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Ethylene production, respiration and gas exchange modelling in modified atmosphere packaging for banana fruits

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Summary A mathematical model was developed from experimental measurements to describe the evolution of the O_2, CO_2 and ethylene in a modified atmosphere packaging system for Cavendish bananas. The respiration and ethylene production in the fruits were experimentally obtained from a closed system method and then represented by Michaelis–Menten equations of enzyme kinetics. The gas transfer through the packaging was described by a Fick's diffusion equation, and the temperature dependence was represented based on the Arrhenius law. The model was validated by packaging the fruit in perforated bags of polypropylene and low density polyethylene at 12 °C for a period of 8 days. With the developed model it was possible to satisfactorily describe the experimental evolution of the gas content in the headspace of the packages, obtaining coefficients of determination (R^2) of 0.93 for the O_2 levels, 0.90–0.91 for the CO_2 levels, and 0.89–0.93 for the ethylene levels.

Keywords Arrhenius, Cavendish banana, Michaelis-Menten kinetics, modified atmosphere packaging, uncompetitive inhibition.

Introduction

Modified atmosphere packaging (MAP) is a preservation method widely used to extend the shelf life of fresh fruits and vegetables (Sandhya, 2010; Banda *et al.*, 2015). The MAP system consists of modifying the concentration of the atmosphere surrounding a packaged product to reach appropriate level of gases, mainly low levels of O_2 and moderate levels of CO_2, which result in decreasing the intensity of the physiological and biochemical processes of ripening and senescence, ethylene production, and the activity and action of spoilage microorganisms, thereby maintaining the quality properties and microbiological safety of the product for a longer period of time (Gorris & Tauscher, 1999; Mangaraj *et al.*, 2015; Banda *et al.*, 2015). The modification of gas levels in the headspace of the packaging is a consequence of the dynamic interaction between two processes: on one hand, the metabolism of the packaged product, mainly respiration and ethylene generation, and, on the other hand, the gas exchange between the headspace of the packaging and the external atmosphere (Mahajan *et al.*, 2007; González-Buesa *et al.*, 2009; Castellanos *et al.*, 2016). Thus, a balance between these two processes is sought to reach an internal equilibrium atmosphere with the adequate concentration of gases.

The rate at which the packaged product consumes O_2 and produces CO_2 and ethylene through metabolic reactions should be adequately described to obtain favourable level of gases in the MAP system and thus determine the permeability required by the package to balance these processes and reach the equilibrium levels. If the balance between metabolism and permeability is not appropriate for obtaining the adequate atmosphere, then shelf life may be decreased instead of extended (Mangaraj *et al.*, 2014; Castellanos *et al.*, 2016).

In the respiration process, various substrates are oxidised to generate the energy required by the product to develop its metabolic activities. In aerobic respiration, the energy released during the respiration process is associated with the energy required to completely oxidise one mole of hexose, approximately 2880 kJ (Brownleader *et al.*, 1997). Given that the respiration process depends on the presence of oxygen, the respiration rate is directly related to the O_2 concentration in the atmosphere surrounding the product. Low partial pressures of O_2 lead to a decrease in the respiration rate and in the amount of chemical energy

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released and available for performing the metabolic processes of the product, delaying ripening (Mir & Beaudry, 2002).

On the other hand, ethylene is a phytohormone that regulates the metabolic processes involved in the growth, development, and response to environmental changes of fruits and vegetables (Klee, 2004). Ethylene in these products is bio-synthesised from methionine in three single steps, involving enzymes S-adenosyl-methionine (SAM) synthetase, 1-aminocyclopropane-1-carboxylate (ACC) synthase and ACC oxidase (Barry & Giovannoni, 2007). ACC oxidase catalyses the formation of ethylene, using ACC and O_2 as substrates, with ascorbate as co-substrate, and Fe^{2+} and CO_2 as cofactors (Sanders & de Wild, 2003). Considering ethylene production depends on O_2 presence, low O_2 levels lead to a decrease in its production rate. Also, due to CO_2 act as inhibitor of ACC oxidase enzyme (De Wild *et al*., 2003).

Respiration in fresh products has been generally represented using enzyme kinetic equations derived from the Michaelis–Menten equation as a function of the O_2 concentration (Fonseca *et al*., 2002; Mangaraj *et al*., 2015). The equation of uncompetitive enzyme kinetics, in which CO_2 is the inhibitor, is one of the most widely used (Bhande *et al*., 2008; Mangaraj *et al*., 2014; Pandey & Goswami, 2012; Kwon *et al*., 2013). Ethylene production has also been represented by simple Michaelis–Menten models and by modified models in which a possible positive cooperativity between the substrate (in this case, the O_2) and the enzymes responsible for ethylene production is considered (De Wild *et al*., 1999; Sanders & de Wild, 2003). The implication is that the binding of the substrate to an active site on the enzyme increases the affinity of other active sites of the enzyme.

Once the respiration rate and ethylene production for the packaged product can be described, the change in the gas level inside the packaging in the MAP system is represented by the differential mass balance for each gas considering the contribution of the product and the mass transfer through the packaging walls (Del-Nobile *et al*., 2007; González-Buesa *et al*., 2009; Kwon *et al*., 2013; Mangaraj *et al*., 2015). The rate of gas exchange through the packaging depends on the permeability of the packaging material and, for perforated or porous packaging, on the permeation through the perforations (González-Buesa *et al*., 2009; Kwon *et al*., 2013).

In flexible packaging such as bags, which are more commonly used due to their lower price, the pressure can be considered constant and equal to atmospheric pressure, and the free volume varies due to the difference between the rates at which each gas (CO_2, O_2, N_2, C_2H_4) passes through the packaging walls (Paul & Clarke, 2002; Castellanos *et al*., 2016). For small packages that weigh 1 kg or less, which are most commonly found on supermarket shelves, it has been assumed that there is no stratification of gases (Mangaraj *et al*., 2014). The effect of temperature on both the respiration and ethylene production of the product and the permeation rate of gases in the packaging has been widely represented using Arrhenius equations (Del-Nobile *et al*., 2007; Mahajan *et al*., 2007; Mangaraj *et al*., 2014; Pandey & Goswami, 2012).

For banana fruits some models to describe respiration and O_2 and CO_2 evolution have been developed. Maneerat *et al*. (1997) developed a model based on Michaelis–Menten kinetics to describe respiration and Fick equations to represent gas exchange through non-perforated polyethylene packages of constant volume. They considered the temperature effect using Arrhenius' Law. Bhande *et al*. (2008), presented a model to describe respiration and O_2 and CO_2 evolution based on Michaelis–Menten Kinetics with uncompetitive inhibition due CO_2. In the model they represent the temperature effect also using the Arrhenius Law in the three parameters of the Michaelis–Menten equations. Heydari *et al*. (2010) developed a similar model, to describe the respiration (O_2 consumption and CO_2 production) of banana at a single temperature (21 °C) in a closed system of constant volume. This model also was based on Michaelis–Menten kinetics. Except the work of Maneerat *et al*. (1997) no other works for banana applied to MAP were found. Except work Maneerat *et al*. (1997), no more works for banana applied to MAP were found. Likewise, as far as the authors of this work know, there are no models available of ethylene production for this fruit in postharvest storage.

In this work a mathematical model to describe the evolution of O_2, CO_2 and ethylene in a MAP system of variable volume for Cavendish bananas (*Musa acuminata* AAA) from experimental data has been developed. In the model was taken into account the respiration and ethylene production by the fruits, the mass transfer of gases through a perforated plastic package, the change in the volume headspace and the influence of the storage temperature in all these processes.

Materials and methods

Fresh fruit

For the experiments, almost ripe banana fruits, with a ripeness five of seven (green cortex area <20%) according to the classification of Chitarra & Chitarra (1990), were used. The fruits were obtained from a plantation in the region of Urabá in the department of Antioquia in Colombia and were transported in the days following to the Post-Harvest Laboratory at The Faculty of

Agricultural Sciences of the National University of Colombia (Bogota, Colombia).

In the laboratory, fruits with evidence of damage were discarded, and fruits with similar characteristics were then selected to ensure uniformity in the size, weight and colour of the sample group. The fruits were subjected to cleaning and disinfection, starting with a wash solution of 2% (v/v) citric acid in water, followed by rinsing, with subsequent crowns immersion in a water solution 2% (v/v) of antifungal Lonlife 20%TM (Adiquim, Bogota, Colombia). Finally the fruits surface was dried at room temperature. After the cleaning and disinfection treatments, the sample group was randomly divided into two groups. The first group was used to experimentally measure the respiration and ethylene production rates, and the second group was used for the MAP tests.

Originally the fruits had a soluble solids content of 3.6 ± 0.2° Brix, a titratable acidity of 0.21 ± 0.01% (expressed as a percentage of malic acid), and a firmness to pulp penetration of 7.7 ± 0.2 kgf as measured in the centre of the fruit with an 8 mm Magness-Taylor type probe at a test speed of 1 mm s^{-1}.

Packages

Polypropylene (PP) (0.025 ± 0.002 mm thickness) and low density polyethylene (LDPE) (0.020 ± 0.002 mm thickness) bags were used for the MAP assays (Rediplast, Bogota, Colombia). The bags had an effective transfer area of 800 ± 20 cm^2. A perforation with an effective diameter of 0.280 ± 0.010 mm was made in each bag using a small needle to fully deplete the O_2 present in the headspace of the packaging and cause anaerobic reactions. The perforation size was determined using an optical microscope (Motic® B1-220A; Speed Fair Co., Ltd., Richmond, BC, Canada) by taking the average of ten measurements.

Determination of the respiration rates

The O_2 consumption and CO_2 production rates of the bananas at different temperatures were determined using a closed system method (Castellanos *et al.*, 2016). Two fruits were placed in hermetically sealed glass containers of 2020 cm^3. The containers were left open for 1 h until the fruit reached the temperature of each experiment. The headspace concentrations of O_2 and CO_2 were measured with a previously calibrated Oxybaby® 6i (Witt-Gasetechnik GmbH & Co. KG, Witten, Germany) electronic gas analyser with gas chromatography. A sample of 1 cm^3 of gas was taken through a rubber stamp set in the container lid, and 1 cm^3 of air was then introduced to replace the withdrawn amount. The experiments were performed in a climatic chamber in which the temperature was controlled to 12, 15, 20 and 25 °C, setting the temperature to a range of ±0.2 °C; measurements were taken at regular intervals for a total period of 1.2 days. All measurements were made in triplicate to record the average value for each concentration.

The respiration, O_2 consumption and CO_2 production rates were calculated using the following equations:

$$r_{O_2}(t) = (V/W)(y_{O_2 t-1} - y_{O_2 t+1})/\Delta t \quad (1)$$

$$r_{CO_2}(t) = (V/W)(y_{CO_2 t+1} - y_{CO_2 t-1})/\Delta t \quad (2)$$

where $r_{O_2}(t)$ and $r_{CO_2}(t)$ are the O_2 consumption and CO_2 production rates, respectively, measured at time t, Δt is the time interval between two successive measurements, $y_{O_2 t-1}$, $y_{CO_2 t-1}$ are the O_2 and CO_2 mole fractions determined in the previous measurement than reported at time t and $y_{O_2 t+1}$, $y_{CO_2 t+1}$ are the O_2 and CO_2 mole fractions determined in the subsequent measurement than reported at time t, respectively.

According to research using several types of fruits conducted by other authors (Bhande *et al.*, 2008; Heydari *et al.*, 2010; Mangaraj & Goswami, 2011; Castellanos *et al.*, 2016), Michaelis–Menten-type equations of enzyme kinetics with uncompetitive inhibition by CO_2 (MMU, eqns 3 and 4) were used to model the experimental behaviour of the respiration process in bananas.

The O_2 consumption and CO_2 production rates are as follows:

$$r_{O_2} = \frac{r_{O_2 \max} y_{O_2}}{K_{m_{O_2}} + y_{O_2}\left(1 + \frac{y_{CO_2}}{K_{mu_{CO_2}}}\right)} \quad (3)$$

$$r_{CO_2} = \frac{r_{CO_2 \max} y_{O_2}}{K_{m_{CO_2}} + y_{O_2}\left(1 + \frac{y_{CO_2}}{K_{mu'_{CO_2}}}\right)} \quad (4)$$

where r_{O_2} and r_{CO_2} are the O_2 consumption and CO_2 production rates, respectively (Fonseca *et al.*, 2002; Castellanos & Herrera, 2015).

The experimental values of r_{O_2}, r_{CO_2}, y_{O_2} and y_{CO_2} measured at each temperature were replaced in the linearised form of eqns 3 and 4 to obtain the different parameters of the equations, $r_{O_2 \max}$, $r_{CO_2 \max}$, K_{mO_2}, K_{mCO_2}, K_{muCO_2} and $K_{mu'CO_2}$, by linear regression.

The temperature dependence was determined using an Arrhenius equation:

$$P_m = P_{m\theta} e^{-E_a/RT} \quad (5)$$

where P_m denotes each of the parameter of the MMU equation, $P_{m\theta}$ is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, and T is the assay temperature. The experimental values of each parameter obtained at the four temperatures of the experiment were replaced in the linearised form of eqn 5 to obtain the activation energy and pre-exponential values by linear regression.

Determination of the ethylene production rate

Measurements of the packaging headspace to determine the ethylene production rate were taken simultaneously with the measurements taken to determine the respiration rate. For each temperature, samples of 1 cm^3 of gas were taken with a syringe through the rubber seal. These gas samples were then immediately analysed by injecting them in an Agilent 7890A gas chromatograph (Agilent Technologies Inc., Santa Clara, CA, USA). The analysis conditions were the following: injector temperature 70 °C, oven temperature 50 °C, and FID detector temperature 250 °C. Helium was used as carrier gas at a flow of 7.0 mL min^{-1}. To determine the concentration of ethylene as a function of the area under the curve obtained in each measurement, a calibration curve was established using different mixtures of ethylene (0–500 ppm) and nitrogen. All measurements were performed in triplicate to record the average value of each ethylene concentration.

The rate of ethylene production was calculated as follows:

$$r_{C_2H_4}(t) = (V/W)(y_{C_2H_4t+1} - y_{C_2H_4t-1})/\Delta t \qquad (6)$$

where $r_{C_2H_4}(t)$ is the ethylene production rate at time t, Δt is the time interval between two successive measurements, $y_{C_2H_4t-1}$ is the ethylene mole fraction determined in the previous measurement than reported at time t and $y_{C_2H_4t+1}$ is the ethylene mole fraction determined in the subsequent measurement than reported at time t, respectively.

Two expressions of Michaelis–Menten enzyme kinetics were used to represent ethylene production in bananas, evaluating at the end the expression that better fits the experimental data obtained. First, a simple Michaelis–Menten enzyme kinetics (MM, eqn 7) proposed by De Wild *et al.* (1999) was used, and second, a Michaelis–Menten kinetics incorporating a cooperativity term (MMC, eqn 8), taking into account the possibility of a positive cooperativity between the substrate (O_2) and the enzyme, was used (Sanders & de Wild, 2003). The implication is that the binding of a substrate molecule to an active site of the enzyme increases the affinity of other active sites for the substrate.

$$r_{C_2H_4} = \frac{r_{C_2H_4max} y_{O_2}}{K_{m_{C_2H_4}} + y_{O_2}} \qquad (7)$$

$$r_{C_2H_4} = \frac{r_{C_2H_4max} (y_{O_2})^h}{(K_{m_{C_2H_4}})^h + (y_{O_2})^h} \qquad (8)$$

In the above equations, $r_{C_2H_4}$ is the ethylene production rate and h denotes the cooperativity degree, known as the Hill coefficient. The integer higher than the estimated h value corresponds to the minimum number of active sites. As before, the experimental values of $r_{C_2H_4max}$ and y_{O_2} measured at each temperature were substituted into eqns 7 and 8 to obtain the different parameters of the equation, r_{O_2max}, r_{CO_2max}, K_{mO_2}, K_{mCO_2}, K_{muCO_2} and $K_{mu'CO_2}$, by linear regression in the case of eqn 7 and by nonlinear regression using the damped least-squares method in the case of eqn 8. To calculate $r_{C_2H_4}$ by non-linear regression, the following equation derived from the MMC equation (eqn 8) was used:

$$\frac{1}{r_{C_2H_4}} = \frac{1}{r_{C_2H_4max}} (K'_{mC_2H_4}(y_{O_2})^h + 1) \qquad (9)$$

where $K'_{mC_2H_4} = (K_{m_{C_2H_4}})^h$.

The above equation makes it easier to reach the parameters compared to directly use the eqn 8 in the nonlinear regression, because h is written only once and not three.

The MM and MMC equations were compared by using an adjusted R^2 (Sanders & de Wild, 2003). The R^2_{adj} allows the comparison between non-linear models and compensates for possible bias due to different number of parameters (Spiess & Neumeyer, 2010).

The dependence of the ethylene production rate with respect to temperature was also obtained using the Arrhenius equation (eqn 5), calculating the activation energies and pre-exponential factors of each parameter in eqns 7 and 8.

Modified atmosphere packaging test

After finding the parameters for the banana respiration and ethylene production equations and selecting the most suitable one between the MM and MMC in the case of ethylene production, an experiment was conducted in which the fruits were packed in PP and LDPE bags to determine the evolution of O_2, CO_2 and ethylene in the headspace of a MAP system. In each bag, 161.5 ± 11.5 g of fruits were packed. The initial volume of the headspace was 186.4 ± 3.3 cm^3 for PP bags and 336.7 ± 8.2 cm^3 for LDPE bags. The bags with the fruits were stored in a cabinet with controlled temperature and relative humidity at 12 ± 0.2 °C for 8 days, maintaining the relative humidity at 80 ± 1%. A perforation with a 0.280-mm effective diameter was made in each packaging bag containing the fruit to prevent the total depletion of O_2 in the headspace. The perforation size was determined using a light microscope (Motic® B1-220A; Speed Fair Co., Ltd.) with the mean value of ten perforations. The measurements of the levels of the three gases were performed as described above for the determination of the respiration and ethylene production rates, using the electronic gas analyser and gas chromatograph. The initial concentration of the headspace of the packaging was equal to the atmospheric concentration.

The permeability coefficients of the two packaging materials to O_2 and CO_2 were determined in a previous work (Castellanos *et al.*, 2016) with steady-state methods. A Mocon® Oxtran 2/21 (MOCON, Inc., Minneapolis, MN, USA) permeation instrument was used for O_2, and a temperature-controlled chamber with a permeation cell connected to a gas chromatograph was used for CO_2.

The permeability coefficients of the two materials to ethylene were determined experimentally at 12, 16, 24 and 33 °C using a static permeation cell with a transfer area of 1074 cm^2. The material was placed between two compartments. The lower compartment with a volume of 755 cm^3, completely sealed except for the material itself, was filled with a mixture of 3400 ppm of ethylene and N_2, whereas the upper compartment was left open to the atmosphere. After filling, the remaining ethylene concentration in the lower compartment was measured at regular intervals by gas chromatography as previously described in the evaluation of the ethylene production rate.

The permeability coefficient $Q_{C_2H_4}$ for the two materials at each temperature was calculated as:

$$Q_{C_2H_4} = \frac{VL}{PAt} \ln\left(\frac{y_{C_2H_4\text{ini}} - y_{C_2H_4\text{out}}}{y_{C_2H_4}(t) - y_{C_2H_4\text{out}}}\right) \quad (10)$$

where V is the volume of the lower chamber, P is the atmospheric pressure, A is the transfer area and $y_{C_2H_4\text{out}}$ is the ethylene concentration in the atmosphere (in this case, 0); $y_{C_2H_4\text{ini}}$ is the initial concentration of ethylene in the chamber, t is the test time, and $y_{C_2H_4}(t)$ is the ethylene concentration at time t.

The temperature dependence was represented by replacing the $Q_{C_2H_4}$ data at each temperature in the linearised form of an Arrhenius-type equation (eqn 11) and estimating the activation energy E_a and the reference permeability coefficient $Q_{C_2H_4\text{ref}}$ by linear regression. The reference temperature T_{ref} was 23 °C.

$$Q_{C_2H_4} = Q_{C_2H_4\text{ref}}\, e^{\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)} \quad (11)$$

To determine the gas transfer through the perforation made in each bag, it was assumed that this process might be described by Fick's diffusion equation with a correction term (ε in eqns 12–15) due to the resistance to diffusion at the perforation (Chung *et al.*, 2003; Castellanos *et al.*, 2016). The transfer rate of each gas through the perforation depends on the cross-sectional area and length (film thickness) of the perforation itself, the diffusivity of the gas in the air (gas mixture in the area to which the gas diffuses), and the concentration difference between the inside and the outside of the package, which is expressed in eqns 12–15 of the differential gas balance.

Modelling of the MAP system

In a package with perforations, the gas levels in the headspace are the result of the metabolic processes of the product, O_2 consumption, CO_2 and ethylene production, and the transfer of gases through the packaging walls and perforations. The gas levels can be represented by the following differential mass balance equations for each gas (Castellanos *et al.*, 2016):

For O_2:

$$V\frac{dy_{O_2}}{dt} + y_{O_2}\frac{dV}{dt} = \frac{APQ_{O_2}}{L}(y_{O_2\text{out}} - y_{O_2}) + \frac{D_{O_2}A_h}{L+\varepsilon}(y_{O_2\text{out}} - y_{O_2}) - r_{O_2}W \quad (12)$$

For CO_2:

$$V\frac{dy_{CO_2}}{dt} + y_{CO_2}\frac{dV}{dt} = \frac{APQ_{CO_2}}{L}(y_{CO_2\text{out}} - y_{CO_2}) + \frac{D_{CO_2}A_h}{L+\varepsilon}(y_{CO_2\text{out}} - y_{CO_2}) + r_{CO_2}W \quad (13)$$

For C_2H_4:

$$V\frac{dy_{C_2H_4}}{dt} + y_{C_2H_4}\frac{dV}{dt} = \frac{APQ_{C_2H_4}}{L}(y_{C_2H_4\text{out}} - y_{C_2H_4}) + \frac{D_{C_2H_4}A_h}{L+\varepsilon}(y_{C_2H_4\text{out}} - y_{C_2H_4}) + r_{C_2H_4}W \quad (14)$$

For N_2:

$$V\frac{dy_{N_2}}{dt} + y_{N_2}\frac{dV}{dt} = \frac{D_{N_2}A_h}{L+\varepsilon}(y_{N_2\text{out}} - y_{N_2}) + \frac{APQ_{N_2}}{L}(y_{N_2\text{out}} - y_{N_2}) \quad (15)$$

where Q_{O_2}, Q_{CO_2}, $Q_{C_2H_4}$ and Q_{N_2} are the permeability coefficients of the bag material and D_{O_2}, D_{CO_2}, $D_{C_2H_4}$ and D_{N_2} are the diffusion coefficients in the air of O_2, CO_2, C_2H_4 and N_2, respectively. y_{O_2}, y_{CO_2}, $y_{C_2H_4}$ and y_{N_2} are the molar fractions of each gas in the packaging headspace. $y_{O_2\text{out}}$, $y_{CO_2\text{out}}$, $y_{C_2H_4\text{out}}$ and $y_{N_2\text{out}}$ are the molar fractions of each gas into the external atmosphere. r_{O_2} is the O_2 consumption rate, and r_{CO_2} and $r_{C_2H_4}$ are the production rates of CO_2 and ethylene, respectively. A is the transfer area of the bag, L is the bag thickness, W is the weight of the fruit, P is the system pressure, V is the headspace of the package, and t is the storage time. A_h is the perforation area (assuming it is circular, $A_h = \pi d^2/4$), and ε is a correction term for the diffusion of gases through the perforations. For the model, the following assumptions were made: a lack of stratification of gases inside the package and that the system pressure corresponds to atmospheric pressure.

The change in volume of the headspace packaging can be obtained by adding eqns 12–15 and considering that the sum of the molar fractions of the four gases is equal to 1, resulting in:

$$\frac{dV}{dt} = W(r_{CO_2} - r_{O_2}) + \sum_{i=1}^{n}\left((y_{i\mathrm{out}} - y_i)\left(\frac{D_i A_h}{L + \varepsilon} + \frac{APQ_i}{L}\right)\right) \quad (16)$$

where i can be O_2, CO_2, C_2H_4 or N_2.

The system of differential eqns 12–16 was solved numerically using a calculation routine built in the Matlab software (MathWorks, Inc., Natick, MA, USA) from the 'ode 15s' function, a multi-step implicit method based on numerical differentiation formulas. The change in the O_2, CO_2 and C_2H_4 concentrations in the headspace was elucidated once the test conditions were defined in the calculation routine. The conditions defined in the calculation routine in this case were: concentration of gases in the atmosphere; atmospheric pressure; fruit weight; type, area and thickness of the bag used for packaging; and initial gas levels and headspace volume the package.

Finally, the data of the concentration of gases generated in the calculation routine were compared with the experimental measurements of the headspace of the bags to evaluate the predictive strength of the integrated model of respiration, ethylene production and mass transfer in the MAP system.

Results and discussion

Respiration rates

The O_2 concentration inside the sealed packages decreased with storage time for the bananas as shown in Fig. 1; simultaneously, the CO_2 concentration increased at the different test temperatures. The rates of O_2 consumption and CO_2 production were higher to the initial concentrations of O_2 (air) and became lower as the O_2 was consumed within the package, as shown in Figs 2 and 3. Similarly, the O_2 consumption and CO_2 production rates increased directly with the temperature, reaching lower concentrations of O_2 (and higher CO_2), as shown in Figs 1–3.

The experimental data of the O_2 consumption and CO_2 production by the bananas fitted well to the proposed Michaelis–Menten uncompetitive inhibition equations (eqns 3 and 4), as shown in Figs 1–3. In these figures, the data generated by the MMU equations correspond to the solid lines. The influence with respect to temperature was, in turn, adequately described using the Arrhenius law for the four test temperatures. The pre-exponential factors and the activation energies for the three parameters of the MMU equations (r_{max}, K_m, and K_{mu}) were determined by linear regression of eqn 5 and are shown in Table 1. The positive values of the activation energies for the three parameters indicate a direct relationship between the temperature and respiration rate. The inhibitory effect of CO_2 was established by the values obtained for the inhibition constants by CO_2, K_{mu}, which proved to be positive, indicating an inverse relationship between the CO_2 concentration and the O_2 consumption and CO_2 production rates. The respiration rate becomes lower at higher levels of CO_2.

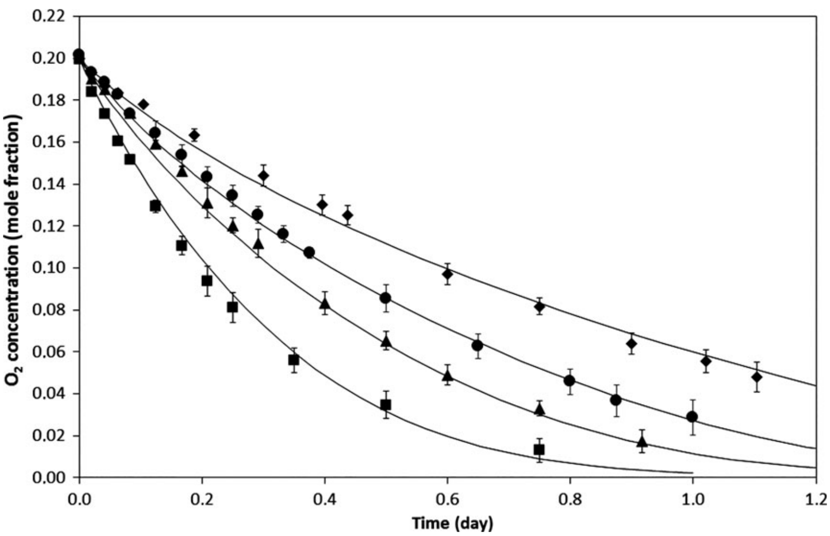

Figure 1 O_2 evolution within the experimental container headspace at 12 °C (●), 15 °C (■), 20 °C (♦), 25 °C (▲) and predicted values using the Michaelis–Menten Uncompetitive equations (—) for banana fruits. Bars represent SD.

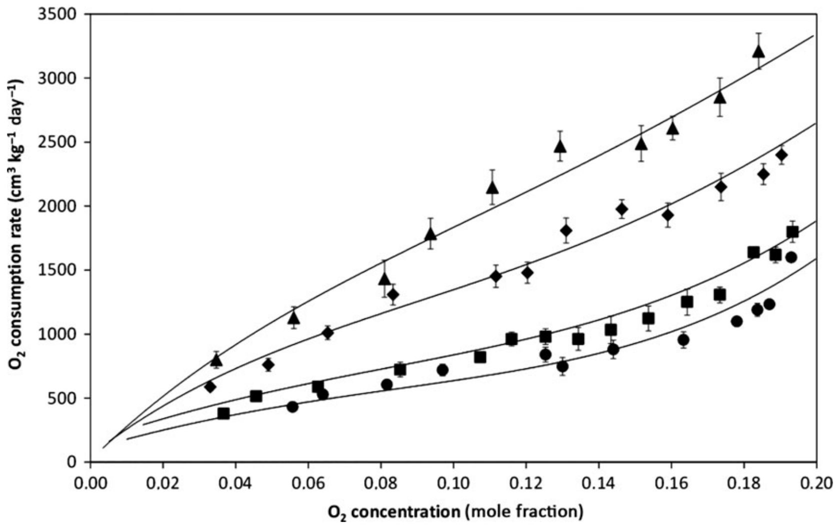

Figure 2 O_2 consumption rate as a function of O_2 concentration within the container headspace at 12 °C (●), 15 °C (■), 20 °C (♦), 25 °C (▲) and predicted values using the Michaelis–Menten Uncompetitive equations (—) for banana fruits. Bars represent SD.

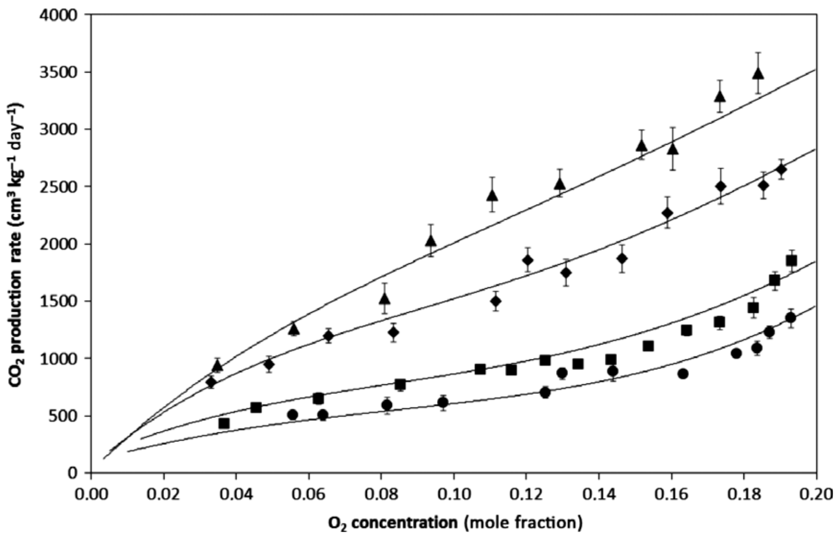

Figure 3 CO_2 production rate as a function of O_2 concentration within the container headspace at 12 °C (●), 15 °C (■), 20 °C (♦), 25 °C (▲) and predicted values using the Michaelis–Menten Uncompetitive equations (—) for banana fruits. Bars represent SD.

For O_2 consumption, the coefficient of determination total R^2 for the MMU equation parameters was 0.961, and for CO_2 production, R^2 was 0.947, showing that the respiration data obtained for bananas correspond to MMU enzyme kinetics. These results are consistent with those reported by Bhande *et al.* (2008) and Heydari *et al.* (2010).

Ethylene production

For the four test temperatures, there was a progressive accumulation of ethylene generated by the fruits inside the packaging. The ethylene production rate was higher at baseline (atmospheric O_2 concentration) and decreased as the O_2 in the packages was consumed by the fruits, as shown in Fig. 4. The effect of temperature was evident in the production of ethylene by the fruits, reaching a $R_{C_2H_4}$ close to 0.36 cm^3 kg^{-1} day^{-1} at 25 °C and 0.04 cm^3 kg^{-1} day^{-1} at 12 °C and atmospheric O_2 concentration, a value that is almost 10 times higher. At 12 and 15 °C, the ethylene production rate did not seem to vary greatly with respect to the O_2 concentration in the package, whereas for higher test temperatures, the effect of the O_2 level on $R_{C_2H_4}$ was more evident, as shown in Fig. 4.

The experimental data of the ethylene production rate fitted well to MMC kinetics (solid lines), as seen in Fig. 4. Similarly, the effect of temperature was also adequately represented by the Arrhenius equation for the parameters $R_{C_2H_4max}$ and K_m of the MMC equation. The parameters of the model are shown in Table 2. For the MMC equation, a total R^2_{adj} of 0.948

Table 1 Estimated parameters of O_2 consumption and CO_2 production rates for the Michaelis–Menten Uncompetitive (MMU) equations

MMU parameters	O_2	CO_2
r_{max} (cm^3 kg^{-1} day^{-1})		
$r_{max\theta}$ (cm^3 kg^{-1} day^{-1})	$1.00 \pm 0.03 \times 10^{14}$	$3.30 \pm 0.15 \times 10^{16}$
E_a (kJ mol^{-1})	58.14 ± 1.74	72.41 ± 3.69
K_m		
$K_{m\theta}$	$2.15 \pm 0.07 \times 10^{10}$	$2.68 \pm 0.14 \times 10^{15}$
E_a (kJ mol^{-1})	62.58 ± 1.88	91.96 ± 4.58
K_{mu}		
$K_{mu\theta}$	$1.13 \pm 0.05 \times 10^{12}$	$1.20 \pm 0.06 \times 10^{13}$
E_a (kJ mol^{-1})	72.87 ± 2.16	78.17 ± 3.96
R^2	0.961	0.947

r_{max}, maximum respiration rate (O_2 consumption or CO_2 production); $r_{max\theta}$, pre-exponential factor, maximum rate; K_m, Michaelis constant; $K_{m\theta}$, pre-exponential factor, Michaelis constant; K_{mu}, Inhibition constant by CO_2; $K_{mu\theta}$, pre-exponential factor, inhibition constant; R^2, coefficient of determination. For each parameter, standard error is included.

was obtained. The value of the cooperative term h obtained for the bananas assessed was 0.96; thus, it can be affirmed that the ethylene production experimental results obtained may be adequately described by simple Michaelis–Menten kinetics. This finding can be seen in Fig. 4, in which the ethylene production rate data obtained from MM kinetics (dotted lines) fit well with the experimental evolution (geometric figures) at the four tested temperatures. For the MM kinetics, R^2_{adj} was 0.938, which was slightly lower than the value obtained for the MMC kinetics. In a study with pears, Sanders & de Wild (2003) also obtained cooperative h terms close to 1 for freshly harvested fruits in their physiological maturity.

Although it is not explicitly raised in the MM and MMC kinetics (eqns 7 and 8), CO_2 may have an effect on the fruit's ethylene production rate. For this experiment, this effect can be considered to be indirect, bearing in mind that, by increasing the concentration of CO_2 around the fruit, its respiration rate decreases and thereby the level of O_2 in the package does not decrease as quickly, thus influencing ethylene generation by the fruit. The above has been described by Génard & Gouble (2005), who assume that CO_2 inhibits ACC oxidase enzyme activity and, in turn, ethylene production in the fruit.

Parameters of gas transfer through the package for the MAP test

As noted above in the Materials and methods section, the permeability coefficients of the packaging films to O_2 and CO_2 were taken from a previous work (Castellanos *et al.*, 2016), whereas the permeability coefficient to N_2 was estimated from information provided by the manufacturers and the literature (Hasbullah *et al.*, 2000; Techavises & Hikida, 2008). The permeability coefficients of PP and LDPE to ethylene were calculated from the concentration data determined in the static permeation cell at the four tested temperatures using eqn 10. The reference permeability coefficients (at 23 °C) and the activation energies of each film were calculated by linear regression, replacing the previous values in the Arrhenius equation (eqn 11). The $Q_{C_2H_4ref}$ obtained for LDPE was almost three times higher than that obtained for PP, and the E_a for LDPE was 46% higher than that for PP. The values of R^2 obtained were 0.996 for PP and 0.989 for LDPE, showing a good fit between the experimental data and

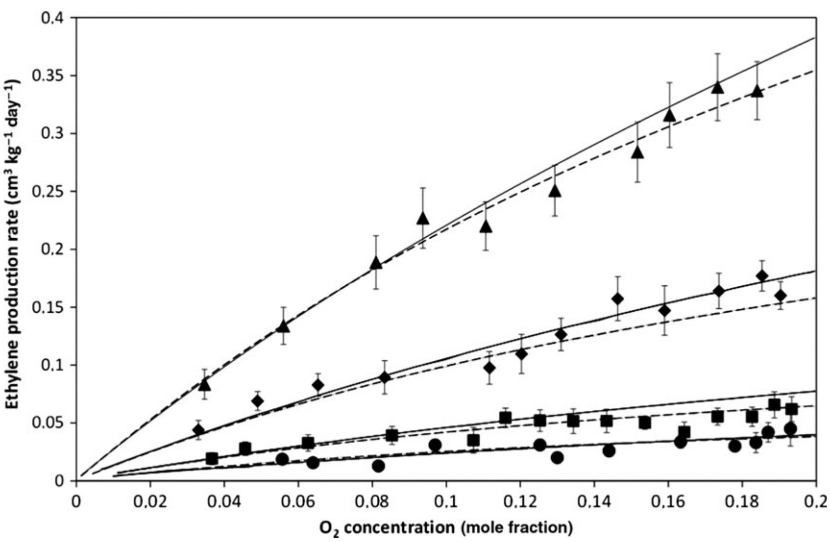

Figure 4 Ethylene production rate as a function of O_2 within the container headspace at 12 °C (●), 15 °C (■), 20 °C (♦), 25 °C (▲) and predicted values using the Michaelis–Menten simple (—) and Michaelis–Menten Cooperative (---) equations for banana fruits. Bars represent SD.

Table 2 Estimated parameters of ethylene production rate by Michaelis–Menten (MM) and Michaelis–Menten Cooperative (MMC) equations

Model parameters	MMC	MM
h	0.96 ± 0.12	–
r_{max} (cm^3 kg^{-1} day^{-1})		
$r_{max\theta}$ (cm^3 kg^{-1} day^{-1})	2.21 ± 0.76 × 10^{21}	1.54 ± 0.17 × 10^{23}
E_a (kJ mol^{-1})	120.74 ± 9.65	132.58 ± 14.01
K_m		
$K_{m\theta}$	1.77 ± 0.48 × 10^2	1.95 ± 0.20 × 10^3
E_a (kJ mol^{-1})	13.94 ± 6.10	21.63 ± 2.26
R^2_{adj}	0.948	0.938

r_{max}, maximum ethylene production rate; $r_{max\theta}$, pre-exponential factor, maximum rate; K_m, Michaelis constant; $K_{m\theta}$, pre-exponential factor, Michaelis constant; E_a: apparent activation energies; h, cooperative term, MMC model; R^2_{adj}, adjusted coefficient of determination. For each parameter, standard error is included.

Table 3 Arrhenius activation energies and reference permeability coefficients of the polypropylene (PP) and low density polyethylene (LDPE) bags for ethylene

Permeability parameters	PP	LDPE
C_2H_4		
Q_{ref}* (cm^3 mm m^{-2} day^{-1} atm^{-1})	92.01 ± 0.46	267.87 ± 2.73
E_a (kJ mol^{-1})	24.41 ± 0.13	35.61 ± 0.38
R^2	0.996	0.989

*T_{ref} = 296.15 K (23 °C).

the parameters obtained from the Arrhenius equation (shown in Table 3).

The permeation of the gases through the perforation in each bag in eqns 12–16 was calculated by estimating the diffusion coefficients of O_2, CO_2, C_2H_4 and N_2 in the air as a function of the temperature from the data reported by Burg (2004) and Xanthopoulos *et al.* (2012), and using a correction factor ε equal to 0.5 times the diameter of the perforation as reported by Castellanos *et al.* (2016).

Modelling gas evolution for the MAP test

After determining the parameters for the kinetics of respiration and ethylene production in the fruits and select the MM kinetics to describe the ethylene production for the reasons stated above, an integrated model to describe the evolution of the O_2, CO_2 and ethylene levels in the headspace for bananas packaged at 12 °C in PP and LDPE bags was constructed. The predicted concentrations of the gas for the conditions in the modified atmosphere test were obtained with the solved model. The respective permeability coefficients of PP and LDPE for each gas, the diffusion coefficients of each gas in the air at 12 °C, and the values of ε and the perforation area required to validate the model are shown in Table 4.

Table 4 Parameters of gas exchange for the perforated PP and LDPE bags at 12 °C

	O_2	CO_2	C_2H_4
Film permeability coefficients			
Q_i/PP (cm^3 mm m^{-2} day^{-1} atm^{-1})	55.3	253.2	62.8
Q_i/LDPE (cm^3 mm m^{-2} day^{-1} atm^{-1})	124.7	977.6	153.3
Parameters of permeation in the perforation			
D_i/air (cm^2 day^{-1})	16 364	12 081	12 105
ε = 0.5 d (mm)	0.14		
$A_h = \pi d^2/4$ (cm^2)	6.16 × 10^{-4}		

Q_i/PP, Q_i/LDPE: polypropylene and polyethylene permeability coefficients. O_2 and CO_2 permeability coefficients taken from Castellanos *et al.* (2016). D_i/air: gas diffusion coefficient in air (adapted from: Burg, 2004; Xanthopoulos *et al.*, 2012). D, perforation diameter; ε, term of correction; A_h, perforation area.

The experimental evolution of the gas concentrations in the bags of PP and LDPE and the values predicted from the integrated model are shown in Figs 5 and 6. For both types of bags, the O_2 concentration decreased, and the CO_2 and C_2H_4 concentrations increased until reaching a steady state (Table 5), establishing a balance between respiration and ethylene production by the fruit and the transfer of gases through the packaging. This behaviour is consistent with the results reported by several authors (Techavises & Hikida, 2008; González-Buesa *et al.*, 2009; Pandey & Goswami, 2012; Castellanos *et al.*, 2016). The equilibrium concentrations were reached approximately 1.2 days after the start of the assay for the PP bags and 1.8 days for the LDPE bags. Figures 5 and 6 shows that a good fit was obtained between the data predicted from the model and the experimental gas concentrations obtained, with the predicted values being slightly higher in all cases. The fitting with regard to the experimental data was better for the PP bags, obtaining determination coefficients between 0.913 and 0.935 for the three gases, whereas for the LDPE bags, the R^2 were between 0.891 and 0.934. Similarly, the ethylene concentrations predicted by the model were further from the experimental values compared to the predicted O_2 and CO_2 concentrations, as shown in Figures 5 and 6 and Table 5. This finding may be due to the inherent variability between the evaluated fruits and the magnitude difference between the concentrations of ethylene compared to the concentrations of the other two gases (and, of course, between the ethylene production and the respiration rates), the former being much lower.

The equilibrium concentrations of O_2, CO_2 and ethylene reached in the assay (Table 5) were lower for the LDPE bags compared with the PP bags. This result is due to the difference in the permeabilities

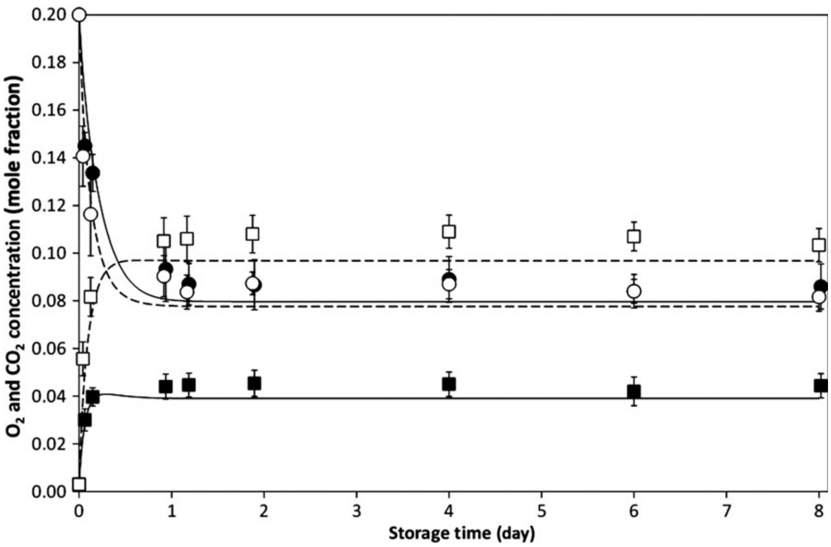

Figure 5 Evolution in the headspace O_2 and CO_2 concentrations for banana fruits packed in polypropylene (PP) (O_2 ○; CO_2 □) and low density polyethylene (LDPE) (O_2 ●; CO_2 ■) bags with one perforation of 280 μm at 12 °C and predicted values by the model (PP ---; LDPE —). Bars represent SD.

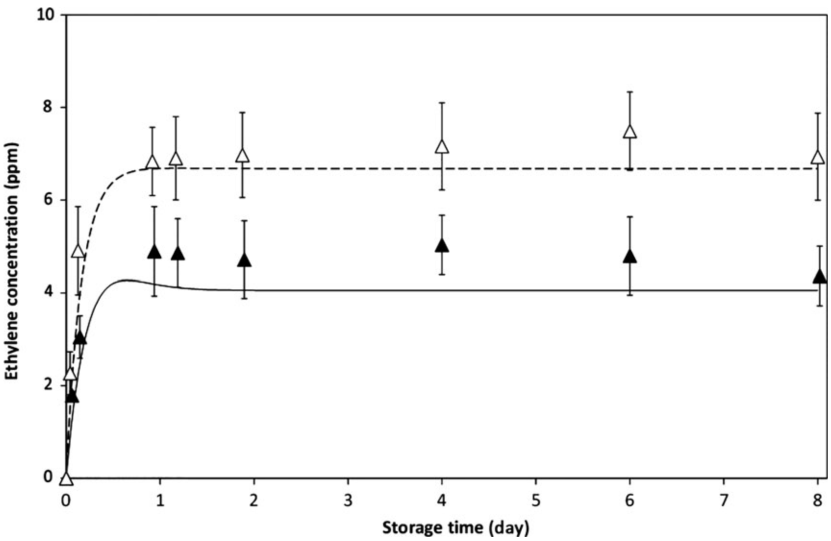

Figure 6 Evolution in the headspace ethylene concentration for banana fruits packed in polypropylene (PP) (Δ) and low density polyethylene (LDPE) (▲) bags with one perforation of 280 μm at 12 °C and predicted values by the model (PP ---; LDPE —). Bars represent SD.

Table 5 Experimental and predicted equilibrium concentrations of O_2, CO_2 and C_2H_4 for the validation experiment in modified atmosphere packaging at 12 °C

Package	$y_{O_2eq-exp}$	$y_{O_2eq-pre}$	R^2	$y_{CO_2eq-exp}$	$y_{CO_2eq-pre}$	R^2	$y_{C_2H_4eq-exp}$ (ppm)	$y_{C_2H_4eq-pre}$	R^2
PP bags	0.082 ± 0.006	0.077	0.935	0.103 ± 0.007	0.097	0.913	6.93 ± 0.74	6.68	0.931
LDPE bags	0.086 ± 0.009	0.080	0.934	0.040 ± 0.006	0.039	0.904	4.36 ± 0.64	4.06	0.891

PP, cast polypropylene bags; LDPE, low-density polyethylene bags; R^2, coefficient of determination of the model in each case.

between the two materials, with LDPE being more permeable to the three gases, and considering that the contribution to the total mass transfer of the permeation through the package walls is significant and of the same range as that through perforation as shown in Table 4 (Castellanos *et al.*, 2016). For PP for example, the less permeable film, the permeation through the film (AQ_iP/L in eqns 12–16) represents 17.6% of the total transfer of O_2, 57.1% of CO_2 and 24.8% of ethylene, with the remainder gas permeation being given through the perforation ($D_iA_h/L+\varepsilon$ in eqns 12–16). For LDPE, the most permeable film, the permeation through the package walls represents 36.9% of the total transfer of O_2, 86.1% of CO_2 and 49.3% of ethylene, respectively. The model adequately predicts the difference between the permeabilities of the two types of bags. Additionally, the gas transfer through the perforation made in each bag was adequately predicted, given the proximity between the predicted and experimental concentrations obtained.

Conclusion

The respiration rate (O_2 consumption and CO_2 production) for the evaluated bananas can be represented using enzymatic Michaelis–Menten kinetics of uncompetitive inhibition by CO_2, given the good fit between the calculated data and those obtained experimentally.

Ethylene production for bananas can be represented satisfactorily and with a good degree of accuracy using simple Michaelis–Menten kinetics, given the good fit between the experimental values and those calculated with the equation, the similarity between the R^2 obtained for the MM and MMC equations, and the proximity to unity of the cooperativity term *h* estimated in the MMC equation. The influence of temperature on the respiration and ethylene production rates was properly described by Arrhenius equations evaluated in the 12–25 °C range.

The MMU respiration and the MM ethylene production kinetic equations were satisfactorily integrated into a mathematical model that was used to describe the change in the gas concentration in a MAP system for bananas. In the model, analytical expressions based on Fick's diffusion equations for estimating the gas transfer through the walls and perforations of the package were employed.

The integrated model adequately described the evolution in the concentration of O_2, CO_2, and ethylene in the headspace of the packaging, satisfactorily predicting the equilibrium concentrations reached for the three gases in the MAP experiment at 12 °C. The integrated model can be used to design MAP systems for bananas under different storage conditions.

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Nomenclature

A: Effective exchange area of the packaging film (m^2)

A_h: Cross-sectional area of the perforations (cm^2)

d: Diameter of the perforation (cm)

d_e: Effective diameter of the perforations (cm)

$D_{O_2}, D_{CO_2}, D_{C_2H_4}$: Diffusion coefficient of O_2, CO_2 and ethylene in air ($cm^2\ day^{-1}$)

E_a: Activation energy ($kJ\ mol^{-1}$)

h: Hill coefficient

$K_{mO_2}, K_{mCO_2}, K_{mC_2H_4}$: Dissociation constants of the enzyme-substrate complex

$K_{muCO_2}, K_{mu'CO_2}$: Constants of uncompetitive inhibition for consumption of O_2 and generation of CO_2, respectively

L: Film thickness (mm)

MM: Michaelis–Menten simple kinetics

MMC: Michaelis–Menten Cooperative kinetics

MMU: Michaelis–Menten Kinetics with uncompetitive inhibition

P: System pressure (atm)

$Q_{O_2}, Q_{CO_2}, Q_{C_2H_4}$: Film permeability coefficient to O_2, CO_2 and ethylene ($cm^3\ mm\ m^{-2}\ day^{-1}\ atm^{-1}$)

R: Universal gas constant (0.008314 $kJ\ mol^{-1}\ K^{-1}$ or 82.057 $atm\ cm^3\ mol^{-1}\ K^{-1}$)

$r_{O_2}, r_{CO_2}, r_{C_2H_4}$: Consumption of O_2 and generation of CO_2 and ethylene rates ($cm^3\ kg^{-1}\ day^{-1}$)

$r_{O_2max}, r_{CO_2max}, r_{C_2H_4max}$: Maximum consumption of O_2 and generation of CO_2 and ethylene rates ($cm^3\ kg^{-1}\ day^{-1}$)

t: Packaging/storage time (day)

Δt: Time elapsing between two successive measurements

T: Temperature (°C, K)

V: Free package volume – headspace (cm^3)

W: Fruit weight (kg)

$y_{O_2}, y_{CO_2}, y_{C_2H_4}$: O_2, CO_2 and ethylene concentrations inside the package

$y_{O_2out}, y_{CO_2out}, y_{C_2H_4out}$: O_2, CO_2 and ethylene concentrations outside the package

$y_{C_2H_4ini}$: Initial ethylene concentration inside the permeation cell *ε: Correction term for gas transmission through perforations (mm)*

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