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# A mathematical model for packaging with microperforated films of fresh-cut fruits and vegetables

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#### ABSTRACT

For the design of modified atmosphere packaging with microperforated films it is necessary to know the respiratory kinetics of the product and the gas interchange through the packaging. The aim of this work was to describe an empirical equation that relates the microperforation area with the transmission rate in order to present a mathematical model, valid for packages of constant volume. The model should take into account the dependency of the respiration rate with the gas composition and the existence of a hydrodynamic flow through the microperforations. The evolution of the gas composition inside the package predicted by the model has been compared with the results of experiments conducted at 4 °C with minimally processed peach ('Andross' and 'Calante' cultivars), fresh-cut cauliflower and whole black truffle, by using seven packages of different number (0-14) and size (from  $90 \times 50 \,\mu\text{m}$  to  $300 \times 100 \,\mu\text{m}$ ) of microperforations. The respiratory kinetics of these products was previously determined in a closed system. It has been established that the rate of  $O_2$  consumption is a potential function of the  $O_2$  concentration, while the production of  $CO_2$  is linear, except in the case of the truffle which showed a linear dependency for O<sub>2</sub> and CO<sub>2</sub>. The experimental data and those predicted by the model showed a satisfactory agreement for the  $O_2$ , while the  $CO_2$  is underestimated for products with RQ < 1 but in agreement when RQ > 1. The reason for this behaviour could be the  $CO_2$  concentration gradient within the package owing to the air flow that moves to compensate pressure differences.

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#### 41

# 42 **1. Introduction**

Modified atmosphere packaging (MAP) of minimally processed 43 fruits and vegetables combined with cold storage are considered as 44 the best way to maintain sensory and microbiological quality of 45 46 fresh-cut produce (Kader et al., 1989; Philips, 1996). Low O2 and elevated CO<sub>2</sub> atmospheres reduce the product respiration rate 47 48 (Watada et al., 1996), while the CO<sub>2</sub> accumulation favours the inhibition of microbial growth responsible for product deterioration 49 (Bennik et al., 1998). 50

Modified atmosphere design (MAP) for fruit and vegetables is a 51 complex task requiring an understanding of the dynamic interac-52 tions established between the product, the atmosphere generated 53 within the package and the package itself (Yam and Lee, 1995). A 54 55 large number of variables should be integrated: the respiration rate 56 of the product as a function of the temperature, the optimum gas composition and tolerance limits, gas transport through the pack-57 age depending on the temperature, gas exchange area, free volume, 58 weight of the product, etc. Mathematical models are useful tools 59 60 for defining the characteristics that a package should have and for predicting the evolution of the gas composition during conservation of the product.

Many of the early models developed for modified atmosphere packaging concentrated on the analysis of equilibrium atmospheres (Mannapperuma et al., 1989; Emond et al., 1991; Cameron et al., 1994; Talasila et al., 1994). However, for minimally processed products in particular, the time required to reach this equilibrium can represent a significant percentage of their short useful life (7–9 days). Furthermore, in some circumstances the CO<sub>2</sub> can reach a maximum concentration different from that of equilibrium, especially if films with a high permeability quotient,  $\beta = Q_{CO_2}/Q_{O_2}$ , are used (Fishman et al., 1995; Salvador et al., 2002). The products are therefore subjected to CO<sub>2</sub> concentrations higher than their tolerance limit, despite the fact that the concentrations in the equilibrium might or might not be adequate.

As the use of perforated films became more widespread as an alternative to overcome the limitations of conventional polymeric films, research works began to be published about the modelling of gas exchange in this type of packaging. However, the majority of these studies (Emond et al., 1991; Fishman et al., 1996; Fonseca et al., 1996; Lange et al., 2000; Paul and Clarke, 2002) referred to quite large perforations (from 0.2 up to 17 mm in diameter). The high respiration rate of minimally processed products requires much greater permeability than that provided by unperforated

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| a1. a2     | constants  | R        |
|------------|--|----------|
| A A        | film area (m <sup>2</sup> )  | Ri       |
| $A_h$      | microperforation area $(m^2)$  | 1        |
| CO2        | carbon dioxide concentration (%)   | Ro       |
| d          | diameter of the microperforation (um)  | 02       |
| Ie         | transmission of gas <i>i</i> across the film (mol s <sup>-1</sup> )                | Rco      |
| Jhi<br>Ihi | flow of gas <i>i</i> through the holes (mol $s^{-1}$ )                             |          |
| Jii<br>Ii  | total permeation flow of gas <i>i</i> through the film (mol s <sup>-1</sup> )      | t        |
| Ji<br>Ini  | hydrodynamic flow of gas i (mol s <sup>-1</sup> )                                  | Ť        |
| Jp,i<br>I. | thickness of the film (m)  | TR:      |
| 2<br>n:    | moles of gas i   | V        |
| $\Omega_2$ | oxygen concentration (%)   | Ŵ        |
| P          | pressure (Pa)  | 2        |
| n:         | pressure (Fu) partial pressure of gas <i>i</i> inside the package (Pa)             | 11       |
| $p_i$      | partial pressure of gas <i>i</i> outside the package (Pa)                          | م<br>adi |
| $Q_i$      | gas <i>i</i> permeability coefficient of the polymeric film $(m^2 s^{-1} Pa^{-1})$ | auj      |

85 films. In addition, perforated films have a permeability quotient 86 close to 1 (Brody, 2005) and this allows the required concentra-87 tions of CO<sub>2</sub> to be reached without anaerobiosis, taking into ac-88 count that the respiration coefficient of the product can fluctuate 89 between 0.7 and 1.3 (Kader, 1987). These factors justify the inter-90 est in using perforated films. However, the size of the perforations 91 normally used in MAP is between 50 and 200 um in diameter. 92 appreciably smaller than the sizes referred to above. The extrapo-93 lation of predictions of gas transmission obtained with the sizes re-94 ferred above to microperforations could lead to errors which 95 directly affect the composition of the package atmosphere. It is 96 therefore important to quantify the influence of the microperfora-97 tion size, total exchange area, equivalent radius and film thickness 98 on the gas transmission rate. In a previous work (González et al., 99 2008), an empirical equation that relates the area of a microperfo-100 ration with the transmission rate of oxygen and carbon dioxide 101 was derived from experimental data. The results were compared 102 with other experimental data (Ghosh and Anantheswaran, 2001) 103 and with those predicted by five other models (Heiss, 1954; Beck-104 er, 1979; Emond et al., 1991; Fishman et al., 1996; Fonseca et al., 1996). The O<sub>2</sub> and CO<sub>2</sub> transmission rates predicted by the empir-105 ical equation were very close to those obtained with the modified 106 Fick's equation in which the total diffusive pass length of a perfo-107 108 ration is considered as the sum of the perforation length and a correction factor, which is approximately 0.5 times the diameter of 109 110 the perforation. Unlike the other proposed equations, this equation can be used for a wide range of conditions (diameters between 111 40 µm and 10 mm, and thicknesses between 30 and 1.5 mm). 112 113 The aim of this work is to verify experimentally the gas exchange 114 predictions through microperforated films with packages containing minimally processed products. To achieve this objective, first 115 the respiration kinetics of the products were determined. These 116 117 measurements are considered necessary for the following reasons: 118 (i) fresh-cut products have a physiology that differs from intact 119 produce (Martinez et al., 2005), (ii) the respiration rates given in 120 the literature do not always take into account their dependence 121 on the gas composition while MAP design for fresh-cut produce re-122 quires a suitable model for the prediction of the respiration rate as 123 a function of the gas composition (Iqbal et al., 2009; Fonseca et al., 124 2002) and (iii) the respiration activity varies with the cultivars. A 125 mathematical model is subsequently proposed that takes into account the physiological activity of the products, the diffusive flow 126 127 through the microperforations, the film permeability, as well as the

gas constant (Pa  $m^3 mol^{-1} K^{-1}$ ) respiration rate expressed as consumption or production of a gas i (m<sup>3</sup> kg<sup>-1</sup> s<sup>-1</sup>) respiration rate expressed as consumption of  $O_2$  (m<sup>3</sup>  $kg^{-1} s^{-1}$ ) respiration rate expressed as production of CO<sub>2</sub> (m<sup>3</sup>  $\mathbf{)}_2$  $kg^{-1} s^{-1}$ ) time (s) temperature (K) gas *i* transmission rate  $(m^3 s^{-1})$ free package volume (m<sup>3</sup>) product mass (kg) molecular mean free path (m) gas viscosity (Pa  $s^{-1}$ ) ustable parameters: *m*, *n*, *q*, *s* 

hydrodynamic flow to compensate for the differences in pressure. 128 Finally, the experimentally measured evolution of the gas compositions in the interior of the packages is compared with those predicted by the model. 131

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# 2. Material and methods

#### 2.1. Preparation of produce

The two cultivars of peach, 'Andross' and 'Calante', were har-134 vested at commercial maturity stage (soluble solids: 13.6 ± 1.7° 135 Brix for 'Andross' and  $11.4 \pm 0.9^{\circ}$  Brix for 'Calante'; acidity: 136 5.1 ± 0.1 g/L in 'Andross' and  $6.1 \pm 1.0$  g/L in 'Calante'; firmness in 137 penetration test with cylindrical punch of 6 mm diameter: 5.7 ± 1.0 kg cm<sup>-2</sup> for 'Andross' and 3.6 ± 0.4 kg cm<sup>-2</sup> for 'Calante'). 138 139 Upon arrival at the laboratory they were refrigerated to a temper-140 ature of 0–1 °C, after which they were disinfected (100 ppm active 141 chlorine, 5 min) to reduce the surface microbial charge and left to 142 drain for 10 min. The peaches were peeled with a semi-automatic 143 peeler (Orange Peel model, Pelamatic). The stones were removed 144 with a manual corer, while a special Granton fruit knife was used 145 to cut them into 10-12 slices. They were immersed during 30 146 min in a cold bath (2 °C) containing 2% ascorbic acid, 1% citric acid 147 and 1% calcium chloride. The segments were then immediately 148 drained cold on a sieve for 15 min. 149

The cauliflower, *Brassica oleracea var. Botrytis* L. of the 'Meridien' cultivar, was supplied by a local distributor (Cooperativa San Lamberto, Zaragoza, Spain). The approximate mass of the cauliflowers was 900 g, with a diameter of 15 cm. The leaves were removed and any cauliflowers with blemishes or in bad condition were rejected. They were cut into 15–20 g pieces with a knife (Granton, UK). Afterwards they were washed (at 2 °C, with 100 ppm of active chlorine, 5 min) and drained for 10 min.

The black truffles (Tuber melanosporum) used in this study were 158 obtained from artificial truffle grounds in Teruel (Spain). The truf-159 fles, dug with the help of trained truffle dogs, were all at a similar 160 stage of maturity and surrounded by a layer of soil in insulated 161 boxes with ice bags and transported immediately to our labora-162 tory. Upon arrival, the soil was removed by brushing the truffles 163 with a wet soft brush. They were then rinsed with tap water and 164 dried in a fluid laminar cabinet. Qualitative selection of the carpo-165 phores was made by discarding truffles with softened texture, dip-166

167 ters and coleoptera larva or those extremely damaged during theharvest.

All the products were cooled to a temperature of 4 °C prior tohaving the respiration rate measured.

#### 171 2.2. Closed system respiration experiments

172 The respiration rate was determined in a closed system at 4 °C. A quantity of product (0.5 kg of peach, 0.345 kg of cauliflower or 173 0.050 kg of truffle) was placed in hermetic containers (1230 mL 174 capacity for peach and cauliflower and 250 mL for truffles), and 175 both the consumption of O<sub>2</sub> and the production of CO<sub>2</sub> were mea-176 sured. The composition of the gas inside the containers was deter-177 mined with a Hewlett Packard 4890 (Geneva, Switzerland) gas 178 179 chromatograph equipped with a thermal conductivity detector 180 and a CP-Carboplot Chrompack (Bergen op Zoom, Norwegian) capillary column of 25 m in length with a film thickness of 25 um, and 181 an internal and external diameter of 0.53 mm and 0.75 mm, 182 respectively. Helium was used as a carrier gas (12.6 mL min<sup>-1</sup>). 183 The monitoring of the evolution of the gaseous composition in 184 185 the interior of the containers was done by triplicate until the O<sub>2</sub> 186 levels reached 1%. The results shown (Figs. 1 and 2) are average values of the three measurements taken. 187

#### 188 2.3. Packages

The Amcor P-Plus (Amcor Flexibles, Ledbury, UK) films used 189 have a polymeric matrix, made up of one layer of low density poly-190 ethylene and another of polyester, and microperforations of differ-191 ent sizes. Using equipment based on the ASTM D3985-05 norm, the 192 permeability coefficients of the matrix, Q<sub>i</sub>, were experimentally ob-193 tained at 4 °C. The thickness of the film, 40 µm, was determined as 194 the average of five measurements with a Mitutoyo (Kawasaki, Ja-195 pan) gauge. The size of the microperforations was measured with 196 a Zeiss (Thornwood, NY, USA) microscope provided with a cali-197 198 brated ocular micrometer. The sizes of the microperforations were 199 between 90  $\times$  50 and 200  $\times$  100 µm.

The products were placed in polypropylene trays wrapped in polyethylene, which can be considered as a barrier to gas transmission effects (during the market life of the product). The upper part of the package (96 cm<sup>2</sup>) was heat sealed with the microperforated film described above. The volume of the package and the weight of the product in each case was: 500 mL and 185 g for 'Andross' peach, 700 mL and 250 g for 'Calante' peach, 600 mL and 200 g



**Fig. 1.** Time course of  $O_2$  depletion in the closed container atmosphere containing fresh-cut peach ( $\blacksquare$  'Calante',  $\Box$  'Andross'), cauliflower ( $\bullet$ ) or truffle ( $\nabla$ ).



**Fig. 2.** Time course of  $CO_2$  accumulation in the closed container atmosphere containing fresh-cut peach ( $\blacksquare$  'Calante',  $\Box$  'Andross'), cauliflower ( $\bullet$ ) or truffle ( $\nabla$ ).

for cauliflower, and 250 mL and 50 g for black truffle. The initial gas composition was similar to that of the atmosphere. Samples were kept in a cold room (4 °C, 80% RH).

### 2.4. Mathematical model

The model was developed for packages whose volume remains constant. The physiological activity of the product together with the gaseous exchange through the film are the two processes that contribute to the change in quantity of moles of a gas  $i(n_i)$  in the interior of a package containing fruit or vegetables:

$$\frac{dn_i}{dt} = R_i W \frac{P}{RT} + J_i \tag{1}$$

where  $R_i$  is the respiration rate, W is the product weight, P the pressure, T the temperature, R the gas constant, and  $J_i$  is the total permeation flow through the film. In the case of microperforated films the total flow is:

$$J_i = J_{fi} + J_{hi} \tag{2}$$

where  $J_{hi}$  is the flow of a gas *i* through the holes and  $J_{fi}$  is the transmission of a gas *i* across the film, and can be expressed as (Geankoplis, 1993):

$$J_{fi} = -\frac{Q_i A(p_i - p_{i,out})}{L} \frac{P}{RT}$$

$$\tag{3}$$

where  $p_i$  and  $p_{i,out}$  are the partial pressures of gas *i* inside and outside the package, *L* is the thickness of the polymeric film, *A* is the film area, and  $Q_i$  is the gas *i* permeability coefficient of the polymeric film.

The flow of the gas *i* through the perforation,  $J_{h,i}$ , has been considered to be produced by two mechanisms (Hernandez, 1997; Del-Valle et al., 2003): ordinary diffusion  $(d/\lambda \ge 100)$  and hydrodynamic flow,  $J_{p,i}$ , resulting from the changes in pressure caused by a respiration coefficient different to one. The diffusion flow is itself the result of two magnitudes: the molar flow resulting from the overall movement of the fluid and the flow resulting from the diffusion superimposed on the overall flow (Bird et al., 2007):

$$J_{h,i} = \frac{p_i}{P} \sum_{i=1}^n J_{h,i} - TR_i \frac{(p_i - p_{i,out})}{RT} + J_{p,i}$$
(4)

where  $TR_i$  is the transmission rate of gas *i* and which according to the results obtained in a previous study (González et al., 2008) can be expressed as:

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$$TR_i = a_{1,i} \cdot A_h^{a_{2,i}}$$
 (5)

 $A_h$  being the microperforation area, and  $a_1$ ,  $a_2$  constants for each gas 249 250 i. The values of the constants are determined from the experimental data obtained at 23 °C ( $a_{1,=} 0.880 \pm 0.111$ ,  $a_{2,=} 0.577 \pm 0.0132$  with 251  $r^2 = 0.988$  for O<sub>2</sub>;  $a_1 = 0.830 \pm 0.111$ ,  $a_2 = 0.577 \pm 0.0132$  with  $r^2 = 0.986$  for O<sub>2</sub>;  $a_1 = 0.830 \pm 0.111$ ,  $a_2 = 0.569 \pm 0.0140$  with  $r^2 = 0.986$  for O<sub>2</sub> and  $a_2 = 1100 \pm 0.017$ 252 = 0.986 for CO<sub>2</sub> and  $a_{1,2} = 1.169 \pm 0.253$ ,  $a_{2,2} = 0.558 \pm 0.0195$  with 253  $r^2 = 0.984$  for N<sub>2</sub>). For its use at another temperature, in respect of 254 ordinary diffusion, the transmission rate is considered proportional 255 256 to  $T^{3/2}$ . The validity of Eq. (5) (experimentally determined for  $L < 60 \times 10^{-6}$  m and  $A_h < 3.8 \times 10^{-8}$  m<sup>2</sup>) has been checked for  $L < 1.5 \times 10^{-3}$  m and  $A_h < 7.8 \times 10^{-5}$  m<sup>2</sup>, comparing it with the 257 258 empirical equations in this interval proposed by other authors 259 (González et al., 2008). 260

The hydrodynamic flow of gas *i* can be described by Poiseuille's law in laminar flow conditions:

If 
$$P_{out} > \underline{P}_{p,i} = \frac{\pi d^4 (P_{out} - P) p_{i,out}}{128 \ \mu L} \frac{1}{RT}$$
 (6)

If 
$$P_{out} < \underline{P}_{p,i} = \frac{\pi d^4 (P_{out} - P) p_i}{128 \ \mu L} \frac{1}{RT}$$
 (7)

where *d* is the microperforation diameter,  $P_{out} - P$  is the pressure differential and  $\mu$  is the gas viscosity.

#### 267 3. Results and discussion

268 The respiratory kinetics have been determined from the results 269 obtained in the closed system experiments. Figs. 1 and 2 show the 270 evolution over time of the O<sub>2</sub> and CO<sub>2</sub> concentrations for the four 271 products. Given that in each case the free yolume/weight ratio of the product (V/W) is different, from these data it is not possible 272 to arrive directly at comparative conclusions regarding the respira-273 tion rate of the various products, though the high CO<sub>2</sub> production 274 275 in the case of the truffle can be remarked on.

The respiration rates for each product were calculated using these equations:

$$R_{0_{2}} = -\frac{1}{W} \frac{V}{100} \frac{dO_{2}}{dt}$$
(8)  
$$R_{CO_{2}} = \frac{1}{W} \frac{V}{100} \frac{dCO_{2}}{dt}$$
(9)



**Fig. 3.** Respiration rate of 'Andross' peach at  $4 \,^{\circ}$ C expressed as  $O_2$  consumption ( $\blacksquare$ ) and  $CO_2$  production ( $\blacktriangle$ ), versus  $O_2$  concentration.



**Fig. 4.** Respiration rate of 'Calante' peach at  $4 \,^{\circ}$ C expressed as  $O_2$  consumption ( $\blacksquare$ ) and  $CO_2$  production ( $\blacktriangle$ ), versus  $O_2$  concentration.



**Fig. 5.** Respiration rate of cauliflower at  $4 \,^{\circ}$ C expressed as  $O_2$  consumption ( $\blacksquare$ ) and  $CO_2$  production ( $\blacktriangle$ ), versus  $O_2$  concentration.



**Fig. 6.** Respiration rate of black truffle at 4 °C expressed as  $O_2$  consumption ( $\blacksquare$ ) and  $CO_2$  production ( $\blacktriangle$ ), versus  $O_2$  concentration.

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Table 1

Parameters *m*, *n*, *q* and *s* (Eqs. (12) and (13)) for the different products.

|  |                                  |                                  |                                  | -                                  |                                  |                                  |
|--|----------------------------------|----------------------------------|----------------------------------|------------------------------------|----------------------------------|----------------------------------|
| Product  | т                                | n                                | r <sup>2</sup>                   | q                                  | S                                | r <sup>2</sup>                   |
| "Andross"<br>"Calante"<br>Cauliflower<br>Truffle | 2.559<br>1.192<br>2.287<br>0.814 | 0.318<br>0.632<br>0.732<br>7.778 | 0.972<br>0.998<br>0.999<br>0.999 | 0.0383<br>0.216<br>0.0399<br>0.936 | 3.753<br>2.230<br>8.158<br>9.751 | 0.998<br>0.999<br>0.997<br>0.999 |

The respiration rates thus obtained are shown in Figs. 3-6. In all 280 281 cases a decrease in the respiration rate was observed as the oxygen 282 concentration diminishes. In air, the respiration rate of the minimally processed 'Calante' peach is greater than that of the 'An-283 dross', but the dependence of the latter on the oxygen 284 concentration is less marked. The cauliflower initially shows a 285 low respiratory quotient,  $R_{CO_2}/R_{O_2} = 0.42$ , but owing to the reduced 286 dependence of the CO<sub>2</sub> production rate on the oxygen concentra-287 288 tion, this ratio increases up to 1.1. The truffle is the product with the highest respiration rate, even though it is not a fresh-cut prod-289 uct, managing to consume oxygen 3.5 times more quickly than the 290 'Andross' peach and to produce CO<sub>2</sub> at a rate 6.5 times greater, 291 292 showing respiration coefficients always greater than 1 (1.18-293 1.20). The respiration of vegetables is an enzymatic process, but 294 it was decided to use equations which provide a good fit with the experimental values without any mechanistic background. 295 296 Using a Michaelis-Mentel type equation resulted in very large values for the  $V_m$  parameter (maximum respiration rate) given that at 297 298 high oxygen concentrations the inverse of the respiration rate has values close to zero. The respiration rate expressed as consumption 299 of O<sub>2</sub> is considered to vary potentially with the O<sub>2</sub> concentration 300 301 for the two peach cultivars and the cauliflower:

$$303 \qquad R_{O_2} = m \cdot O_2^n \tag{10}$$

while for the truffle the dependence is linear. In all cases, the rate of 304 305 CO<sub>2</sub> production is also linear:

307  $R_{\rm CO_2} = q \cdot O_2 + s$ (11)

308 The values of the parameters *m*, *n*, *q* and *s* are shown in Table 1 for the different products. 309

310 Taking the above equations into account, and specifying for 311 each of the gases involved, the differential equations that describe 312 the variation over time of the number of moles of  $O_2$ ,  $CO_2$  and  $N_2$ 313 inside a microperforated package containing a product with a specific respiratory activity are: 314

$$\frac{dn_{O_2}}{dt} = \frac{TR_{O_2}}{RT} (p_{O_2}, out - p_{O_2}) + \frac{p_{O_2}}{P} (J_{h,O_2} + J_{h,CO_2} + J_{h,N_2}) 
+ \frac{Q_{O_2}}{RT} \frac{A \cdot P}{L} (p_{O_2}, out - p_{O_2}) - R_{O_2} \frac{P}{RT} W + J_{p,O_2}$$
(12)
$$\frac{dn_{CO_2}}{RT} = \frac{TR_{CO_2}}{RT} (p_{O_2}, out - p_{O_2}) + \frac{p_{CO_2}}{RT} (I_{A_1} + I_{A_2} + I_{A_2})$$

$$\frac{m_{CO_2}}{dt} = \frac{IR_{CO_2}}{RT} (p_{CO_2}, out - p_{CO_2}) + \frac{P_{CO_2}}{P} \left( J_{h,O_2} + J_{h,CO_2} + J_{h,N_2} \right) + \frac{Q_{CO_2}}{RT} \frac{A \cdot P}{L} (p_{CO_2}, out - p_{CO_2}) + R_{CO2} \frac{P}{RT} W + J_{p,CO_2}$$
(13)

$$\frac{dn_{N_2}}{dt} = \frac{TR_{N_2}}{RT} (p_{N_2}, out - p_{N_2}) + \frac{p_{N_2}}{P} (J_{h, 0_2} + J_{h, C0_2} + J_{h, N_2}) + \frac{Q_{N_2}}{RT} \frac{A \cdot P}{L} (p_{N_2}, out - p_{N_2}) + J_{p, N_2}$$
(14)

Given that the volume of the package has been considered to re-318 319 main constant, the pressure in its interior, P, can be calculated with the expression: 320 321

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$$P = \frac{(n_{O_2} + n_{CO_2} + n_{N_2})RT}{V}$$
(15)

| Table | 2 |
|-------|---|
|-------|---|

Values of the parameters used in Eqs. (12)-(14).

| $\begin{array}{l} Q_{0_2} \ (m^2 \ s^{-1} \ Pa^{-1}) \\ Q_{CO_2} \ (m^2 \ s^{-1} \ Pa^{-1}) \\ Q_{N_2} \ (m^2 \ s^{-1} \ Pa^{-1}) \\ Q_{N_2} \ (m^2 \ s^{-1} \ Pa^{-1}) \\ P_{out} \ (Pa) \end{array}$ | $\begin{array}{c} 4.04\times10^{-19}\\ 1.32\times10^{-13}\\ 4.22\times10^{-13}\\ 98,792 \end{array}$ | $\begin{array}{l} 4.04\times 10^{-19} \\ 1.32\times 10^{-18} \\ 4.22\times 10^{-19} \\ 98,792 \\ TR\ (m^3\ s^{-1}\times 10^{11}) \end{array}$ |       |  |  |  |
|--|--|---|-------|--|--|--|
| Hole   | $TR (m^3 s^{-1})$  |   |       |  |  |  |
|  | 02   | CO <sub>2</sub>   | $N_2$ |  |  |  |
| One 90 $	imes$ 50 $\mu$ m  | 102  | 90  | 117   |  |  |  |
| Two 90 × 50 μm   | 204  | 180   | 234   |  |  |  |
| Two 125 × 75 μm  | 234  | 205   | 259   |  |  |  |
| One 200 × 130 μm   | 282  | 246   | 311   |  |  |  |
| One 210 × 135 μm   | 298  | 259   | 327   |  |  |  |
| Two $200 \times 120 \mu m$   | 404  | 349   | 438   |  |  |  |
| Three $200 \times 100 \mu m$   | 458  | 397   | 496   |  |  |  |
| Fourteen $150 \times 80 \ \mu m$   | 830  | 712   | 882   |  |  |  |
|  |  |   |       |  |  |  |

A fourth-order Runge-Kutta method has been used for the numerical solution of these differential equations. Table 2 shows the values of the parameters used in the calculations. The solution allows the prediction of the evolution of the gas composition inside the microperforated package.

To verify the suitability of the model, and to check whether it is capable of a good prediction of the behaviour of the package atmosphere, the experimental results have been compared with those obtained from the Eqs. (12)–(15). The model gives a correct description of the evolution of the oxygen concentration in all the products and films used (Figs. 7-10). For the two varieties of peach, extreme permeability conditions have been used ranging from a small package microperforation (90  $\times$  50 µm) or even packages without microperforations, to three microperforations of relatively large sizes  $(200 \times 100 \,\mu\text{m})$ . This meant that it was possible to obtain very different equilibrium gas compositions for the different types of packages tested and simulated, checking the validity of the proposed model for a large number of situations. Anoxia conditions were reached quickly with films without micoperforations, while for packages with high effective permeability the concentration of oxygen in equilibrium is higher than would be recommended for this type of product (Gorny et al., 1999). In the case of the truffle (Fig. 10), a wide disparity was recorded in the experimental results due to the peculiarities of a very heterogeneous product. In any case, the theoretical predictions were within the interval defined by standard deviation.



Fig. 7. Experimental and predicted evolution of O2 composition for different 'Andross' peach packages: without microperforation (
, continuous line), one  $90 \times 50 \ \mu\text{m}$  hole ( $\Box$ , dash line), two  $90 \times 50 \ \mu\text{m}$  holes ( $\bigcirc$ , dash dot line), one  $210 \times 135 \ \mu\text{m}$  hole ( $\bullet$ , dot line), two  $125 \times 75 \ \mu\text{m}$  holes ( $\blacktriangle$ , continuous thick line), three 200  $\times$  100  $\mu$ m holes ( $\Delta$ , dash dot dot line).

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**Fig. 8.** Experimental and predicted evolution of  $O_2$  composition for different 'Calante' peach packages: without microperforation ( $\blacksquare$ , continuous line), one  $90 \times 50 \ \mu\text{m}$  hole ( $\Box$ , dash line), two  $90 \times 50 \ \mu\text{m}$  holes ( $\bigcirc$ , dash dot line), one  $200 \times 130 \ \mu\text{m}$  hole ( $\blacklozenge$ , dot line), two  $200 \times 120 \ \mu\text{m}$  holes ( $\blacktriangle$ , dash dot dot line).

Regarding CO<sub>2</sub>, the model is not able to describe its evolution 350 351 when there are microperforations in the packages of peach and 352 cauliflower (Figs. 9, 11 and 12). For example, for the 'Andross' vari-353 ety the estimated CO<sub>2</sub> concentration for packages with perforations of  $90 \times 50 \,\mu\text{m}$  correspond to the experimental results when 354 there are two perforations of this same size. For the 'Calante' vari-355 ety, the predictions for packages with a perforation of 356 357  $200 \times 130 \,\mu\text{m}$  agree with the experimental results for two perfora-358 tions of  $200 \times 120 \,\mu\text{m}$ . These discrepancies are also observed for 359 the cauliflower, where again the calculated results are lower than the experimental values. The respiratory kinetics do not appear 360 361 to be the reason given that the model provides acceptable predictions of data obtained for packages without microperforations. The 362 363 coefficient between the transmission rates of the  $CO_2$  and the  $O_2$  is 364  $0.89 \pm 0.05$ , coming within values obtained by other authors 365 (Emond et al., 1991; Silva et al., 1999). However, it was observed 366 experimentally that when a microperforation of  $90 \times 50 \,\mu\text{m}$  is 367 incorporated, the CO<sub>2</sub> concentration changes very little compared 368 to that obtained when there are no microperforations, while the 369  $O_2$  concentration is more substantially modified. The reduction of



**Fig. 9.** Experimental and predicted evolution of gas composition for cauliflower inside packages with fourteen  $150 \times 80 \,\mu\text{m}$  holes: O<sub>2</sub> ( $\blacksquare$ , continuous line) and CO<sub>2</sub> ( $\blacktriangle$ , dash line).



**Fig. 10.** Experimental and predicted evolution of  $O_2$  composition for black truffle packages: without microperforation ( $\blacksquare$ , continuous line), two 90 × 50 µm holes ( $\Box$ , dash line).

the CO<sub>2</sub> transport through the microperforations compared to the 370 estimated value, which brings about a greater accumulation of this 371 component, could be due to the entry of a continuous air flow in-372 side the package as a consequence of a difference in pressure gen-373 erated by the respiratory activity of the product. The respiratory 374 coefficient of the peach and the cauliflower is lower than 1, which 375 causes a depression inside the package that is immediately com-376 pensated for by the entry of air from the outside through hydrody-377 namic flow. This entry of air can generate in the area around the 378 perforation a CO<sub>2</sub> concentration appreciably different to that exist-379 ing inside the package. The real diffusive flow of CO<sub>2</sub> through the 380 perforation would be lower than the estimated value if on the 381 internal side of the perforation the concentration was the same 382 as that existing near the product. The hydrodynamic flow would 383 also have an effect on the oxygen, but in this case the 'sweeping' 384 effect of the air to the entrance would be lower given that the dif-385 fusion goes in the same direction as the hydrodynamic flow. If the 386 difference in pressure between the exterior and the interior of the 387 package was null, or rather if the hydrodynamic flow went in the 388



**Fig. 11.** Experimental and predicted evolution of CO<sub>2</sub> composition for different 'Andross' peach packages: without microperforation ( $\blacksquare$ , continuous line), one 90 × 50 µm hole ( $\square$ , dash line), two 90 × 50 µm holes ( $\bigcirc$ , dash dot line), one 210 × 135 µm hole ( $\bullet$ , dot line), two 125 × 75 µm holes ( $\blacktriangle$ , continuous thick line), three 200 × 100 µm holes ( $\triangle$ , dash dot dot line).

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**Fig. 12.** Experimental and predicted evolution of CO<sub>2</sub> composition for different 'Calante' peach packages: without microperforation ( $\blacksquare$ , continuous line), one 90 × 50 µm hole ( $\Box$ , dash line), two 90 × 50 µm holes ( $\bigcirc$ , dash dot line), one 200 × 130 µm hole ( $\bullet$ , dot line), two 200 × 120 µm holes ( $\blacktriangle$ , dash dot dot line).

389 opposite direction, it ought to be possible to model the CO<sub>2</sub> con-390 centration correctly. A product such as the truffle whose CO<sub>2</sub> pro-391 duction exceeds its O<sub>2</sub> consumption could approach the conditions of this supposition. The respiratory coefficient of the truffle is high-392 er than 1 and therefore the hydrodynamic flow would go from the 393 interior to the exterior of the package. Theoretically, the O<sub>2</sub> ex-394 change through the microperforation could be difficult in this case, 395 396 but is unlikely in fact due to the continuous movement of air in the 397 storage rooms where the product is kept. The experimental evolu-398 tion of the CO<sub>2</sub> in the packages with truffle coincides with the mod-399 el predictions, Fig. 13. This appears to suggest that the reasons for 400 the lack of agreement between the experimental and calculated 401 values are those given above.

402 The value of a correction factor, k', has been estimated by 403 which the transmission rate of the CO<sub>2</sub>,  $TR_{CO_2}$ , should be multi-404 plied in order to obtain the correct fit of the experimental re-405 sults. For the three products with respiratory coefficients lower 406 than 1, and for all the films used, the value of k' was between 407 0.40 and 0.55. Figs. 14 and 15 show the evolution of the CO<sub>2</sub> pre-



**Fig. 14.** Experimental and predicted evolution of CO<sub>2</sub> composition, modified with a correction factor, for different 'Andross' peach packages: without microperforation ( $\blacksquare$ , continuous line), one 90 × 50 µm hole ( $\Box$ , dash line), two 90 × 50 µm holes ( $\bigcirc$ , dash dot line), one 210 × 135 µm hole ( $\blacklozenge$ , dot line), two 125 × 75 µm holes ( $\blacktriangle$ , continuous thick line), three 200 × 100 µm holes ( $\triangle$ , dash dot dot line).

dicted by the model modified with the correction factors for 'Andross' and 'Calante' peaches, respectively. Despite the fact that the consumption and transmission rates of O2 do not depend on the CO<sub>2</sub> concentration, the oxygen concentration can be seen to be slightly modified by a change in the CO<sub>2</sub> composition. This is due to the fact that a greater accumulation of CO<sub>2</sub>, originated by the inclusion of the correction term  $\underline{k}$ , produces a reduction in the difference of pressure between the interior and the exterior, and therefore in a higher hydrodynamic flow. However, this influence is very small and in all cases the term k' modifies the evolution of the  $O_2$  concentration by less than 3.2%. Obviously the introduction of a correction factor, although useful, should be considered as a temporary solution. Future models need to be developed that are devoid of such factors in which the dependence of the concentration of the different gases with the spatial coordinates is taken into account.



**Fig. 13.** Experimental and predicted evolution of  $CO_2$  composition for black truffle packages: without microperforation ( $\blacksquare$ , continuous line), two 90 × 50 µm holes ( $\Box$ , dash line).



**Fig. 15.** Experimental and predicted evolution of CO<sub>2</sub> composition, modified with a correction factor, for different 'Calante' peach packages: without microperforation ( $\blacksquare$ , continuous line), one 90 × 50 µm hole ( $\Box$ , dash line), two 90 × 50 µm holes ( $\bigcirc$ , dash dot line), one 200 × 130 µm hole ( $\bullet$ , dot line), two 200 × 120 µm holes ( $\blacktriangle$ , dash dot dot line).

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## 424 4. Conclusion

425 The model proposed for describing the evolution of the gas 426 composition in packages with microperforated films and with constant volume, taking into account the permeation through the 427 films, the diffusive and hydrodynamic flow through the microper-428 forations and the respiration rate of the packaged product, is a use-429 430 ful tool for predicting the evolution of O<sub>2</sub> composition. The 431 predictions of the model represent an acceptable match with the 432 experimental O<sub>2</sub> composition for all the products and packages 433 tested. The main novelty of this model lies in the inclusion of a potential relation between the microperforation area and the trans-434 435 mission rate, (Eq. (5)). However, the CO<sub>2</sub> levels estimated by the model are lower than the experimental values for products with 436 respiratory coefficients lower than 1 ('Andross' and 'Calante' pea-437 ches, and cauliflower), but in agreement when the CO<sub>2</sub> production 438 is greater than the O<sub>2</sub> consumption (truffle). It is postulated that 439 440 the reason for this is the existence of an air current flowing from outside the package that reduces the CO<sub>2</sub> concentration around 441 the microperforation. 442

#### 443 5. Uncited references

444 Q1 \_\_\_\_\_ aggar et <u>al. (1992)</u> and <u>Song et al. (1992)</u>.

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