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Modified Atmosphere Packaging: Design and Optimization Strategies for Fresh Produce

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Abstract

Modified atmosphere packaging (MAP) is a useful preservation system that allows to significantly increase the shelf life of fruits and vegetables. The MAP results of changing the composition of the atmosphere in the packaging headspace due to the dynamic interaction between the metabolic processes of the packaged product on the one hand, in which O_2 is consumed and another gases such as CO_2 and water vapor are generated, and on the other hand, by transferring all of these gases through the package. The aim of the system is to balance these two processes in such a way that constant levels of these different gases are reached in the packaging headspace and that these equilibrium levels are as favorable as possible to preserve the product. This chapter describes design strategies to obtain a satisfactory gas transfer capacity in the MAP system through the configuration of several related variables such as the type of packing material, its thickness, the transfer surface area and the required number and diameter of perforations. For this, the necessary steps are proposed to estimate the appropriate transfer capacity according to the equilibrium gas concentrations desired to longer preserve the product by using the mass balance equations of the MAP system.

Keywords: packaging configuration, gas transfer capacity, perforation, preservation, fruits, vegetables

1. Introduction

After harvest, the fresh produce undergoes a series of biochemical transformations that lead to the development of color, aroma and characteristic flavors, reduction of acidity and tissue softening [1, 2]. These processes continue until the substrates that support them are consumed, after which follows the deterioration or senescence phase. The postharvest period involves a series of biochemical reactions or metabolic activities that can lead to an increase in the concentration of organic acids, lipids, phenolic compounds, generation of

volatile compounds (aroma), variations in the activity of enzymes, degradation of chlorophyll and biosynthesis of pigments, degradation of pectins and conversion of starch in sugars, which will cause loss of firmness and weight, and increase in the sweetness perception [1, 3–5]. In the case of edible products, all previous processes lead to the development of characteristics that make them acceptable for consumption [1, 6]. In this period, the plant cells continue their respiratory activity, using oxygen from the surrounding atmosphere and releasing carbon dioxide as result of a series of oxide-reduction reactions of the substrates present [7, 8].

The respiratory response of fresh produce in postharvest and the development of ripening and senescence processes depends on the temperature, of the atmosphere surrounding the stored product and also on the levels of gases such as O_2 , CO_2 , ethylene and water vapor, which strongly influence its metabolism. For this reason, by regulating the temperature and gas concentrations in the atmosphere surrounding the product, it is possible to reduce the development of its different biochemical processes and increase its preservation time [9–11]. Likewise, the growth of microorganisms that may cause deterioration or other potentially pathogenic organisms will also be closely related to environmental conditions due to their development, and activity can be controlled by modifying these conditions [9].

1.1. Modified atmosphere packaging

Modified atmosphere packaging (MAP) has been constituted as a preservation method that allows to significantly increase the shelf life of fruits and vegetables. The MAP results of changing the composition of the atmosphere surrounding the product in order to reduce its natural deterioration and the microbial spoilage [9, 12]. In a MAP system, there is a change in the concentration of gases in the packaging headspace due to the dynamic interaction between the metabolic and biochemical processes of the packaged product on the one hand, in which O_2 is consumed and CO_2 , ethylene and water vapor are generated, and on the other hand, the transfer of all of these gases through the packaging. Accordingly, O_2 from the external atmosphere will be entering through the packaging to replace that the product is consuming and the other gases will be leaving out through the packaging system as surplus [11, 13–15]. The aim of the system is to balance these two processes in such a way that constant levels of these different gases are reached in the packaging headspace and that these equilibrium levels are as favorable as possible to preserve the product [9].

In the first MAP systems, a reference was made to active and passive atmospheres depending on whether a volume of gas with a different atmospheric concentration was introduced at the time of sealing the package (active MAP), or simply the bag was sealed with atmospheric air (passive MAP). This is of limited utility if it is not considered that regardless of the initial concentration of gases in the packaging headspace, the final concentration of these will depend on the interaction between the metabolic processes of the product (and possible microorganisms present) and the exchange of gases through the packaging. Failure to know the different rates at which these processes are carried out will result in an inadequate MAP, resulting in concentrations of gases that do not contribute to preserving the product at the best or that

directly increase its deterioration at the worst [9, 14]. For this reason and in order to obtain a satisfactory MAP, it is necessary to design the packaging system previously, and this basically consists of determining the gas transfer capacity in the packaging that is required to balance the metabolic processes of the product to be packed and in this way, to achieve favorable gas concentrations for its preservation [13].

After packing a fruit or vegetable, the O₂ concentration in the headspace will decrease, and the CO₂ concentration will increase until reaching constant values once the equilibrium is reached. In these conditions of reduced O₂ and high CO₂, the metabolic processes of the product and the microbial activity slow down increasing its shelf life. Likewise, as the storage temperature decreases, there is also a reduction in the development of these processes resulting in an additional increase of the produce shelf life [11]. On the other hand, low O₂ levels, high CO₂ levels and above all, low temperatures in the packaging system can significantly decrease the growth of microorganisms that cause deterioration in the product and of other ones potentially pathogenic [16]. In these unfavorable circumstances for microbial growth (low O₂, high CO₂ and low temperature), a competition is established between the produce, natural microflora and other external and potentially pathogenic microorganisms that has an inhibitory effect for the development of the latter ones [17]. As shown in **Table 1**, for a wide range of fresh produce, the most favorable levels in the packaging headspace for preservation are between 1 and 10% of O₂, 5 and 15% of CO₂ and 80 and 90% RH, with temperatures as low as possible (0–15°C) but without inducing chilling injury [9, 18, 19].

1.2. MAP uses to preserve vegetables and fruits

MAP has been successfully applied to preserve several vegetables including broccoli, cauliflower, carrots, garlic and others [20]. The effect of the packaging has been studied on the quality of broccoli [21] and cauliflowers [22]. In order to preserve these products, micro or macro perforated polyethylene and polypropylene bags have been used to compensate for the respiration and transpiration of the packed product and to achieve favorable equilibrium gas levels for its preservation [11, 23]. Other vegetables have been successfully preserved in MAP systems, including cabbage [24], cucumber [25], onion [26], spinach [27] and tomato [28]. Refrigeration temperatures were used in all cases, although at room temperatures, the packaging system may continue to have a preservation effect, although somewhat lower [1, 9].

As for fruits, MAP systems have been used successfully to preserve apple [29], banana [30], breba [31], blueberry [32], feijoa [18], grape [33], guava [34], mandarin [10], medlar [15], papaya [35], pear [36], pomegranate [37], strawberry [38] and others. In all these cases, it was possible to increase the product shelf life between 40% and up to twice with respect to atmospheric conditions. Recommended O₂ and CO₂ concentrations in the MAP system are shown in **Table 1** for various fruits and vegetables.

1.3. Packaging materials used in MAP

Most MAP systems consist of flexible or semiflexible structures, bags of different sizes and thicknesses with and without perforations [39]. The most widely used polymer films for MAP

Produce	O ₂ (%)	CO ₂ (%)
<i>Fruits</i>		
Apple	2–3	1–3
Avocado	2–5	3–10
Banana	2–5	2–8
Feijoa	5–11	7–12
Mango	3–7	5–8
Orange	5–10	5–8
Pear	2–3	2–5
Strawberry	5–10	5–15
<i>Vegetables</i>		
Broccoli	2–3	5–10
Carrot	2–5	2–5
Lettuce	2–3	1–3
Onion	2–5	2–10
Pepper	3–5	1–3
Radish	2–5	2–5
Spinach	15–20	10–20
Tomato	3–5	5–11

Data compiled from [2, 11, 12, 18].

Table 1. Suitable O₂ and CO₂ concentrations in MAP for different fruits and vegetables.

are synthetic polyolefins, low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polyesters, polyethylene terephthalate (PET), polyvinylidene chloride (PVDC), ethylene-vinyl alcohol (EVOH), polyamide (Nylon), polyvinyl alcohol (PVOH), ethylene vinyl acetate (EVA), cellulose-derived plastics such as cellophane and natural biodegradable polymers like polylactic acid (PLA) [11, 19]. Each of these polymeric materials offers different mechanical characteristics and fundamentally different permeability to O₂, CO₂ and water vapor. Depending on the specific requirements of gas permeation, materials of very low permeability to O₂ and CO₂ such as polyamide, of moderate permeability such as polypropylene and EVA, or of high permeability as LDPE can be selected or even combinations of these materials can be made in several layers to adjust the MAP system to the produce respiration and transpiration [9, 39]. In addition, in order to avoid the accumulation of moisture inside the package while maintaining a reduced permeability to O₂ and CO₂, it is possible to use PLA or EVOH, which have a high permeability to water vapor [39, 40]. In **Table 2**, permeability (Q) coefficients to O₂, CO₂ and water vapor are for different polymeric materials.

Polymeric material	Q_{O_2}	Q_{CO_2}	Q_{N_2}	$Q_{H_2O}^*$
Low-density Polyethylene (LDPE)	190–200	1050–1250	100–150	5500–6000
High-density Polyethylene (HDPE)	40–70	160–190	14–20	2100–2500
Cast Polypropylene (PP)	80–95	250–280	17–25	4000–4200
Oriented Polypropylene (OPP)	40–50	180–200	10–15	1800–2200
Polylactic Acid (PLA)	60–80	150–190	20–30	300000–350000
Ethylene vinyl acetate (EVA)	300–330	1100–1300	120–150	10000–15000
Polyamide (PA)	1–5	3–10	0.3–1	20000–30000

* Permeability coefficient to water vapor
 Estimated from [9, 11, 13, 39, 40, 64]

Table 2. Permeability coefficients ($\text{cm}^3 \text{ mm m}^{-2} \text{ atm}^{-1} \text{ d}^{-1}$) at 20°C for different packaging materials.

2. Dynamics of a MAP system

In the design of MAP systems for fresh produce, it is necessary to understand the dynamics of the interactions established between the product, the atmosphere generated in the packaging headspace and the packaging system itself. Each MAP design must be optimized for a specific product, since agricultural products have different metabolisms to each other and, as mentioned above, the MAP system must balance the processes of respiration, transpiration and gas permeation through the packaging that will be occurring simultaneously. Factors that affect both the metabolism of the packaged product and the gas permeation through the packaging should be considered for the design of the MAP system [9, 14, 41]. Among these factors are the type of produce and ripening stage, the characteristics of the packaging system and the storage conditions [10, 13, 42]. With regard to the packaged product, it is also necessary to know in advance its transpiration, oxygen consumption and CO_2 and ethylene generation rates at the packaging conditions and the optimum concentrations of these gases and relative humidity that favor the increase of its shelf life [10, 41, 43].

For the proper design of the MAP system, different mathematical models have been developed to represent the processes of respiration, transpiration and ethylene production for a variety of horticultural products [14, 44, 45]. In these models, it is intended to represent the rates of O_2 consumption and CO_2 , ethylene and water vapor generation from the product as a function of the storage temperature, the concentration of these gases in the packaging headspace and the weight of the packaged product. In some studies, these metabolic processes developed in the fresh produce are described by using enzymatic kinetics equations [37, 46, 47], while in other studies, empirical or semiempirical equations are used to represent them [10, 48, 49]. As for the transfer of gases through the packaging and the perforations that it may have, generally have been developed models derived from the Fick's law, stating the mass balances for each gas in the system and considering the influence of the temperature at the gas permeation rates [14, 50].

2.1. Mathematical representation of the MAP system

The change in the composition of each gas in the packaging headspace will depend on the metabolic processes of the packaged product and the gas transfer through the packaging system.

$$\left[\begin{array}{c} \text{Accumulation or} \\ \text{decrease rate of gas in} \\ \text{the packaging headspace} \end{array} \right] = \left[\begin{array}{c} \text{Transfer rate of} \\ \text{gas through the} \\ \text{packaging system} \end{array} \right] + \left[\begin{array}{c} \text{Generation or} \\ \text{consumption rate of} \\ \text{gas from the product} \end{array} \right] \quad (1)$$

As mentioned above, when the product is packaged will begin to consume O_2 from the packaging headspace and to generate CO_2 due its respiration, water vapor due its transpiration and ethylene. This will create a concentration differential between the inside and outside of the package resulting in an O_2 inlet and an outlet of the other gases to the external atmosphere. The composition of the different gases will be changing until a balance is reached between the metabolic processes in the product and the transfer of gases through the package (Eq. (2)). At this point, the MAP system becomes an equilibrium modified atmosphere packaging (EMAP), which is a kind of self-sustaining controlled atmosphere system that will be maintained until the product substrates are consumed or until storage conditions such as temperature are altered.

$$\left[\begin{array}{c} \text{Generation or} \\ \text{consumption rate of} \\ \text{gas from the product} \end{array} \right] = \left[\begin{array}{c} \text{Transfer rate of} \\ \text{gas through the} \\ \text{packaging system} \end{array} \right] \quad (2)$$

2.1.1. Respiration rate

Fresh produce shelf life depends on its respiration rate. Fruits such as mango and banana that have high respiration rates are highly perishable [7]. The energy released during respiration is associated with the energy required to completely oxidize a mole of substrate to CO_2 and H_2O . In the case of a mole of hexose that is the most common carbohydrate, approximately 2880 kJ are released. Each hexose molecule is oxidized to 6 CO_2 molecules, using 32 molecules of adenosine diphosphate (ADP) and six molecules of O_2 to form 12 water molecules (Eq. (3)). Under normal physiological conditions, 50 to 60% of this energy is chemically captured to form 32 molecules of adenosine triphosphate (ATP), which are required for subsequent cell metabolic processes [12, 45, 51]. As respiration is a series of oxidation reactions, the rate at which it is carried out will be related to the O_2 concentration in the medium, and when this concentration decreases, the energy released will also be reduced [52].



In the case of carbohydrates such as glucose or fructose, when these are completely oxidized, the O_2 volume used per unit time will be practically the same as the volume of generated CO_2 per unit time [12, 45]. For organic acid oxidation, more CO_2 volume is produced than the used O_2 and for lipids oxidation, less CO_2 volume is generated than O_2 used. From the above, the respiratory quotient (RQ) is defined as the ratio of CO_2 produced to O_2 consumed per unit

time [53, 54]. The RQ values range between 0.7 and 1.3 for the majority of fresh produce [12]. High RQ values usually indicate anaerobic respiration in produce tissues or microbial activity that produces aldehydes and alcohols through fermentation. In such cases, a rapid change in the RQ can be used as an indication of the shift from aerobic to anaerobic respiration [2]. **Table 3** shows estimated O₂ consumption, CO₂ production rates and RQ values for different fruits and vegetables.

Produce	r _{O₂}	r _{CO₂}	RQ
Apple	340–380	350–450	1.02–1.20
Avocado	3500–3800	2400–2700	0.70–0.72
Banana	3400–3600	2600–2700	0.75–0.76
Broccoli	2200–2400	2000–2150	0.88–0.90
Feijoa	4500–4800	3600–3800	0.79–0.80
Guava	850–1000	800–950	0.95–0.98
Strawberry	1050–1150	1000–1100	0.94–0.96
Tomato	640–680	700–730	1.05–1.07

Estimated from [12–14, 41, 47, 54, 57]

Table 3. O₂ consumption and CO₂ production rates (cm³ kg⁻¹ d⁻¹) and respiratory quotient at 20°C and atmospheric air for different fresh produce.

Many mathematical models and equations have been used to represent the respiration process in fresh produce and the effect of the O₂ and CO₂ levels and storage temperature. These models include empirical equations, chemical kinetics and enzyme kinetics equations based on the Michaelis-Menten (MM) model [14, 42, 45, 47, 54–57]. Among these equations stand out the Michaelis-Menten kinetics that have been successfully used for many products, specifically the equation of uncompetitive inhibition (MMU) wherein the inhibitor (CO₂ in this case) reacts with the enzyme-substrate complex, reducing the overall respiration rates at high concentrations. Nevertheless, the maximum O₂ consumption or CO₂ production rates are not influenced by the CO₂ levels in the atmosphere surrounding the product [14, 45, 55, 58–60].

In the MMU kinetics, the rates of O₂ consumption and CO₂ generation are, respectively:

$$r_{O_2} = \frac{r_{O_{2max}} y_{O_2}}{K_{m_{O_2}} + y_{O_2} \left(1 + \frac{y_{CO_2}}{K_{mu_{CO_2}}} \right)} \quad (4)$$

$$r_{CO_2} = \frac{r_{CO_{2max}} y_{O_2}}{K_{m_{CO_2}} + y_{O_2} \left(1 + \frac{y_{CO_2}}{K_{mu'_{CO_2}}} \right)} \quad (5)$$

where r_{O₂} and r_{CO₂} are the O₂ consumption and CO₂ production rates, respectively (in cm³ kg⁻¹ d⁻¹); r_{O_{2max}} and r_{CO_{2max}} are the maximum rates of O₂ consumption or CO₂ production,

K_{mO_2} and K_{mCO_2} are the dissociation constants of the enzyme-substrate complex, and K_{muCO_2} and $K_{mu'CO_2}$ are the inhibition constants due to CO_2 [14, 45, 47]. In other cases, competitive, non-competitive or combined MM models have been used to represent the respiration rates [45, 12].

Respiration rates are also directly influenced by temperature. As temperature increases, O_2 consumption and CO_2 production becomes higher, and this relationship has been satisfactorily described by considering each of the parameters of the Michaelis-Menten kinetics dependent on temperature by using the Arrhenius' Law [14, 47].

2.1.2. Transpiration rate

The transpiration rate can be defined as the water lost or evaporated in the product per unit time. The transpiration and water loss can be considered as a consequence of the heat transferred to and from the product and the vapor pressure difference between the product and the surrounding atmosphere [41, 46, 61, 62]. When the vapor pressure in the atmosphere is less than the vapor pressure in the product, it could be considered that both processes will contribute to transpiration [44]. When the vapor pressures become equal, transpiration only will be seen as a consequence of the heat exchange to and from the product. This heat will be transferred to evaporate the product moisture mainly from the fraction of dissipated energy in the respiration process (that than is not used in the product metabolism), and from the temperature difference between the product and the surrounding atmosphere in the process of cooling [41, 46]. Some part of this energy transferred will change the product temperature as sensible heat, while another part will be converted to latent heat through moisture evaporation. If the system is in thermal equilibrium, as in a temperature-controlled chamber, the only heat that contributes to the moisture evaporation in the product will be the dissipated fraction of its respiratory heat. Thus, considering the above, the transpiration rate in a fresh produce can be expressed as follows:

$$r_{H_2O} = \frac{q}{\lambda} \left(\frac{RT}{PM_{H_2O}} \right) + k(a_{wp} - a_{wat}) \quad (6)$$

where r_{H_2O} is the transpiration rate (in $cm^3 \text{ kg}^{-1} \text{ d}^{-1}$), q is the total heat transferred to the product (kJ d^{-1}), λ is the latent heat of moisture evaporation (kJ kg^{-1}), R is the gas constant, T is the temperature, P is the pressure, and M_{H_2O} is the water molar mass. In addition, k is total mass transfer coefficient due the water vapor differential ($cm^3 \text{ kg}^{-1} \text{ d}^{-1}$), a_{wp} is the water activity in the product, and a_{wat} is the water activity in the surrounding atmosphere. The coefficient k will be influenced by temperature, and this relation can be expressed using the Arrhenius' Law [41]. If the packing system is not in thermal equilibrium, it may be assumed that the effective heat contributing to the evaporation of water besides the water activity gradient is the dissipated fraction of respiratory heat to simplify the calculations in Eq. (6). In that case, it is necessary to write the energy balance of the packaging system to estimate the temperature change in the product [61].

In case that the vapor pressure in the atmosphere (in the packaging headspace) becomes equal to the saturation pressure at the storage temperature, the water lost by the product as vapor

will be condensed almost instantly inside the package [63]. On the other hand, as a result of transpiration, the weight of the packaged product will be decreasing over the storage time which can bring undesirable effects on its quality. This weight loss can be quite significant when the differences in water activities between the product and the surrounding atmosphere are large or when the storage time is long, and for this reason, it should be considered in the modeling of the MAP system [41].

2.1.3. Gas permeation through the packaging film

The permeability of a material to different gases will be determined by its molecular structure, thickness, surface area available for mass transfer, concentration gradient, pressure differential and temperature [13, 39, 64]. For some biopolymers, the relative humidity should also be considered [40]. When the film structure is uniform, without cracks or perforations, the gas will flow through the material by molecular diffusion. First, the gas will be adsorbed to the near face of the film, then the gas will diffuse through the film due to the concentration differential (from the point of greatest concentration to the point of lowest concentration), and thereafter, it will be desorbed from the farthest face from the film [12, 39].

The permeation or transfer of a gas i through the material constituting the packaging system can be expressed as follows [13, 65]:

$$J_{fi} = - \frac{Q_i A (p_{i,in} - p_{i,out})}{L} \frac{P}{RT} \quad (7)$$

where J_{fi} is the gas permeation through the continuous packaging film (mol d^{-1}), Q_i is the permeability coefficient of gas i in the packing material ($\text{cm}^3 \text{ mm m}^{-2} \text{ atm}^{-1} \text{ d}^{-1}$), and p_i and $p_{i,out}$ are the partial pressures of gas i in and out of the package (atm). P is the local pressure (atm), A is the film surface area (m^2), and L is the thickness of the packaging material (mm). The permeability of the packaging films will depend on the storage temperature, and this can be represented by using the Arrhenius' Law considering the permeability coefficient Q_i as a function of temperature [43].

2.1.4. Gas transmission through perforations in the packaging system

The gas transfer through perforations made in each packaging film can be described by using the Fick's diffusion equation with a correction term (ϵ in Eq. (8)) due to the resistance to diffusion at the perforation [13, 66]. Thus, the transmission rate of gas i through the perforation (K_{TRI} in $\text{cm}^3 \text{ d}^{-1}$) can be defined as follows:

$$K_{TRI} = \frac{D_i A_h}{L + \epsilon} \quad (8)$$

where D_i is the diffusion coefficient of the packaging film to gas i , A_h is the cross-sectional area of the perforations, L is the film thickness, and ϵ is the correction term due the diffusion resistance in the perforation channel. The correction term ϵ can be estimated as approximately 0.5 times the effective diameter (d_e) of the perforations, the effective diameter being related to

the diameter of each perforation and to the total number of perforations through the expression $d_e = N^{1/2}d$ [10, 13, 59].

The transmission 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 headspace and the external atmosphere [13, 48]. The dependence of the diffusion coefficients with respect to temperature can be described in the same way as the permeability coefficients using Arrhenius' law.

2.2. Balance equations for the MAP system

In the headspace of a MAP system, the change in the O_2 , CO_2 , H_2O and N_2 concentrations can be described by using the mass balance equations for each gas considering the respiration and transpiration rates, the gas transfer through the packaging material, the gas transmission through the perforations in the package and the changes in volume or pressure. To write the equations, it is necessary to consider whether the packaging system is flexible or rigid [13, 48, 50].

If the packaging system is flexible (such as a bag), the packaging headspace will be varying with the change in the number of moles of gases in the system, while the pressure can be considered constant and equal to the atmospheric pressure. In this case, the balance equations will be as follows:

For O_2 ,

$$V \frac{dy_{O_2}}{dt} = K_{TRO_2}(y_{O_{2Out}} - y_{O_2}) + \frac{APQ_{O_2}}{L}(y_{O_{2Out}} - y_{O_2}) - r_{O_2}W - y_{O_2} \frac{dV}{dt} \quad (9)$$

For CO_2 ,

$$V \frac{dy_{CO_2}}{dt} = K_{TRCO_2}(y_{CO_{2Out}} - y_{CO_2}) + \frac{APQ_{CO_2}}{L}(y_{CO_{2Out}} - y_{CO_2}) + r_{CO_2}W - y_{CO_2} \frac{dV}{dt} \quad (10)$$

For H_2O

$$V \frac{dy_{H_2O}}{dt} = K_{TRH_2O}(y_{H_2O_{out}} - y_{H_2O}) + \frac{APQ_{H_2O}}{L}(y_{H_2O_{out}} - y_{H_2O}) + r_{H_2O}W - y_{H_2O} \frac{dV}{dt} \quad (11)$$

For N_2 ,

$$V \frac{dy_{N_2}}{dt} = K_{TRN_2}(y_{N_{2Out}} - y_{N_2}) + \frac{APQ_{N_2}}{L}(y_{N_{2Out}} - y_{N_2}) - y_{N_2} \frac{dV}{dt} \quad (12)$$

where y_{O_2} , y_{CO_2} , y_{H_2O} and y_{N_2} are the O_2 , CO_2 , water vapor and N_2 concentrations in the packaging headspace, respectively; $y_{O_{2Out}}$, $y_{CO_{2Out}}$, $y_{H_2O_{out}}$ and $y_{N_{2Out}}$ are the gas external concentrations, V is the headspace volume (cm^3), W is the product weight (kg), and t is the storage time (d).

The headspace volume change over time can be written as follows:

$$\frac{dV}{dt} = W(r_{\text{CO}_2} - r_{\text{O}_2} + r_{\text{H}_2\text{O}}) + \sum_{i=1}^4 \left((y_{i\text{Out}} - y_i) \left(K_{\text{TR}i} + \frac{APQ_i}{L} \right) \right) \quad (13)$$

where i is O_2 , CO_2 , water vapor or N_2 .

If the headspace atmosphere is saturated ($\text{RH} = 100\%$ and $y_{\text{H}_2\text{O}} = P_s/P$, where P_s is the saturation pressure), the change in the water vapor concentration with the storage time in the headspace will be zero, and the water evaporated in the product due to its transpiration ($r_{\text{H}_2\text{O}}$) will be condensing inside the package. In this case, the Eq. (11) can be written as:

$$\frac{dy_{\text{H}_2\text{O}}}{dt} = 0 \quad (14)$$

In this case, the contribution of $r_{\text{H}_2\text{O}}$ to the volume change in the packaging headspace is not considered in Eq. (13).

If the packaging system is rigid, the packaging pressure will be varying with the change in the moles of gases in the system while the headspace volume can be considered constant along the storage time. In this case, the balance equations will be as follows:

For O_2 ,

$$V \frac{dy_{\text{O}_2}}{dt} = K_{\text{TRO}_2} (y_{\text{O}_{2\text{Out}}} - y_{\text{O}_2}) + \frac{APQ_{\text{O}_2}}{L} (y_{\text{O}_{2\text{Out}}} - y_{\text{O}_2}) + \frac{N\pi d^4 (P_{\text{out}} - P) y_{\text{O}_2}}{128\mu L_h} - r_{\text{O}_2} W - y_{\text{O}_2} \frac{V dP}{P dt} \quad (15)$$

For CO_2 ,

$$V \frac{dy_{\text{CO}_2}}{dt} = K_{\text{TRCO}_2} (y_{\text{CO}_{2\text{Out}}} - y_{\text{CO}_2}) + \frac{APQ_{\text{CO}_2}}{L} (y_{\text{CO}_{2\text{Out}}} - y_{\text{CO}_2}) + \frac{N\pi d^4 (P_{\text{out}} - P) y_{\text{CO}_2}}{128\mu L_h} + r_{\text{CO}_2} W - y_{\text{CO}_2} \frac{V dP}{P dt} \quad (16)$$

For H_2O

$$V \frac{dy_{\text{H}_2\text{O}}}{dt} = K_{\text{TRH}_2\text{O}} (y_{\text{H}_2\text{O}_{\text{out}}} - y_{\text{H}_2\text{O}}) + \frac{APQ_{\text{H}_2\text{O}}}{L} (y_{\text{H}_2\text{O}_{\text{out}}} - y_{\text{H}_2\text{O}}) + \frac{N\pi d^4 (P_{\text{out}} - P) y_{\text{H}_2\text{O}}}{128\mu L_h} + r_{\text{H}_2\text{O}} W - y_{\text{H}_2\text{O}} \frac{V dP}{P dt} \quad (17)$$

For N_2 ,

$$V \frac{dy_{\text{N}_2}}{dt} = K_{\text{TRN}_2} (y_{\text{N}_{2\text{Out}}} - y_{\text{N}_2}) + \frac{APQ_{\text{N}_2}}{L} (y_{\text{N}_{2\text{Out}}} - y_{\text{N}_2}) + \frac{N\pi d^4 (P_{\text{out}} - P) y_{\text{N}_2}}{128\mu L_h} - y_{\text{N}_2} \frac{V dP}{P dt} \quad (18)$$

where $P_{\text{out}} - P$ represents the difference in pressure between the packaging headspace and the external atmosphere, which results in a gas flow through the packaging system that can be described by using the Poiseuille's Law [50, 59]. N is the number of perforations, d is the perforation diameter, μ is the viscosity of the gas mixture (which can be considered as air), and L_h is the effective length of the perforations ($L + \epsilon$).

The headspace pressure change over time can be written as follows:

$$\frac{dP}{dt} = P \left(W(r_{\text{CO}_2} - r_{\text{O}_2} + r_{\text{H}_2\text{O}}) + \sum_{i=1}^4 \left((y_{i\text{Out}} - y_i) \left(K_{\text{TRI}} + \frac{APQ_i}{L} \right) + y_i \frac{N\pi d^4 (P_{\text{out}} - P)}{128\mu L_h} \right) \right) \quad (19)$$

where i is again O_2 , CO_2 , water vapor or N_2 .

As before, if the headspace atmosphere is saturated ($\text{RH} = 100\%$), the change in the water vapor concentration with the storage time in the headspace will be zero, and the water evaporated in the product due to its transpiration will be condensing inside the package. In this case, the Eq. (17) will be equal to Eq. (14). In this case again, the contribution of $r_{\text{H}_2\text{O}}$ to the pressure change in the packaging headspace is not considered in Eq. (19).

The weight change in the packed product over time can be determined as follows [41]:

$$\frac{dW}{dt} = -W r_{\text{H}_2\text{O}} \left(\frac{PM_{\text{H}_2\text{O}}}{RT} \right) \quad (20)$$

where W is the product weight, $r_{\text{H}_2\text{O}}$ is the transpiration rate, P is the packaging pressure, R is the gas constant, T is the temperature, and $M_{\text{H}_2\text{O}}$ is the water molar mass.

2.3. Model considerations and numerical solution

By using the mass balance equations for the MAP system in combination with the equations to represent the product respiration and transpiration and the transfer of the gases through the package and perforations, it is possible to represent the change in the composition of the packaging headspace along the time under defined conditions. However, for the set of equations to be useful and achieve a numerical solution, it is required to establish several considerations and assumptions in the MAP model [14, 41, 48, 50]:

- During the packaging time, it can be assumed that the respiration and transpiration rates in the product are not affected by ripening or senescence considering that in general, at this time, the product is expected to remain in a kind of pseudoequilibrium state while consuming the substrates that allow the development of these processes.
- After reaching the thermal equilibrium in the packaging system, this is conserved throughout the storage.
- All temperature dependent processes can be modeled based on Arrhenius' law.

- The stratification of gases inside the package is negligible considering that at the sizes of packaging usually used in MAP, the concentration gradients are small due to the similarity in diffusivities of the gases involved and the small lengths of gas diffusion.
- The flexible packaging system acts as a kind of cylinder-piston when there is a change in the composition and the amount of gas in the packaging headspace, keeping the pressure approximately constant. Also in the rigid packaging system, the volume remains approximately constant throughout the storage time.
- The amount of moisture gained by the product is negligible with respect to the amount lost due to its transpiration.

The equations for the MAP system can be solved numerically by using a suitable program routine to integrate multiple differential equations [13, 43, 48]. Whereas some components of the model solution, such as O_2 and CO_2 concentrations in headspace will change more rapidly than others such as water vapor concentration, headspace volume or product weight, the equations of the MAP system are characterized by being stiff or numerically unstable unless very small step sizes are used in the iteration process to find the solution. For this reason, it is recommended to use multistep implicit methods based on numerical differentiation formulas (NDF) [41]. When the packaging conditions such as concentration of gases and relative humidity in the external atmosphere, atmospheric pressure, product weight, packaging material, area and thickness of the flexible or rigid package and initial gas levels, headspace volume and pressure are defined, it is possible to estimate the change in the headspace atmosphere composition for a determined storage time.

3. Configuration of a suitable MAP

Each MAP design must be optimized for a specific product, since agricultural products have different metabolisms to each other, and as mentioned above, the MAP system must balance the processes of respiration, transpiration, ethylene production and gas permeation through the packaging that will be occurring simultaneously. Taking all of this into account, factors that affect both the metabolism of the packaged product and the gas permeation through the packaging should be considered for an optimal design of the MAP system [9, 14, 18]. Among these factors are firstly, the product maturity and ripeness stage, its weight and geometry and if it is whole or cut into fractions and secondly, the characteristics of the packaging system such as material, surface area, film thickness and headspace volume, and finally, the storage conditions such as temperature and external relative humidity [10, 13, 42]. With regard to the packaged product, it is also necessary to know in advance its transpiration, respiration rates at the packaging conditions and the optimum concentrations of these gases and relative humidity that increase its shelf life [10, 18, 43].

Once the rates of the metabolic processes and characteristics of the packaged product are known, it is also necessary to determine the gas levels and temperature that are most favorable for its preservation. In this way, it is possible to determine the configuration of the packaging

system in which the different processes are balanced, and the appropriate gas levels are reached steadily over the storage time [10, 18, 67].

The design methodology of a successful MAP system can follow the steps shown in **Figure 1**.

First, it is necessary to define the product to be preserved and to determine its relevant characteristics such as maturity and ripeness stage, and configuration (whole or cut). It is then necessary to determine a suitable storage temperature that does not result in product deterioration (generally, it will be the most favorable temperature, but according to the specific conditions of distribution can be higher or even room temperature). Likewise, it is required to evaluate the levels of gases favorable for longer preserve the produce: O_2 , CO_2 and HR. In order to determine these suitable conditions of temperature and gas concentrations, it may be required to perform experimental tests at various storage conditions or consult available data from literature for the product to be preserved.

To determine the gas transfer capacity required in the MAP system, it is necessary to pre-estimate the respiration and transpiration rates of the product to be packed. These rates can be determined as a function of gas levels and temperature by using Eqs. (4)–(6) and knowing previously the parameters of each equation that must be obtained experimentally or from other studies [41, 45, 47].

Once the aspects corresponding to the product to be preserved are known, then the configuration of the packaging system for its preservation is followed. First, it is necessary to evaluate of the packaging material to be used and estimation of its permeation rates to the different gases. This evaluation will of course depend on the transfer capacity required to properly balance the metabolism of the product. For a product with high respiration rates, a packing material with high permeability to O_2 and CO_2 is required. Likewise, for a product with high transpiration rate, a packing material with a high permeability to water vapor will be necessary. Other considerations must be made such as the availability and cost of the packaging material. Many biodegradable polymers such as PLA or EVOH are suitable for MAP systems but their availability on the market is still limited, and their cost is still high compared to synthetic materials such as PP and LDPE.

To determine the required transfer capacity in the package to reach the suitable gas levels (O_2 , CO_2 or RH), it is necessary to estimate the transfer area of the packaging material and/or the size of the perforations required by using the mass balance equations of the MAP system in steady state [13, 43]. If the gas transfer capacity in the package is enough to compensate the produce respiration and transpiration, after a certain time an atmosphere of equilibrium will be reached inside the MAP system and for a flexible packaging, for example, Eqs. (9)–(12) may be rewritten as follows:

$$\left(K_{TRO_2} + \frac{APQ_{O_2}}{L} \right) (y_{O_{2Out}} - y_{O_{2eq}}) - r_{O_2} W - y_{O_{2eq}} \frac{dV}{dt} = 0 \quad (21)$$

$$\left(K_{TRCO_2} + \frac{APQ_{CO_2}}{L} \right) (y_{CO_{2Out}} - y_{CO_{2eq}}) + r_{CO_2} W - y_{CO_{2eq}} \frac{dV}{dt} = 0 \quad (22)$$

$$\left(K_{\text{TRH}_2\text{O}} + \frac{APQ_{\text{H}_2\text{O}}}{L} \right) (y_{\text{H}_2\text{O}_{\text{out}}} - y_{\text{H}_2\text{O}_{\text{eq}}}) + r_{\text{H}_2\text{O}} W - y_{\text{H}_2\text{O}_{\text{eq}}} \frac{dV}{dt} = 0 \quad (23)$$

where $y_{\text{O}_2 \text{ eq}}$, $y_{\text{CO}_2 \text{ eq}}$ and $y_{\text{H}_2\text{O} \text{ eq}}$ are the equilibrium O_2 , CO_2 and water vapor concentrations. The change in the free package volume over time dv/dt , is substituted from Eq. (13). The N_2 balance is not necessary since N_2 concentration (molar fraction) is a function of the O_2 , CO_2 and water vapor concentrations considering that the sum of all concentrations must be equal to 1, and that the presence of other gases is negligible. In the case of rigid packages, Eqs. (14)–(17)

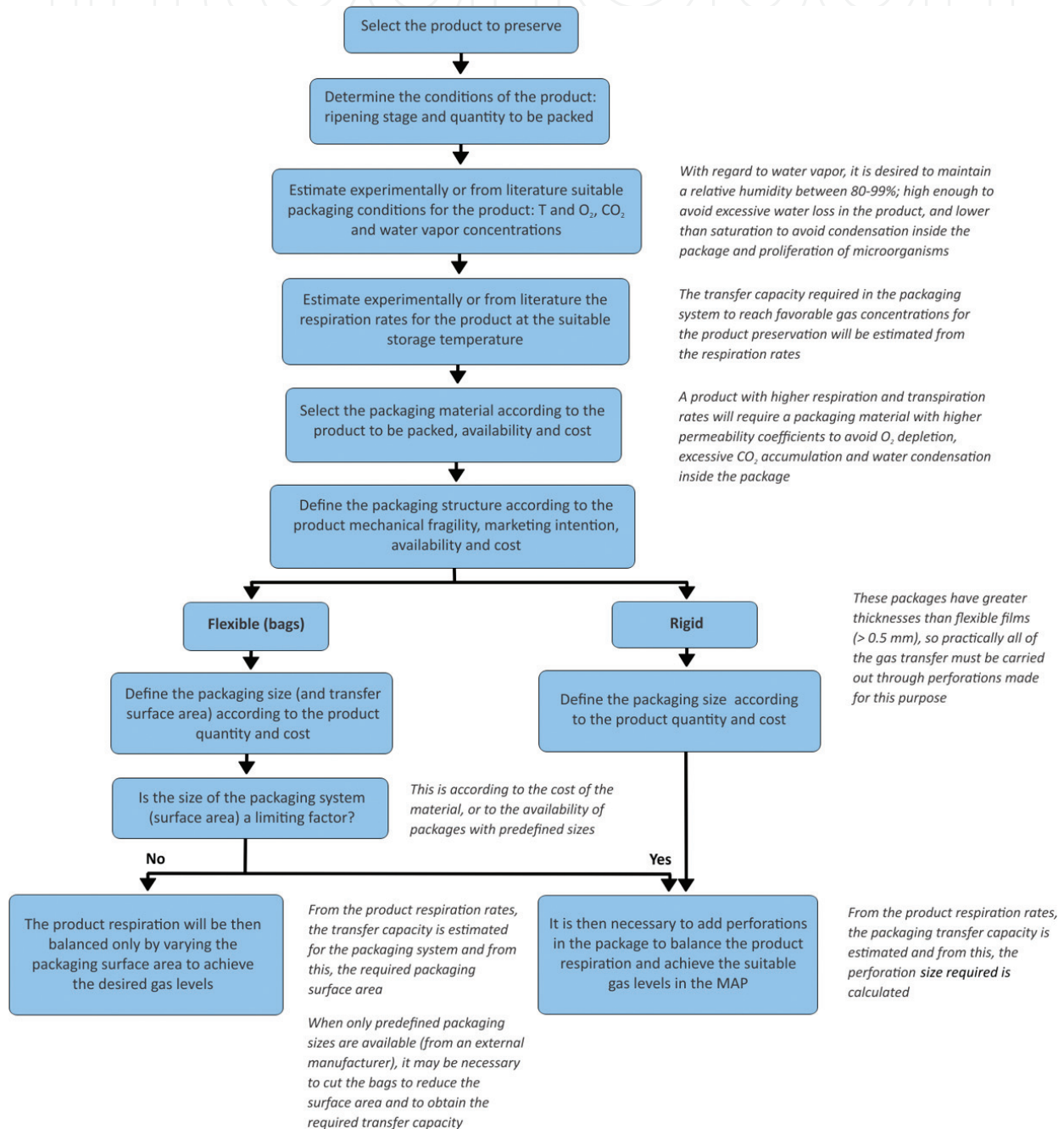


Figure 1. Schematic diagram for the configuration of a suitable MAP system.

can be rewritten similar to Eqs. (20)–(23) with the change in concentration of each gas with respect to time equal to zero in steady state. In that case, the change in the headspace pressure over time dP/dt is substituted from Eq. (19).

The meaning of Eqs. (21)–(23) is that to reach a determined steady concentration of gas, a given transfer capacity by the package will be required to match the produce respiration and transpiration. To achieve this transfer capacity, the type of packaging material, the package surface area and the number and size of perforations can be modified. By knowing the produce respiration and transpiration rates, it is possible to define a packaging system to achieve a self-sustaining controlled atmosphere with favorable gas levels [13].

Depending whether the size of the package is defined or not, two possible configurations arise. In the first configuration, if the size is not defined, it is possible to achieve the required transfer capacity of the package simply by increasing the film surface area. In this case, the K_{TR} values of each gas are zero in the absence of perforations and four variables will be taken: the equilibrium O_2 , CO_2 and water vapor concentrations, y_{O_2eq} , y_{CO_2eq} , y_{H_2Oeq} and the required surface area. As there are four variables and three independent equations, fixing one of the former, zero degrees of freedom are left, and the remaining three variables are determined in the calculation. What this means is that it is only possible to configure the system to specifically set only a gas concentration, that of O_2 , CO_2 or water vapor. If it is wanted to set the equilibrium O_2 concentration in the MAP system, for example, the equilibrium CO_2 and water vapor concentrations (and of course the surface area) will be already defined and cannot be set. As it is not possible to isolate A and y_{O_2eq} in Eqs. (21)–(23), it is necessary to calculate the value of the former (and the other concentrations) iteratively.

It is worth noting that the water vapor concentration in the packaging headspace will be about 1% (mole fraction) in almost all situations due to its low saturation pressure with respect to the atmospheric pressure at the typical storage conditions (e.g., at 10°C and 1 atm, 1.21% water vapor is equivalent to 100% RH). Considering this, it is possible to somehow simplify calculations to set a defined O_2 concentration and find the required area by assuming the water vapor concentration (between 1 and 2% mole fraction) and run iterations using only two equations instead of three.

In the second configuration, if the size of the package is defined, the surface area will be constant and to achieve the required transfer capacity is necessary to make perforations. In this case, the equilibrium gas concentrations, y_{O_2eq} , y_{CO_2eq} , y_{H_2Oeq} and the transmission coefficients through the perforation, K_{TRO_2} , K_{TRCO_2} , K_{TRH_2O} and K_{TRN_2} will be taken as variables. However, from Eq. (8), it can be seen that just as the diffusion coefficients of each gas in the atmosphere, the thickness of the bag and the ϵ correction term are already defined, the real variables are the diameter and the number of perforations in the package. If the number of perforations is fixed, only the diameter is variable, and if the perforation diameter is fixed, only the number of these may be varied, although it is better to define the diameter to estimate an integer number of perforations [13]. Four variables will then be taken: the equilibrium O_2 , CO_2 and water vapor concentrations, y_{O_2eq} , y_{CO_2eq} , y_{H_2Oeq} and the diameter or number of perforations. As in the first setting, when one of the concentrations is fixed, zero degrees of freedom are left, and the remaining concentration and the diameter or the number of perforations are determined in the iterative calculation.

In general, for n independent components in the packaging headspace, it will be $n + 1$ variables (counting the variable related to the transfer capacity in the package, e.g., the diameter of perforations), and n independent equations. By setting one of the gas concentrations, the system can be solved.

In the case of rigid packages where a higher transfer capacity is given by the perforations, the same procedure explained for the second configuration can be followed. Depending on the configuration defined for the MAP system and the initial gas concentrations in the headspace, it can take more or less time to reach a steady state and obtain the desired gas concentration. It can then be quite convenient to seal the package with an initial concentration close to the desired one to achieve equilibrium more quickly [13].

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