

Mathematical Models for the Representation of Some Physiological and Quality Changes during Fruit Storage

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Abstract

In fruits and vegetables, certain physiological processes, such as respiration and transpiration, and quality properties, such as color, firmness or weight, are used as consumer-based criteria of acceptability and shelf-life indicators. Changes in the rates of oxygen consumption, carbon dioxide and water vapor generation and product quality properties result from a series of biochemical processes. These processes are affected by internal conditions such as the ripening state and by external conditions such as temperature or environmental gas concentration. Understanding the time-progress of these processes and properties, according to variables that affect the product, and the mathematical models that regulate them, would be beneficial in selecting the most appropriate storage and preservation conditions to meet determined quality and shelf-life requirements. This manuscript describes the effect of postharvest storage conditions on biochemical and physiological processes related to respiration and transpiration and on quality property changes. Moreover, equations developed by many authors that describe the changes in these processes and properties according to storage conditions are reported.

INTRODUCTION

Consumers of fruits and vegetables have recently developed greater interest in the importance of the quality of these products (Batt, 2006; Fearn et al., 2006; Hewett, 2006). Thus, it has become increasingly essential for producers and distributors to use tools for the rapid and easy monitoring of the changes in fruit quality during the postharvest period. An effort has been made to correlate changes in product properties during the postharvest period (mainly during storage) with quality and shelf-life decline (Schouten et al., 2007; Lukasse and Polderdijk, 2003). These correlations could be beneficial in the development of models with the capacity to predict product future behavior under a wide range of conditions. The objective of this article is to review the models that describe respiration and transpiration processes, color evolution and firmness as a function of storage conditions in fruits in the postharvest stage.

THE EFFECT OF ENVIRONMENTAL CONDITIONS ON QUALITY PROPERTIES

Fruits, once harvested, are subject to chemical modifications that are mainly affected by environmental conditions, such as temperature. The concentration of gases, such as oxygen, carbon dioxide, ethylene and water vapor, directly affect the biochemical processes that these products undergo during ripening. These conditions should be

considered in the postharvest storage of fruits by establishing the most suitable limits to reduce the deterioration rate (Kader et al., 1989; Lee and Kader, 2000). Herein, some factors are presented.

Temperature

Temperature is the factor that most substantially affects the rate of various metabolic reactions. Once the temperature increases, respiration, enzymatic processes and several reactions related to sensory properties such as firmness, color and flavor also increase, leading to a state of senescence. Likewise, as the temperature decreases, these processes slow down.

Fruits must be preserved at the lowest temperature that the product can tolerate to delay the ripening rate without lowering it more than the critical storage temperature to avoid chilling injury (CI) problems in the fruit (Kader, 2002; Thomson et al., 2002). Some products such as avocados, bananas, grapes, lemons, limes, papayas and tomatoes do not tolerate low temperatures, and their optimum storage temperature is approximately 10 °C (Kader 1997; Lukatkin et al., 2012; Saltveit, 2003). For example, softening is enhanced in tomatoes stored to low temperatures due to CI and loss of turgor pressure (Biswas et al. 2014). When mangos were stored at 12 °C, mild cold

damage was caused in the skin of the fruit, expressed as red spots around lenticels (Pesis et al., 2000). In the case of Pawpaw fruits, storage temperature of 4 °C led to a fail to ripen (Galli et al., 2009).

An increase in temperature also results in an increase in the transpiration rate and moisture loss and a simultaneous increase in the capacity of the air around the product to contain water and decrease in its relative humidity (Kang and Lee 1998). Moreover, low temperature storage causes a decrease in the activity of the enzymes 1-aminocyclopropane-1-carboxylic (ACC) oxidase and ACC synthase, which participate in the conversion reactions of ACC to ethylene, reducing its production. By transferring the fruit to room temperature, ACC oxidation continues, and more ethylene will be produced, enhancing ripening (Larrigaudiere et al., 1997; Zhou et al., 2001).

Each 10 °C of temperature increase results in a double to triple increase of certain respiration-related biological reaction rates (Sandhya, 2010). Temperature fluctuation must also be considered given that can cause extensive damage due to condensation and metabolic and ripening disorders (Tano et al., 2007).

Oxygen

Oxygen is fundamental for aerobic respiration and numerous metabolic reactions. A decrease in the oxygen concentration results in a decrease in the rate of the reactions in which it is involved. In fruits, when the O₂ concentration around the fruit is decreased below 8%, ripening slows down (Sandhya, 2010).

A low oxygen level slows down ripening by inhibiting ethylene generation and function; at O₂ levels of 2.5%, ethylene generation is reduced by approximately half (Satyan et al., 1992; Ščetar et al., 2010). O₂ concentrations of approximately 2% or less may result in anaerobic respiration reactions that lead to undesirable products, according to each particular anaerobic compensation point that can vary depending on several factors such as specie, cultivar, etc. Moreover, fruits exposed to such low O₂ levels may lose their normal ripening ability once placed again at normal levels (Ke and Kader, 1989; Sandhya, 2010).

CO₂

CO₂ is produced by the oxidation of respiration substrates. The CO₂ production rate is proportional to the respiratory intensity (RI), and an increase in its concentration generally causes various effects on fruits and vegetables in the postharvest state. CO₂ concentrations greater than 1% in the atmosphere around the fruit retards ripening and leads to a decrease in RI (Watada et al., 1996). High CO₂ levels (for example in MA storage) may enhance the inhibition of the growth of microorganisms that are responsible for product deterioration (Bennik et al., 1998). Kubo et al. (1990) observed an RI decrease in some climacteric fruits and broccoli after exposure to a 60% CO₂ atmosphere but an RI increase in eggplants, cucumbers, peas, spinach and lettuce. Enzymatic activity declined in pears stored under 10% CO₂ (Kerbel et al., 1988). Liu et al. (2004) demonstrated that in bananas stored under 60% CO₂, respiratory climacteric was suppressed, and the pyruvate, 2-oxoglutarate, and malate contents decreased.

Ethylene

Ethylene is a naturally synthesized hormone in plants and is associated with the onset of ripening (Watkins, 2003); it is physiologically active at concentrations of 0.1 ppm and below. Non-climacteric fruits generate a small amount of ethylene as a product of their metabolic processes (Wu, 2010). In climacteric fruits such as bananas, mangos or apples, which complete their ripening in the postharvest state, ethylene exposure contributes to the acceleration of their ripening. These fruits also produce higher quantities of ethylene because of their metabolic processes (Kader, 1988). In this type of fruit, ethylene is the main volatile component produced (50 – 75% of the total carbon content of all volatiles), and by not having a strong aroma, it does not contribute to typical fruit characteristic flavor (Kader, 1999).

Exposure to high CO₂ (for example, air + 20% CO₂) or low O₂ (for example, 0.25% O₂) concentrations greatly suppresses C₂H₄ biosynthesis in climacteric fruit tissue. A decrease in O₂ levels to concentrations less than 8% leads to a significant inhibition of the C₂H₄ biosynthesis in fresh fruits and vegetables (Kader, 1986). 'Golden Delicious' apples maintained at 2.5% O₂ have exhibited a suppressed internal C₂H₄ concentration and ACC (1-aminocyclopropane-1-carboxylic acid) accumulation (Gorny and Kader, 1996).

Finally and although is not the purpose of this review, is good to consider the influence of storage conditions under modified atmosphere packaging. Barrier properties (permeability) of the package containing the fruit coupled with respiration will determine the concentration of gases in the atmosphere that surrounds it and this in turn will affect fruit physiological behavior, so that is necessary to take into account the interaction between film and produce when selecting one that offers favorable storage conditions.

USE OF MODELS TO REPRESENT PHYSIOLOGICAL AND QUALITY CHANGES IN HARVESTED FRUITS ACCORDING TO STORAGE CONDITIONS

The use of models is an efficient tool to predict characteristic changes in a biological system affected by various environmental conditions, without the need to assess these conditions in real time. For the successful use of a model, it is necessary that the model can accurately represent the desired physical phenomenon. A model requires previous validation, which means that its parameters must have been identified or adjusted based on experimental data (Tijssens and Schouten, 2009).

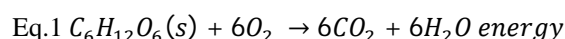
Many models have been developed to assess changes in fruits stored under various conditions (Caleb et al., 2012; Hertog et al., 2003; Hertog et al., 2004; Lukasse and Polderdijk, 2003; Schouten et al., 2007; Verdijck and Lukasse, 2000). However, few models consider the interactions among the principal storage variables (temperature, storage atmosphere composition, relative humidity, product ripening during storage, etc.).

Each particular fruit has properties that reflect its quality and ripening changes; in general, properties that are easy to measure, representative throughout the product's shelf-life non-destructive, if possible, and affected by storage conditions should be investigated. For certain products, color, texture, moisture, weight loss and respiration rates are the most used properties (Hertog et al., 2001; Jha, 2010; Mangarat and Goswami, 2011; Tijssens and Schouten, 2009).

Respiratory Intensity (RI)

Respiration is a metabolic process that provides the plant with the necessary energy to perform its biochemical processes. Respiration substrates oxidized to produce CO₂ and water. Fruit shelf-life

after harvest depends on RI; fruits such as mango and banana that have an increased RI are severely perishable (Paliyath and Murr, 2008b). The energy released during respiration is associated with the energy required to completely oxidize a mole of hexose (Brownleader, 1997; Taiz and Zeiger, 1998). A mole of hexose releases approximately 2880 kJ during respiration. Each glucose molecule is oxidized to 6 CO₂ molecules, using 32 molecules of adenosine diphosphate (ADP) and six molecules of O₂ to form 12 water molecules (Eq. 1). 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. The respiratory metabolism is limited at low partial O₂ pressure, which leads to a decrease in the chemical energy produced during respiration (Mir and Beaudry, 2002).



By the time carbohydrates such as glucose or fructose are completely oxidized, the O₂ volume used per unit time will be practically the same as the volume of generated CO₂ per unit time (Kader et al., 1987; Renault et al., 1994). For organic acid oxidation, more CO₂ volume is produced than the used O₂. From the above, the respiratory quotient (RQ) is defined as the ratio of CO₂ produced to O₂ consumed per unit time. The RQ values range between 0.7 and 1.3 for the majority of vegetables (Kader et al., 1989). High RQ values usually indicate anaerobic respiration in produce tissues that produce ethanol. In such tissues, a rapid change in the RQ can be used as an indication of the shift from aerobic to anaerobic respiration (Salveit, 2004).

Many mathematical models have described the respiration process and how O₂ and CO₂ levels affect this process. These models can be grouped into two large categories: empirical models (lineal, polynomial or exponential) and models based on Michaelis-Menten enzyme kinetics (Fonseca et al., 2002). The simplest empirical model is the lineal model. In this model, the O₂ consumption rate is determined by its concentration only, as shown in Eq. 2:

$$\text{Eq. 2 } r_{O_2} = a_1 + a_2 y_{O_2}$$

Where r_{O_2} is the O₂ consumption rate, y_{O_2} is the O₂ mole fraction (or, in general, the O₂ concentration in appropriate units) and a_1 and a_2 are constants.

Fishman et al. (1996) used this type of equation to model mango respiration.

In exponential models, the O_2 concentration is the only one mainly considered in determining the respiration rate (Eq. 3), although the CO_2 concentration could also be considered (Eq. 4):

$$\text{Eq. 3 } r_{O_2} = a_1 + a_2 \exp(a_3 y_{O_2})^{a_4}$$

$$\text{Eq. 4 } r_{O_2} = a_1 + a_2 \exp(a_3 y_{O_2} y_{CO_2})^{a_4}$$

Where y_{CO_2} is the CO_2 mole fraction (or, as before, the CO_2 concentration in appropriate units), y_{O_2} is the O_2 concentration and a_1 , a_2 , a_3 and a_4 are constants. Eq. 3 has been used to model the respiration of tomatoes (Cameron, et al., 1989), blueberries (Beaudry et al., 1992; Emond et al., 1993) and strawberries (Talasila et al., 1992). Eq. 4 has been used to model the respiration of apples, slightly processed under modified atmosphere (MA; Rocculi et al., 2006), and slightly processed packaged kiwi, banana and pears (Del Nobile et al., 2007).

Some authors like Finnegan et al. (2013) propose that respiration rate will not be constant throughout the storage time, and that this will be increased with increasing physiological age of the fruit, representing this process through a model based on exponential decay (for CO_2 production):

$$\text{Eq. 5 } r_{CO_2} = r_{CO_2}^{eq} + (r_{CO_2}^i - r_{CO_2}^{eq}) e^{-\alpha t}$$

Where r_{CO_2} is the respiration rate at any time (t); $r_{CO_2}^i$ is the initial respiration rate; $r_{CO_2}^{eq}$ is the respiration rate at equilibrium time; t is the storage time and α is a constant coefficient.

Polynomial models include equations of different orders and multiple adjustable coefficients that consider the O_2 concentration and time. Gong and Corey (1994) used a polynomial equation to determine tomato respiration according to O_2 concentration. Dash et al. (2012) used second-order polynomial equations, obtained by regression, to determine O_2 consumption and CO_2 generation in packaged sapote based on O_2 and CO_2 concentrations. Morales-Castro et al. (1994) considered O_2 and CO_2 concentrations, temperature and time for the respiration of sweet corn and obtained polynomial equations by regression to calculate CO_2 generation and O_2 consumption.

Previous models however, do not provide an analytical representation of the mechanisms of the respiration processes being useful in very specific cases, so that other models based on the Michaelis-Menten equations have been used as a good alternative to describe the effect of O_2 and CO_2 concentrations during respiration (Fonseca et al., 2002; Geysen et al., 2005; Gomes et al., 2010; Ho et al., 2013). Eq. 6 illustrates the simplest mechanism of enzymatic kinetics; the model is based on a limiting enzymatic reaction where the substrate is O_2 :

$$\text{Eq. 6 } r_{O_2} = \frac{r_{O_2}^{max} y_{O_2}}{K_m + y_{O_2}}$$

Where r_{O_2} is the O_2 consumption rate (or CO_2 production, r_{CO_2} , $cm^3 kg^{-1} d^{-1}$), r^{max} is the maximum rate of O_2 consumption or CO_2 production ($cm^3 kg^{-1} d^{-1}$) and K_m is the dissociation constant of the enzyme-substrate complex (dimensionless). This equation has been used to model the respiration of apples (Andrich et al., 1998; Lakakul et al., 1999), blueberries (Song et al., 2002) and cauliflower (Ratti et al., 1996).

The basic Michaelis-Menten equation is transformed into one of the following equations depending on the type of inhibition produced by the generated CO_2 (Fonseca et al., 2002; Gomes et al., 2010; Heydari et al., 2010; Lee et al., 1996; Maneerat et al., 1997; Peppelenbos and van't Leven 1996):

Competitive inhibition:

$$\text{Eq. 7 } r_{O_2} = \frac{r_{O_2}^{max} y_{O_2}}{K_m \left(1 + \frac{y_{CO_2}}{K_{mCO_2}}\right) + y_{O_2}}$$

Non-competitive enzyme inhibition but competitive inhibition for the enzyme-substrate complex:

$$\text{Eq. 8 } r_{O_2} = \frac{r_{O_2}^{max} y_{O_2}}{K_{mO_2} + y_{O_2} \left(1 + \frac{y_{CO_2}}{K_{mCO_2}}\right)}$$

Non-competitive inhibition:

$$\text{Eq. 9 } r_{O_2} = \frac{r_{O_2}^{max} y_{O_2}}{(K_m + y_{O_2}) \left(1 + \frac{y_{CO_2}}{K_{mCO_2}}\right)}$$

A mixed non-competitive and competitive inhibition for the enzyme-substrate complex:

$$\text{Eq. 10 } r_{O_2} = \frac{r_{O_2}^{\max} y_{O_2}}{K_m \left(1 + \frac{y_{CO_2}}{K_{mcCO_2}}\right) + y_{O_2} \left(1 + \frac{y_{CO_2}}{K_{muCO_2}}\right)}$$

K_{mcCO_2} , K_{muCO_2} and K_{mmCO_2} are constants representing the competitive enzyme, non-competitive enzyme and non-competitive inhibitions, respectively. Competitive inhibitions occur when the inhibitor (CO_2) and the substrate compete for binding to the same active site on the enzyme. Thus, at high CO_2 concentrations, there is a lower maximum RI. Non-competitive enzyme inhibition occurs when the inhibitor reacts with the enzyme-substrate complex; in this case, the maximum RI is not very affected by high CO_2 concentrations. This type of enzymatic kinetics has been successfully used for many products (Bhande et al., 2008; Heydari et al., 2010; Mangarat and Goswami, 2011; McLaughlin and O’Beirne, 1999). Non-competitive inhibition occurs when the inhibitor reacts not only with the enzyme but also with the enzyme-substrate complex (Lee et al., 1996; Maneerat et al., 1997).

Temperature has an effect on respiration processes that can be considered in mathematical models (Fonseca et al., 2002). All the constants appearing in equations 6 to 10, together with the maximum O_2 consumption rate and CO_2 generation, depend on the temperature. This dependence has been described in the Arrhenius equation (Fonseca et al., 2002; Gomes et al., 2010) as follows (in this case for the maximum oxygen consumption rate):

$$\text{Eq. 11 } r_{O_2}^{\max} = r_{O_2ref}^{\max} e^{E_a/RT}$$

Where E_a is the activation energy ($kJ\ mol^{-1}$), R is the universal gas constant ($kJ\ mol^{-1}\ K^{-1}$) and T is the temperature (K). Other authors (Oluwafemi et al., 2012; Iqbal et al., 2009) have used the O_2 consumption rate and CO_2 generation rate as solely depending on temperature, using a reference temperature in the Arrhenius equation (T_{ref} , in K):

$$\text{Eq. 12 } r_{O_2} = r_{O_2ref} e^{\left(\frac{-E_a}{R}\right)\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}$$

Transpiration rate (TR) and moisture loss

A low relative humidity can increase transpiration damage and lead to excessive dehydration, RI increase and finally to a loss of product quality. Alferez et al. (2005) and Kader (1985) state that

relative humidity should be maintained at approximately 85-95% during handling and storage. Lower values cause fruit dehydration with subsequent weight loss, while higher values could speed up fruit spoilage because part of the water vapor can build up in the product packaging due to storage temperature fluctuations, favoring microbial growth (Kader, 1988). However, there are fruits such as papaya or ‘mountain papaya’ that can be well preserved at less than 40% relative humidity (Baiyewu and Amusa, 2005).

During ripening, there is a continuous loss of water due to transpiration and disassembly of the different components of the cell wall (Brummell, 2006; Kissinger et al., 2005), degradation of pectic compounds and changes in turgor pressure (Abera et al., 2014; Saladie et al., 2007). Thus, their permeability to water that leaves the cell increases, which also produces wilting and excessive pulp smoothness when the loss is high (Wills et al., 2007). Cellular membrane deterioration is also a key factor for the weight loss. It is critical the first day at harvest in all the produce due to the effect of cutting and to the high respiration rate and transpiration associated with cutting, stress and handling. Some authors have not considered the first day in order to have a linear trend in weight loss (Conesa et al., 2014).

Thus, TR is the quantity of water loss from a plant tissue per unit time. This parameter is affected by the own properties of the fruit (morphological characteristics, surface-to-volume ratio, ripening state, damage) and by environmental factors (temperature, relative humidity, air speed and pressure; Kader, 1992). The TR of a fruit is initially expressed by its weight loss (Leonardi et al., 1999):

$$\text{Eq. 13 } r_{H_2O}^{trs} = \frac{W_0 - W}{t(W_0/1000)}$$

Where $r_{H_2O}^{trs}$ is the TR ($g\ kg^{-1}\ h$), t is the transpiration time (h), W_0 is the initial weight of the fruit (g) and W is the weight of the fruit at the given time t (g).

The most basic model to determine TR considers that the driving force for transpiration is the difference in water vapor pressure between the product surface and its surroundings. This relationship is expressed through the following equation (Becker and Fricke, 1996):

$$\text{Eq. 14 } r_{H_2O}^{trs} = k_i (p_s - p_{at})$$

Where k_i is the transpiration coefficient, $(p_s - p_{at})$ is the deficit in vapor pressure, p_s is the vapor pressure at the surface of the product and p_{at} is the vapor pressure in its surroundings. The values of k_i for different products can be found in the ASHRAE Handbook (2006).

Mahajan et al. (2008) developed a model for TR based on the above considerations. Their model considers a) the difference between the relative humidity of the medium and the fruitwater activity and b) the effect of temperature on the transpiration process:

$$\text{Eq. 15 } r_{H_2O}^{trs} = k_i(a_{wat} - a_w)(1 - e^{-bT})$$

Where a_w is the fruit's average water activity, a_{wat} is the water activity of the medium (RH/100), k_i is the mass transference coefficient, T is the temperature ($^{\circ}\text{C}$) and b is a constant. The weight of the fruit at a given time-point can be calculated by combining equations 13 and 15, which results in the following equation (Sousa-Gallager et al., 2013):

$$\text{Eq. 16 } W = W_0 - k_i(a_{wat} - a_w)(1 - e^{-bT})\left(\frac{tW_0}{1000}\right)$$

The amount of water that the fruit loses during transpiration can be related to the respiratory heat and to the heat convection through the energy balance of the process (Becker and Fricke, 2001; Kang and Lee, 1998; Song et al., 2002):

$$\text{Eq. 17 } qW + hA_p(T_{at} - T_p) = m_{H_2O,gen}\lambda + c_pW\frac{dT_p}{dt}$$

Where q is the respiratory heat ($\text{kJ kg}^{-1} \text{h}^{-1}$), W is the weight of the product (kg), h is the convective heat transfer coefficient ($\text{kJ m}^{-2} \text{ }^{\circ}\text{C}^{-1} \text{h}^{-1}$), c_p is the specific heat of the product ($\text{kJ kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$), λ is the latent heat of moisture evaporation (kJ kg^{-1}), A_p is the surface area of the produce (m^2), T_{at} is the ambient temperature ($^{\circ}\text{C}$), T_p is the produce temperature ($^{\circ}\text{C}$) and $m_{H_2O,gen}$ is the mass of lost water/water vapor generated (kg h^{-1}).

The heat transferred through natural convection from ambient air and the heat generated from respiration inside the product both increase the temperature of the fruit, as sensible heat, and are converted to the latent heat of moisture evaporation in transpiration (Kang and Lee, 1998). This water loss in the produce can be expressed as:

$$\text{Eq. 18 } m_{H_2O,gen} = qW + \frac{hA_p(T_{at} - T_p) - c_pW\frac{dT_p}{dt}}{\lambda}$$

Respiration heat is obtained by the oxidation of glucose into products and energy (Eq. 1). Thus, the respiration heat (in $\text{kJ kg}^{-1} \text{h}^{-1}$) can be estimated by the respiration reaction and by considering the respiration rate as the average of the O_2 consumption rate (R_{O_2} , in $\text{mol kg}^{-1} \text{h}^{-1}$) and CO_2 conversion (R_{CO_2} ; Kang and Lee, 1998):

$$\text{Eq. 19 } q = \left(\frac{2816}{6 \text{ mol}}\right)\left(\frac{R_{\text{O}_2} + R_{\text{CO}_2}}{2}\right)$$

The above expression is multiplied by a correction factor to correct for the respiration energy dissipated as heat and to consider that glucose is not the only substrate during respiration (Song et al., 2002). For a 100% conversion (supposing that glucose is the only substrate), α will be 1. The latent heat of moisture evaporation λ (in kJ kg^{-1}) is obtained from the equation (Brooker, 1967):

$$\text{Eq. 20 } \lambda = 2502,535 - 2,386(T - 273,16)$$

Where T is expressed in Kelvin.

Finally, the transpiration rate (in moles per kg of fruit hour) can be expressed as water loss in the stored fruit by multiplying the mass of generated water vapor (product water loss) with the ideal gas equation:

$$\text{Eq. 21 } R_{H_2O}^{trs} = m_{H_2O,gen} \left(\frac{RT}{WPM_{H_2O}}\right)$$

Where M_{H_2O} is the molar mass of water in kg mol^{-1} , R is the gas constant, T is the refrigeration temperature, W is the weight of the fruit and P is the pressure.

The establishment of the existing difference between the vapor pressure of water of the product surface area (p_s) and the vapor pressure of water in the produce surroundings is necessary to effectively use transpiration models. The vapor pressure of the surface area of the product will be a consequence of the surface temperature (T_{ps}) and the effect of the vapor pressure deficit (VPD) caused by the dissolved substances. Thus, the vapor pressure of the surface will be (Becker and Fricke, 1996)

$$\text{Eq. 22 } p_s = \text{VPD} * p_{sT_{ps}}$$

The VPD values for different vegetables were determined by Chau et al. (1987) and Beck et al. (1995).

Firmness changes

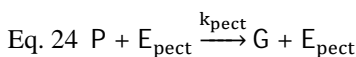
Firmness declines as ripening continue to a minimum level when product senescence is reached. Firmness loss can be attributed to various factors, including disassembly of polysaccharide networks, pectin degradation, hydrolysis of starch, celluloses and hemicellulose in cellular walls (Paliyath and Murr, 2008a; Van Dijk and Tijskens, 2000), and like some authors suggest (Biswas et al., 2014; Saladie et al., 2007), decline in cellular turgor and water loss by transpiration product of these changes in cell architecture. Fruits such as peaches, pears, tomatoes and strawberries can excessively lose their firmness because they have increased levels of endopolygalacturonase activity (which cleaves the pectin sequence at intermediate points in contrast to exopolygalacturonase, which removes galacturonic acid fractions at terminal sequence points). Other fruits such as apples maintain their firmness because they do not undergo this activity (Daas et al., 2000).

During postharvest storage, some compounds are affected while others are not. Thus, firmness (F, measured in N or in kg_f) can be considered to have a fixed (F_{fix}) and a variable (F_{var}) component:

$$\text{Eq. 23 } F = F_{\text{fix}} + F_{\text{var}}$$

The compounds that do not undergo degradation or that are broken down slowly, such as celluloses and hemicelluloses, contribute to the fixed firmness. The compounds that undergo degradation, such as pectins, or that are lost, such as moisture, contribute to the loss of turgor pressure, and from this to the variable firmness (Biswas et al., 2014).

Gwanpua et al. (2012) developed a firmness model considering that its variable part depends on the degradation of pectins (P) by pectic enzymes (E_{pect}), which results in galacturonic acid (G) through a simple irreversible reaction (similar to the proposal of Tijskens and Schouten, 2009):

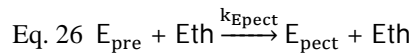


Thus, the firmness is:

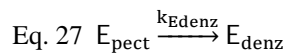
$$\text{Eq. 25 } F = F_{\text{fix}} + \gamma[P]$$

Where [P] is the pectin concentration (nmol⁻³ m³), F_{fix} is the fixed firmness component and is not affected by enzymatic degradation and γ (N m³ nmol⁻¹) is a correction factor that relates firmness (F) to the non-hydrolyzed pectin during enzymatic degradation ([P]).

The presence of ethylene (Eth) in the fruit directly affects the pectic enzyme concentration (Lin et al., 2009). This relationship, which includes complex mechanisms, has been explained in a simplified manner by Gwanpua et al. (2012), as a group of amino acids (E_{pre}) that are converted by ethylene in pectic enzymes (E_{pect}).



Pectic enzyme degradation (E_{pect}) into other compounds (E_{denz}) should also be considered (Johnston et al. 2009). In that case:



Changes in the concentration of pectins and pectic enzymes over time are described through first order kinetics equations:

$$\text{Eq. 28 } \frac{d[P]}{dt} = -k_{\text{pect}}[P][E_{\text{pect}}], \text{ where } [P](t = 0) = [P]_0$$

$$\text{Eq. 29 } \frac{d[\text{Eth}]}{dt} = \frac{r_{\text{Eth}}^{\text{max}} y_{\text{O}_2}}{K_{\text{mO}_2, \text{Eth}} + y_{\text{O}_2} \left(1 + \frac{y_{\text{CO}_2}}{K_{\text{mCO}_2, \text{Eth}}} \right)} + P_{\text{Eth}} A ([\text{Eth}]_{\text{out}} - [\text{Eth}]), \text{ where } [\text{Eth}](t = 0) = [\text{Eth}]_0$$

Where [P] is the pectin concentration (nmol³ m⁻³), [E_{pect}] is the concentration of pectic enzymes, [Eth] is the endogenous ethylene concentration, k_{pect} is the pectin degradation rate constant (s⁻¹) and k_{E_{pect}} and k_{E_{denz}} are the pectic enzymes generation and degradation rate constants, respectively (Gwanpua et al., 2012).

The changes in ethylene concentration are calculated based on the O₂ and CO₂ concentrations in the surroundings of the product using a Michaelis-Menten modified model of non-competitive inhibition for CO₂ (Eq. 30), which is similar to Eq. 3 (Génard and Gouble, 2005; Gwanpua et al., 2012;

Sanders and de Wild, 2003). Génard and Gouble (2005) in their simulation model ETHY, considers that the respiration process has not a significant influence on the generation of ethylene and that its emission is highly dependent on temperature, only slightly sensitive to air O₂ concentrations and almost insensitive to CO₂ concentrations. The above suggests that the respiratory climacteric may not be required for ripening and apparently is not important for modeling.

$$\text{Eq.30} \quad \frac{d[\text{Eth}]}{dt} = \frac{r_{\text{Eth}}^{\text{max}} y_{\text{O}_2}}{K_{\text{mO}_2, \text{Eth}} + y_{\text{O}_2} \left(1 + \frac{y_{\text{CO}_2}}{K_{\text{muCO}_2, \text{Eth}}}\right)} + P_{\text{Eth}} A ([\text{Eth}]_{\text{out}} - [\text{Eth}]),$$

where $[\text{Eth}](t = 0) = [\text{Eth}]_0$

Where $r_{\text{Eth}}^{\text{max}}$ is the maximum ethylene generation rate (nmol m⁻³ s⁻¹), $K_{\text{mO}_2, \text{Eth}}$ is the Michaelis constant for ethylene production, $K_{\text{muCO}_2, \text{Eth}}$ is the constant for the non-competitive inhibition for CO₂, y_{O_2} is the molar fraction of O₂ in the surroundings of the product, y_{CO_2} is the molar fraction of CO₂, P_{Eth} is the permeability of ethylene in the product peel (m⁻² s⁻¹), A is the surface area of the product (m²) and $[\text{Eth}]_{\text{out}}$ is the concentration of ethylene around the product (nmol⁻³ m³). The constants $r_{\text{Eth}}^{\text{max}}$, $K_{\text{mO}_2, \text{Eth}}$ and $K_{\text{muCO}_2, \text{Eth}}$ depend on temperature through an Arrhenius relationship such as that in Eq. 29 (Gwanpua et al., 2012).

Other authors have described the variable part of firmness through a first-order model (Eq. 31, Hertog et al., 2004; Lana et al., 2005; Pinheiro et al., 2013; Schouten et al., 2007) or a logistic model (Eq.32, Hertog et al., 2003). In these models, these authors considered that the variable part depends on respiration, the O₂ and CO₂ concentrations in the surroundings of the product and the temperature. F_0 is the initial firmness, and F_{fix} is the equilibrium firmness. k represents the firmness loss rate and can depend on O₂ and CO₂ levels through Michaelis-Menten relationships (Peppelenbos et al., 1996; Hertog et al., 2001; Hertog et al., 2004) that consider respiration as oxidative and fermentative (Eq. 33) or can depend only on temperature through a Arrhenius relationship such as that in Eq. 34 (Sila et al., 2004; Schwaab and Pinto, 2007):

$$\text{Eq. 31} \quad F = F_{\text{fix}} + (F_0 - F_{\text{fix}})e^{-kt}$$

$$\text{Eq. 32} \quad F = \frac{F_{\text{fix}}}{1 + (F_0 - F_{\text{fix}})e^{-kt}/F_0}$$

$$\text{Eq.33} \quad k = \frac{k_f^{\text{max}} r_{\text{CO}_2(f)}^{\text{max}}}{1 + y_{\text{O}_2}/K_{\text{mCO}_2(f)}} + \frac{k_o^{\text{max}} r_{\text{O}_2}^{\text{max}} y_{\text{O}_2}}{K_{\text{mO}_2 + y_{\text{O}_2}} \left(1 + \frac{y_{\text{CO}_2}}{K_{\text{muCO}_2}}\right)}$$

$$\text{Eq. 34} \quad k = k_{\text{ref}} e^{\left(-\frac{E_a}{R}\right) \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)}$$

In these equations, k_f^{max} and k_o^{max} are the maximum rates of firmness loss related to fermentative and oxidative processes, respectively, and K_{muCO_2} is the Michaelis-Menten constant for firmness loss inhibition related to oxidation by CO₂; k_f^{max} and k_o^{max} are functions of temperature attributed to Arrhenius relationships, and $r_{\text{CO}_2(f)}^{\text{max}}$ and $r_{\text{O}_2}^{\text{max}}$ are the maximum rates of anaerobic CO₂ production and O₂ consumption, respectively, which are also temperature-dependent through Arrhenius equations (Eq. 34). k_{ref} is the constant reference rate for the reference temperature (T_{ref}), E_a is the activation energy and R is the gas constant. Castellanos and Algecira (2012) used a simplified version of equation (33) for ‘Sucrier’ banana storage. In this case, the contribution of the fermentative process to the firmness loss rate was negligible because the O₂ concentrations during storage were greater than zero. For other fruits, such as avocados (Hertog et al., 2003), a similar approach was applied.

Color change

Color change in fruits is the most evident indicator of ripening (Will et al., 2007). Chlorophyll (Chl) is degraded by the action of three Chl catabolic enzymes, chlorophyllase, pheophorbide *a* oxygenase (PAO) and red Chl catabolite reductase (RCCR; Dangi et al., 2000; Hortensteiner, 2006), and reveals carotenoids, such as lycopene and carotene, that are present in the cortex, which result in the characteristic fruit color. In some fruits, there are other compounds, products of secondary metabolism, such as anthocyanins that are responsible for the color of grapes, blueberries and apples (Paliyath and Murr, 2008b).

The color of an object can be described by various color models such as the RGB (red, green and blue) model, which is used in color monitors, Hunter Lab, CIE (International Commission on Illumination) L*a*b*, CIE XYZ, CIE L*u*v*, CIE Yxy. These differ in the color space symmetry and in the coordinate system used to define the points in this space. The tristimulus methods of the CIE and of the similar Hunter model are of the greatest importance

for instrumental measurements. According to CIE concepts, the human eye has three-color receptors: red, green, and blue and all of their combinations. Many food studies use CIE $L^*a^*b^*$ color coordinates and their derived psychophysical parameters C^* (chroma) and h (hue; tone) or Hunter Lab coordinates (Hunter Lab, 2008). McGuire (2012) noted that it is difficult to separately interpret the values of the coordinates a^* and b^* and that, most likely, these are not independent variables. He proposed the use of C^*_{ab} and h_{ab} as more suitable color measurements. It is also important to clearly establish the brightness, calibration standards and viewing angle to accurately interpret color data.

The CIE 1976 $L^*a^*b^*$ (CIELAB) color space is defined when the coordinates for luminosity, L^* , and chromaticity, a^* , b^* , are presented in a three-dimensional space. L^* represents the luminosity of the color or clarity and is the vertical axis with values ranging between 100, for white, and zero, for black. The axes for a^* and b^* have no specific numeric limits. Positive values for a^* represent red/magenta, and negative values represent green. Similarly, positive values for b^* represent yellow, and negative values represent blue (HunterLab, 2008).

The following equation defines the total color difference (ΔE^*_{ab}) between two different points measured in the same sampling using the geometrical distance in a spherical space:

$$\text{Eq. 35 } \Delta E^*_{ab} = ((L^*)^2 + (a^*)^2 + (b^*)^2)^{1/2}$$

The psychophysical parameters chroma, C^*_{ab} , and tone (hue), h_{ab} , stem from luminosity-chromaticity coordinates (L^* , a^* , b^*) defined by CIELAB space as follows:

$$\text{Eq. 36 } C^*_{ab} = ((a^*)^2 + (b^*)^2)^{1/2}$$

$$\text{Eq. 37 } h_{ab} = \arctan\left(\frac{b^*}{a^*}\right)$$

Ren et al. (2006) assessed the kinetics of color changes in broccoli stored under refrigeration. These authors observed that b^* and ΔE^*_{ab} changes could be presented by a first-order exponential model, as follows:

$$\text{Eq. 38 } b^*(t) = b^*_0 \exp(-k_b t)$$

$$\text{Eq. 39 } \Delta E^*_{ab}(t) = \Delta E^*_{ab_0} \exp(-k_{\Delta E} t)$$

Where b^*_0 and $\Delta E^*_{ab_0}$ are the values at the beginning of storage, and k is the constant of the storage temperature-dependent rate, expressed by an Arrhenius relationship.

In addition, these authors describe changes during storage time for a^* and h_{ab} using the following second-order polynomial functions:

$$\text{Eq. 40 } a^*(t) = c_1 t^2 + c_2 t + c_3$$

$$\text{Eq. 41 } h_{ab}(t) = d_1 t^2 + d_2 t + d_3$$

In the previous equations, c_1 , c_2 , c_3 , d_1 , d_2 and d_3 are specific constants based on the stored fruit and the storage conditions.

In studies about postharvest banana storage (Chen and Ramaswamy, 2002) and ‘baby banana’ (Castellanos and Algecira, 2012), peel color changes were described by Hunter Lab system color coordinates based on the O_2 concentration and temperature over time. The coordinate L was described by a logistic growth model (Eq. 42), a was described by a zero-order model (Eq. 43), and b was described by a first-order model (Eq. 44):

$$\text{Eq. 42 } L = U_0 + \frac{U}{1 + \exp(-k_L(t - t_{1/2}))}$$

$$\text{Eq. 43 } a = a_0 + k_a t$$

$$\text{Eq. 44 } b = b_0 \exp(-k_b t)$$

In the previous equations, a_0 and b_0 are the values of these coordinates at the beginning of storage, U_0 is a constant related to the initial value of luminosity L , U is a value related to the equilibrium value, $t_{1/2}$ is the time needed for the L value to increase or decrease to half of the equilibrium value and k is the constant rate that depends on the gas concentration and temperature of each coordinate. Chen and Ramaswamy (2002) also presented the ΔE value using a logistic model (Eq. 37), where all the constant rates only depend on temperature. The regression coefficients (R^2) for all the coordinates and ΔE were higher than 0.96.

Jha et al. (2007) defined a ripening index for mango that was independent of color coordinates. These authors considered the ripening index obtained by the total soluble solids and the optimum value, or 100 %.

For mangoes, they consider the ripening index to be a function of a and b color coordinates according to the following equation:

$$\text{Eq. 45 } I_m = j_1 + j_2 a + j_3 b + j_4 ab$$

Where j_1 , j_2 , j_3 and j_4 are the equation constants. The values of a and b coordinates depend on the storage variables through equations 43 and 44. Gómez and Camelo (2002) defined an average color index based on the L^* , a^* and b^* coordinates of the CIELAB space, equally dependent on the storage conditions.

$$\text{Eq. 46 } I_{cm} = \frac{2000 \times a^*}{L^* \times ((a^*)^2 + (b^*)^2)^{0.5}}$$

For the postharvest storage of tomatoes and limes, Hertog et al. (2004) and Pranamornkith (2009), respectively, presented a logistic model for the color tone h_{ab} based on time (Eq. 49). This behavior can be viewed as the consequence of two parallel processes: the exponential increase of enzymatic activity during ripening and the effect of enzymatic activity on color (Tijsskens and Evelo 1994).

$$\text{Eq. 47 } h(t) = h_{+\infty} + \frac{h_{-\infty} - h_{+\infty}}{1 + e^{kt(h_{-\infty} - h_{+\infty}) \frac{h_{-\infty} - h_0}{h_0 - h_{+\infty}}}}$$

Here, $h_{-\infty}$ and $h_{+\infty}$ are the tone minimum and maximum values (balanced) in degrees, h_0 is the tone value at time zero and k is the constant temperature-dependent rate in days^{-1} . This dependency is represented by an Arrhenius relationship (Eq. 11).

Dixon and Hewett (1998) studied two apple varieties with a first-order model (Eq. 44). These authors studied the time-evolution of tone values h_{ab} depending only on temperature and used a combined Arrhenius model and Boltzmann enzyme distribution function to calculate the constant rate, k_h :

Eq. 48

$$k_h = k_h^{\max} \exp\left(-\frac{E_a}{RT}\right) + \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right)$$

where k_h is the constant rate of h_{ab} change, k_h^{\max} is the maximum rate of change, E_a is the activation energy (kJ mol^{-1}), R is the gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), T is the temperature (K), ΔS is the entropy change ($\text{kJ mol}^{-1} \text{K}^{-1}$) and ΔH is the enthalpy change (kJ mol^{-1}).

No effort has been made to model the functions of other quality indicators, such as aroma and taste, based on environmental conditions because of the great difficulties involved. This unexplored area creates a wide range of new possibilities in which multidisciplinary groups of scientists and engineers specialized in fresh food preservation field can work in the future.

CONCLUSION

Properties such as color, firmness and moisture provide valuable information for the monitoring of quality changes in postharvest fruits because of their reliability and rapid and easy measurement. These changes are consequences of many biochemical and physiological processes that occur during fruit ripening, such as respiration and transpiration. In addition, these changes depend on the external conditions to which the fruit is exposed. Understanding the mechanisms in which these conditions affect quality changes processes is of great importance because it allows their appropriate modification to maintain quality and maximize preservation time.

To date, many authors have developed and used various mathematical models for particular cases of respiration and transpiration. They have presented, in a trustworthy manner, the progression of respiration and transpiration processes as well as the progression of quality properties, such as temperature activity, O_2 , CO_2 and H_2O concentrations around products during postharvest storage. Based on this information, it is possible to monitor these progressions during storage and determine the availability (or quality) of the product at a given time. In addition, it is possible to simulate specific storage situations and to obtain concrete values of these quality properties when previously requested.

However, the application of these particular models is often limited. Only a few models for general use have been developed, such as the Michaelis-Menten enzyme kinetics model for the description of respiration (and in some cases of the firmness loss rate) or the combined model of mass transfer and respiration heat. Thus, more studies by multidisciplinary groups of chemists, biologists and engineers are necessary to develop more general and complex models for the description of quality properties.

These models should consider the characteristics of the product under study, for example, if it is climacteric or not, and how the conditions to which the product is exposed affect the biochemical and physiological processes. These processes result in respiration, transpiration, and quality properties changes. Moreover, it is necessary that these models also consider other quality indicators such as aroma and taste.

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