at reference temperature $T_{ref}$ ($=15^\circ$C); $Ea_{O_2}$ is the energy of activation (J·mol$^{-1}$) of the maximum $O_2$ consumption rate $r_{O_2}^{max}$. $Km_{O_2}$ is the Michaelis constant for $O_2$ consumption (kPa).
<table>
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</thead>
<tbody>
<tr>
<td>$r_{CO_2,ref}^{max}$</td>
<td>$RQ_{ox}$</td>
<td>$r_{CO_2,ref}$</td>
<td>0.0067 (7.5)</td>
</tr>
<tr>
<td>$Ea_{CO_2}$</td>
<td></td>
<td>$Ea_{CO_2}$</td>
<td>39869 (15)</td>
</tr>
<tr>
<td>$Km_{O_2(f)}$</td>
<td></td>
<td>$Km_{CO_2(f)}$</td>
<td>0.1 (--)</td>
</tr>
<tr>
<td>$R^2_{adj}$</td>
<td>96.1</td>
<td>$n$</td>
<td>840</td>
</tr>
</tbody>
</table>

* Fixed value; no standard error.

* $R^2_{adj}$ is the percentage variance accounted for.

* $n$ is the number of observations.

Differences between the two batches can be due to differences in fruit maturity related to the different harvest dates. This raises the interesting possibility of a strong maturity effect on the activation energy of respiration. If this were shown to be consistent across crop types, this would provide an interesting interaction effect in MAP. Climacteric fruits, by analogy, could have a very different activation energy for their climacteric respiration than that of the basal pre-climacteric process upon which it builds.

5. Conclusions

Integrated approaches, like the one presented here, enhance the understanding of complex systems like MA-packed fruits, enabling us to further explore and optimise MA treatments for capsicums. The permeability of the LDPE film to both $O_2$ and $CO_2$ matched the respiration characteristics of the packed capsicums from the perspective of generating temperature-stable gas conditions inside the package. However, the potential variation in activation energy of respiration between batches emphasises the need for batch-dedicated MAP design.

Fig. 5. Temperature effects on respiration of two separate batches of green capsicums. The dotted line is based on the respiration of those fruit used in the packaging experiment. The symbols and the solid line are for an additional batch of later harvested fruit measured in air.
References


