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Modeling the respiration rate of Golden papayas stored under different atmosphere conditions at room temperature

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ABSTRACT

The present study aimed to measure the respiration rate of papayas (cv. Golden) stored under controlled atmosphere at room temperature, with decreasing O_2 and increasing CO_2 levels, in order to identify mathematical models capable of predicting respiration rate throughout storage. A model was proposed based on the Michaelis–Menten equation with uncompetitive inhibition and kinetic parameters that change during storage time. A second-order nonlinear regression model was used as reference for the mathematical approach. Nine experiments with three replicates were conducted under different controlled atmospheres to generate respiration data. A closed system method was used to measure the respiration rate at 2 d intervals over 13 d of storage at ambient temperature (23 °C). Peel color measurements indicated total ripening of fruit stored in high O_2 atmospheres, whereas ripening was minimal in atmospheres containing low O_2 and high CO_2 levels. The respiration rate remained at the lowest value, but gradually increased during storage at the lowest O_2 level associated with the highest CO_2 concentration. The nonlinear regression model obtained the lowest *AICc* value with VarPow variance, indicating a better fit than the Michaelis–Menten model. However, the latter, whose kinetic parameters change according to a polynomial second-order equation (MM_Q), displayed a better fit than the nonlinear regression model evaluated by homoscedastic variance. Additionally, MM_Q was more sensitive than nonlinear regression in detecting the real change in respiration rate in a biological system as a function of different gas compositions during storage.

1. Introduction

Brazil is the world's second largest producer of papaya (*Carica papaya* L.), with production totaling 1,463,770 t over 30,445 ha in 2015 and the states of Bahia and Espírito Santo accounting for over 70% of this volume (IBGE, 2017).

Papaya is classified as a climacteric fruit whose respiration rate increases significantly after harvest, prompting immediate ripening and resulting in losses caused by fungi, insects, improper handling, transport and inadequate storage, among others (Paull et al., 1997). Its quality is directly influenced by the temperature and composition of the atmosphere during storage, which can be controlled to extend the shelf life of the fruit (Martins and Resende, 2013).

Off-odor and/or flavor is a common problem in papaya storage under a controlled and modified atmosphere. The Golden papaya exhibits disturbances in sensorial quality when stored under an atmosphere with less than 3% O_2 and more than 6% CO_2 (Martins and Resende, 2015).

Respiratory activity is influenced by fruit physiology and changes as fruit ripen after harvesting, with temperature and atmosphere conditions during storage exerting a significant influence (Martins et al., 2014). Knowing the respiration rate is an important tool in controlling maturation to ensure quality after harvesting (Barbosa, 2013). This knowledge makes it possible to establish models that predict the respiration rate in response to fruit maturation stages, an important element in developing suitable packaging (Fonseca et al., 2002).

According to Rahman et al. (2013), modeling fruit respiration rate is a convenient way to evaluate the respiratory kinetics of fruit in order to predict their respiratory coefficient. Most mathematical models reported in the literature focus on enzyme kinetics or adsorption theories, and use regression models. More recently, the respiration rate has been expressed using the Michaelis–Menten equation, which describes the quantitative relationship between enzyme kinetics and substrate concentration.

The main respiratory gases (O_2, CO_2, ethylene) can be regulated using controlled atmospheres, but the effect of CO_2 in the respiration process can change according to the type of inhibition in enzymatic reactions (Peppelenbos et al., 1996). Models based on

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Michaelis–Menten kinetics suggest that respiration rate can be mediated by three inhibition mechanisms: competitive inhibition, which occurs when the inhibitor (CO_2) and the substrate compete for the same active site of the enzyme, leading to a reduction in the respiration rate at high CO_2levels; uncompetitive inhibition, when the inhibitor reacts with the enzyme-substrate complex, meaning that high concentrations of CO_2 do not affect the respiration rate; and noncompetitive inhibition, whereby the inhibitor reacts with both the complex and the enzyme, which lie in between those obtained by the previously described inhibition models (Peppelenbos and van't Leven, 1996). However, none of these inhibition models can be deemed the most suitable since they do not cover all types of inhibition, and more than one model showed a good fit to the experimental data. Thus, respiration can be mediated by various inhibitory pathways based on Michaelis–Menten kinetics (Fonseca et al., 2002).

Respiration rate is known to depend on different product-related factors and atmosphere conditions. Respiration rate models reported in the literature consider atmosphere composition and temperature effects. Michaelis–Menten type equations have been used to describe respiration rate dependence on O_2 and CO_2 compositions, and Arrhenius-type equations to account for the influence of temperature (Barrios et al., 2014). However, the influence of temperature is quantified by modeling the maximum respiration rate according to the Arrhenius equation, whereas Michaelis–Menten inhibitory constants are considered to exhibit no temperature dependence. This is because these constants are derived from kinetic parameters related to the inhibition of enzyme-substrate interactions or the enzyme-substrate complex, thereby negating the effect of temperature on these kinetic parameters (Hertog et al., 1998).

In the current state of the art, mathematical modeling of the respiration rate does not consider the change in Michaelis–Menten parameters according to fruit ripening stages. This is especially important in climacteric fruit, whose respiration rate increases after harvesting at the pre-climacteric stage. Thus, the aim of this study was to evaluate the goodness of fit of the respiration rate model considering Michaelis–Menten parameters remaining constant, changing linearly or nonlinearly with ripening during storage of papayas under different controlled atmospheres at room temperature. A nonlinear regression model was used as reference to evaluate the three models of parameters for the Michaelis–Menten equation.

2. Material and methods

2.1. Raw material

Papayas ('Golden' cultivar) were selected at a fruit export company (Caliman Agricola SA) in Linhares (Espirito Santo state, Brazil, 19.3908°S, 40.0719°W). Fruit were harvested when approximately 10–15% of the peel was yellow, with an average weight of 0.35 kg, washed in chlorinated water (100 mol L^{-1} active chlorine) and treated in a hydrothermal bath (48 °C 20 min^{-1}), then immersed in Prochloraz fungicide solution for 2 min. Selected papayas were packed in corrugated cardboard boxes and transported under refrigeration to the laboratory, where the experiments were conducted 36 h after harvest.

2.2. Experimental conditions

The papayas were weighed on an electronic balance (Gehaka, model 2000 BCE, Brazil) and peel color was assessed using a Hunter colorimeter (Spectrophotometer MiniScanHunterLab, USA), calibrated according to a standard white and black calibration plate. A D65 illuminant and a 10° standard observer were employed. Measurements were taken at two equidistant points in the equatorial region of the light-exposed and non-exposed sides of the fruit, in accordance with Martins and Resende (2013). The results were expressed according to the Hunter L, a, b color scale, which characterizes the lightness, greenness and yellowness of the fruit during storage.

The papayas (20 kg per chamber) were stored in small chambers (made from polyvinyl chloride plates covered with multilayered polyethylene, and acrylic doors sealed under pressure with rubber and resin) with controlled atmospheres, kept at room temperature (23 °C) and 85–95% RH (CLIMASUL, Brazil). The chambers were previously tested against air leakage, under the lowest O_2 or highest CO_2 level, after evaluating the pressure difference in the water column using a manometer connected to the line between the chamber and the external environment. The homogeneity of the atmospheres was maintained by a small fan in the upper section of the chamber. Gas levels were set at decreasing O_2 (17%, 6% and 3%) combined with increasing CO_2 levels (0.6%, 5% and 10%). These gas concentrations were based on Martins and Resende (2013, 2015), who evaluated the optimum gas composition range for Golden papaya storage.

The atmospheres were established by flushing with N_2 and CO_2 at the beginning of the storage period until the required gas levels were obtained. The O_2 and CO_2 concentrations were controlled by flushing with nitrogen and adding CO_2. The selected levels were kept constant by scrubbing excess CO_2 produced by respiration and adding air for O_2. Gas concentrations were monitored daily using computerized analyzers with paramagnetic (O_2) and infrared detection (CO_2). Ethylene adsorption was achieved by intermittently (1 h interval) pumping air through a permanganate sorption column connected to the chamber.

2.3. Respiration rate assessment

The respiration rate was assessed every 2 d over 13 d of storage at ambient temperature (23 °C), starting on the 1stday. Levels of O_2 (paramagnetic sensor) and CO_2 (infrared sensor) were measured directly from the suction line that sucks air samples from the chambers. During measurement, the control parameters O_2 and N_2 injection, as well as CO_2 and ethylene adsorption were disabled for 5 h, allowing for five gas concentration measurements, in line with Barbosa (2013). Linear data fitting allowed the determination of respiration rate in% kg^{-1} h^{-1}. These values were corrected based on the gas volume in the empty space of the chamber to determine the respiration rate in μmol kg^{-1} s^{-1}, according to Eq. (1).

$$R_{resp} = (\Delta_{\%}/\Delta_t)(V_{es}/100)(1/m)(d_g/M_g) \quad (1)$$

Where R_{resp} is the rate of O_2 consumption or CO_2 production (μmol kg^{-1} s^{-1}), $\Delta_{\%}$ the variation in O_2 or CO_2 concentration over time (%), Δ_t the time interval used to measure gas levels (s), m the mass of fruit inside the chamber (kg), V_{es} the volume of void space inside the chamber (L), d_g the density of the gas (O_2 or CO_2) (kg L^{-1}), and M_g its molecular mass (kg $kmol^{-1}$).

The empty air space inside the chambers was calculated by subtracting the volume of the shelf supporting the fruit (0.65 L) and the volume of fruit itself from the total volume of the chamber (102.85 L). The volume of the fruit was determined based on the mass and density of a representative sample of papayas with the same shape and ripeness. Density was obtained based on the correlation between fruit mass and the volume of distilled water displaced by immersing the fruit in a calibrated glass beaker (Martins et al., 2014).

2.4. Respiration rate modeling

The respiration rate profiles were interpreted by comparing two approaches: a numerical approach based on a second-order nonlinear model as a function of the varying O_2 and CO_2 concentrations during storage; and a model based on enzyme kinetics as described by the Michaelis–Menten equation, which considers the effect of O_2 and CO_2 levels as well as the uncompetitive inhibition effect of CO_2 on the enzyme-substrate complex, in accordance with Peppelenbos and van't Leven (1996). In addition, model parameters were also evaluated by fitting three approaches: constant parameters, linearly variable