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Evaluation of the *Papaya´s* maturation degree by electrical impedance

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The economic importance of *Papaya* for fruit producers reinforces the idea of alternative (non-invasive and low cost) strategies to measure fruit ripening. In this work, it has been evaluated the kinetics of ripening degree of *Papaya* based on alternative and non-invasive electrical impedance method that is compared with conventional techniques (mechanical assays, determination of total soluble solids and titratable acidity). It was observed that a single point measurement of real part of impedance (1 MHz) returned relevant information concerning the kinetics of *Papaya* ripening. These results were in agreement with the firmness of fruit (mechanical assays) and the corresponding variation in total soluble solids, providing advantages for identification of ripening degree and depreciation of *Papayas*.

Keywords: electrical impedance, *Papaya*, ripening degree, bulky resistance

INTRODUCTION

The *Papaya* (*Carica papaya* L.) is a product of great importance in the economic scenario of Brazilian fruit. This tropical fruit is the seventh most exported natural fruits in the South America (25 % of world production, with 1.6 million tons per year), considered the largest producer of *Papaya* in the world and the third largest exporter to the USA (El-Gewely, 2008). *Papaya* is a climacteric fruit with high respiratory rate and strong ethylene production after harvest, presenting a high degree of perishability if stored under ambient conditions (Martins et al., 2014). As a consequence, the ripening degree monitoring is a critical process for the post-harvest and following distribution to commercial centers. Conventional chemical and biochemical analyses for fruit ripening determination are based on destructive assays, characterizing a strong drawback to be circumvented (Miloski et al., 2008) since these methods are often laborious and expensive. As a consequence, it is required the developing low cost and non-destructive assays (Islam et al., 2018).

The electrical impedance spectroscopy (EIS) technique has been applied in the evaluation of quality control and

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ripening of fresh fruit such as tomato, banana, cucumber and mango (Souza Junior et al., 2015; Figueiredo Neto et al., 2017). The EIS of nanostructured, organic and biologic systems returns information about charge transport and accumulation at interfaces–electrode/ material and field-dependent mechanisms in structures. These processes are critically dependent on the current pathways created by ionic channels (resistance) and charge accumulation at surfaces (capacitance) can be conveniently measured by direct inspection of the real and imaginary parts of impedance. The transposition of these concepts to the fruit ripening process favors the association of physical parameters with information about physiological and biochemical changes in fruit (Chowdhury et al., 2015). The tissue composition, anatomy and health of fruit compose and determine the complex bioelectrical system (Schwann, 2002) that provide the electrical path for current circulation and charge accumulation. This condition favors the detection of fruit bruising by direct measurement of impedance in anisotropic fruit. Harker and Forbes (1997) reported the use of EIS applied on persimmons (cultivar Fuyu) at 50 Hz for identification of the ripening degree.

Grossi and Riccò (2017) reported the study of impedance changes of mangoes due the ripening process in the frequency range 1 to 200 kHz using a resistor and a capacitor in parallel as an electrical model. The effective resistance presented strong variation at 1 kHz with an increase in the first phase of the ripening process, reaching a maximum after 5 d and then decreasing with further ripening.

If considered that interfacial phenomena are conveniently explored at low frequency range and that bulk properties are explored at high frequency, the ripening degree (that involves primary bulky properties) can be addressed by impedance data measured at the high frequency region. In a previous work of our group (Figueiredo Neto et al., 2017), the ripening stage of mangos was explored from the direct measurement of bulk electrical resistance of samples, normalized by the diameter that provides an intrinsic parameter that is independent on the fruit size.

Based on those important findings, the kinetics of the *Papayas* ripening was evaluated by impedance analysis. Thus, in this paper it is provided the comparison of EIS data with intrinsic physical properties of fruit (such as total soluble solid, loss of weight and mechanical properties) as a function of the ripening stage.

MATERIALS AND METHODS

Samples preparation

The experiments were carried out at the agricultural experimental field of the Technology and Social Science Department of the Bahia State University/DTCS of the State University of Bahia/UNEB, located in Juazeiro, BA, 09°24' latitude and 40°30' WGr longitude and altitude of 368 m. All the samples were collected during early morning from May to August 2018 in Vertissolo soil. The climate of the region is semi-arid according to the Koppen classification. The meteorological data of the area were collected (each week) during the period of the experiments and these are scrutinized in Table 1.

The collected *Papayas* were taken to the Post-Harvest Technology Laboratory of the Federal University of the São Francisco Valley in cardboard boxes with four fruit in each one. The *Papayas* (average weight of 0.4 kg) were washed and dried before the procedure for storage for 12 days at 25 ± 2°C/(65 ± 3) %RH.

After harvest, the samples were taken to the laboratory and immediately weighed individually to obtain the fresh mass (FM). In order of obtained the dry mass (DM) of *Papayas*, the fruit were sectioned in small pieces and placed to dry in a forced ventilation oven with a temperature of (65 ± 5)°C. The fruit were kept in an oven until constant weights were obtained. The drying time was fixed in 24 h. After drying, the fruit were rested in airtight plastic boxes to cool and avoid additional variation of weight.

Characterization techniques

The physical assays, titratable acidity and total soluble solids, were evaluated using three to five fruit per day (during overall ripening stage). The fruit were pulped and mixed to obtain a homogeneous sample and evaluated in triplicate.

The absorbance index was acquired by a DA-meter® – (DA - index of the state of maturation of the fruit) (Turoni/Italia), calculated by the difference between the measured absorbance at 670 and 720 nm (chlorophyll peak) (Noferini et al., 2009).

The measurement of total soluble solids (TSS) was obtained by homogenizing the pulp. Then, a drop (10 ∟ L) of the resulting solution was placed on the lens of an Atago digital refractometer model PR 201 allowing the direct determination of TSS (%). Titratable acidity (TA) assays were evaluated by titrating an aliquot (10 mL) of *Papaya* juice with 0.1 M NaOH solution in the presence of phenolphthalein until pH 8.0 was obtained, providing the results in mg of citric acid per 100 mL of juice (AOAC, 1992).

The water content of the fruit was determined by direct subtraction between FM and DM. The results are presented as water weight in grams (g) and percentage of water in the fruit (%).

The electrical characterization of samples was performed in a Potentiostat/Galvanostat Metrohm Autolab AUT302N applying an AC voltage of 100 mV and a frequency range from 1 Hz to 1 MHz. The electrical contact with the fruit surface was established by using two electrodes of Ag/AgCl (MedLevensohn) disposed on opposite side of fruit (equatorial zone of samples) as shown in Figure 1.

The compression test was performed in an electromechanic universal machine EMIC model DL 10000 and registered by a computer furnished with a TESC software version 3.04 adapted for experiments with agricultural products. *Papayas* (at different ripening stage) were disposed between parallel plates (diameter 30 cm) and subjected to a compression of 5 mm min^{-1} until the final strength was reached. The complete epicarp disruption, providing a direct relationship between force (N) and deformation (mm) of the samples.

The modulus of elasticity (E) of the papayas was calculated according Equation 1 that used the Hertz model, applied in the determination of the maximum surface pressure and elastic modulus of a body pressed between two flat plates (Khodabakhshian and Emadi, 2011).

$$E = 0{,}75F(1-\mu^2) * \frac{1}{D^{3/2}} * \frac{1}{R^{1/2}} \qquad (1)$$

Table 1. Average of air temperature (T), relative humidity (RH) and precipitation (p), from May to August 2018 measured every morning in the corresponding period.

Month	T (°C)	RH (%)	p (mm)
May	25.7	59.1	17.3
June	24.7	58.7	3.3
July	24.5	53.7	0.5
August	25.3	18.6	1.0

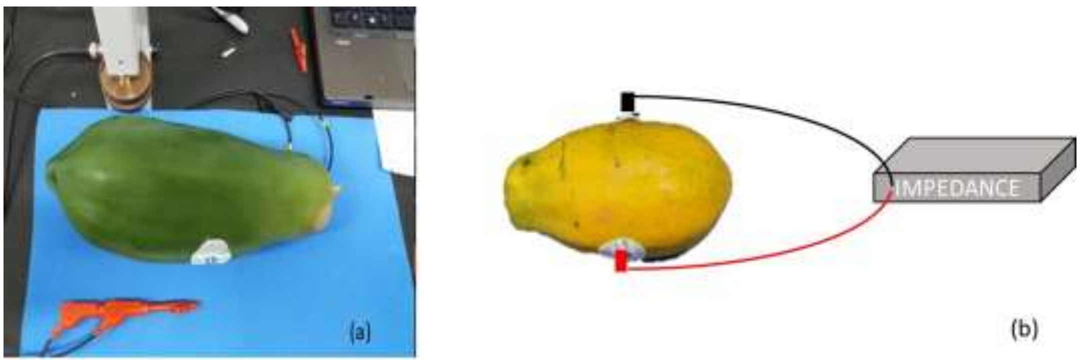

Figure 1. Disposition of electrodes for electrical characterization of samples at different ripening degree (a) 0 d and (b) 4 d- with corresponding connections to impedance analyzer.

where, F is the force in Newton, ∟ is the Poisson's ratio, R is the radius of the theoretical sphere (m), representing the fruit and D is the deformation (m).

Hencky's stress (σ_H) and strain (ε_H) were determined by Equations 2 to 4, as reported by Costa et al. (2017), Ferrari et al. (2011) and Linares et al. (2013). The breakdown stress is calculated considering the peak value of the stress-strain curve (Equations 1, 2 and 3).

$$\sigma_H = \frac{F(t)}{A(t)} \tag{2}$$

$$\varepsilon_H = -\ln\left(\frac{H(t)}{H_0}\right) \tag{3}$$

$$A(t) = \frac{A_0 H_0}{H(t)} \tag{4}$$

where, σ_H is Hencky stress (N m^{-2}); ε_H is Hencky strain (%); F(t) is Force (N) as a function of time t (s); A is Area (m^2) versus time (s); A_0 is initial sample area (m^2); H_0 is initial sample height (m) and H(t) is sample height (m) versus time (s).

Five groups of experiments were performed at different period of time after harvest (0, 2, 4, 6 and 8 d) considering four fruit per day. As a consequence, each point in experimental data refers to the average of 4 assays in different fruit. The error bar expressed in Tables and Figures was calculated from measurement in quadruplicates.

RESULTS AND DISCUSSION

Beyond the typical modification in parameters such as total soluble solids, titratable acidity, elasticity and water concentration, there are important implications on electrical properties of resulting material under progressive ripening. The correlation between parameters was evaluated as the following.

Physico-chemical characterization

Physical properties of *Papayas* during ripening process are summarized in Table 2. It is worth mentioning that each letter in the side of corresponding value reveals the parameter level in the overall range of variation and the degree of statistical significance in assays. Averages with the same letter do not differ statistically from each other. The Tukey test was applied at a 5% probability level for averages considering quadruplicates.

As we can see, the TSS presents a positive variation as a function of time. According to Oliveira Junior et al. (2006) and Fonseca et al. (2003), a good indicator of ripening is established at a condition of high TSS (between 10.8 and 12.75%) and a slight decrease in AT (8.27 and 6.17 g kg^{-1} of citric acid in juice). If considered,

Table 2. Quantification of physico-chemical of stored *Papaya* (the variation coefficient was calculated from experiments in four different fruit per day)

Parameter	Days of storage					Variation coefficient
	0	2	4	6	8	
TSS (%)	8.025[c]	8.65[c]	9.9525 [b]	10.8[b]	12.75[a]	CV% = 4.10
TA (g kg^{-1})	8.95[a]	8.85 [a]	8.275 [b]	7.675[c]	6.175[d]	CV % = 2.47
TSS/TA	8.966e	9.774[d]	12.042[c]	14.047[b]	20.682[a]	CV % = 3.52
AI	2.34[a]	2.005 [b]	1.505 [c]	1.205[d]	0.605e	CV% = 8.20
LFW (%)	0e	7.085[d]	8.835 [c]	11.575[b]	14.29[a]	CV% = 6.71

TSS: Total soluble solids, TA: Titratable acidity, AI: Absorbance index, LFW: Loss of weight in fresh fruit.

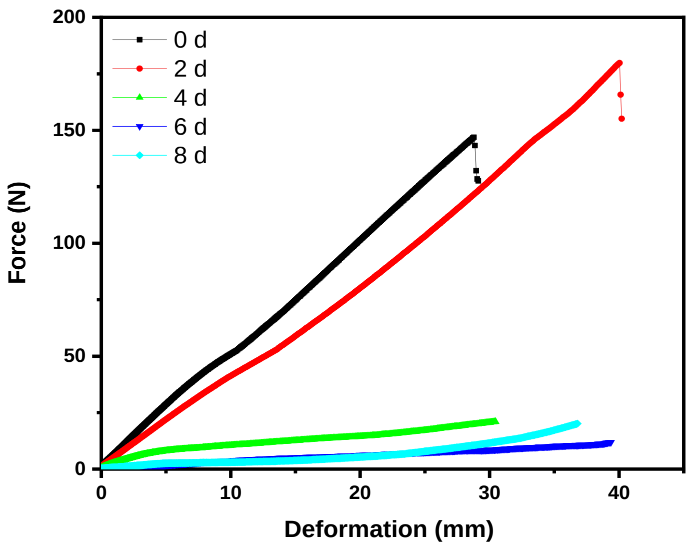

Figure 2. Dependence of force versus deformation in papayas at different post-harvest period.

the ratio TSS/AT makes it possible to verify a strong variation between the fourth and sixth day, in response of a combined increase of TSS and a decrease of AT. In the case of a climacteric fruit, it was observed that the maintenance of the fruit conservation is related to the quality parameters.

On the eighth day, extreme values were observed for fruit, with a higher TSS / AT ratio (20.682), a strong decrease in AT (6.175 g kg^{-1}, a TSS (12.75%) and an absorbance index (0.605), indicating that the fruit were already entering to senescence phase. Similar results were found by Oliveira Junior et al. (2006) with *Papaya* 'Sunrise alone'. It was observed an increase in the fresh mass loss during storage and according to Santos et al. (2008) a loss over 5 % of it is sufficient to depreciate *Papaya* fruit. In this work, that level (5%) of LFW occurred after 2 d of harvest, presenting a considerable statistical growth during storage, corroborating with the corresponding level described by Dias et al. (2011).

Mechanical assays

The mechanical resistance of *Papaya* at different ripening stages introduces important information related to the quality of fruit after harvest. One of the most significant parameters for quality of *Papaya* for consumers is its firmness since it reflects the ripening stages of the fruit (Jha et al., 2010).

Results of mechanical assays performed with fruit at different ripening degree (0, 2, 4, 6 and 8 d after harvest) are summarized in Figure 2. As we can see in Figure 2, a strong force is required to provide a lower level of deformation in fruit at first day. The complete epicarp disruption is reached for a force in the order of 150 N and a corresponding deformation of 30 mm characterizing the firmness of fruit. With progressive ripening, it is observed that is possible to increase the maximum force applied on the fruit surface, due to an increase in the maximum deformation, the elasticity of fruit increases with the ripening process. The elasticity is the capacity of a material for taking elastic or recoverable deformation. In this sense, this variation observed in elasticity as the fruit matures indicates that the resistance to bruising and damage is slightly lowered. In the following step of maturation, specifically at the third day but before the fourth after harvest, a remarked variation takes place in the mechanical properties of fruit (in agreement with previous data, about physico-chemical characterization) indicating that an accelerated depreciation of fruit takes place during this period.

After the fourth day, a minimal variation in force and deformation is observed, due to senescence and severe depreciation of fruit as it is observed in the low variation of mechanical resistance during the following days of ripening. That fact reduces the potential use of the mechanical assays for a clear evaluation of the overall

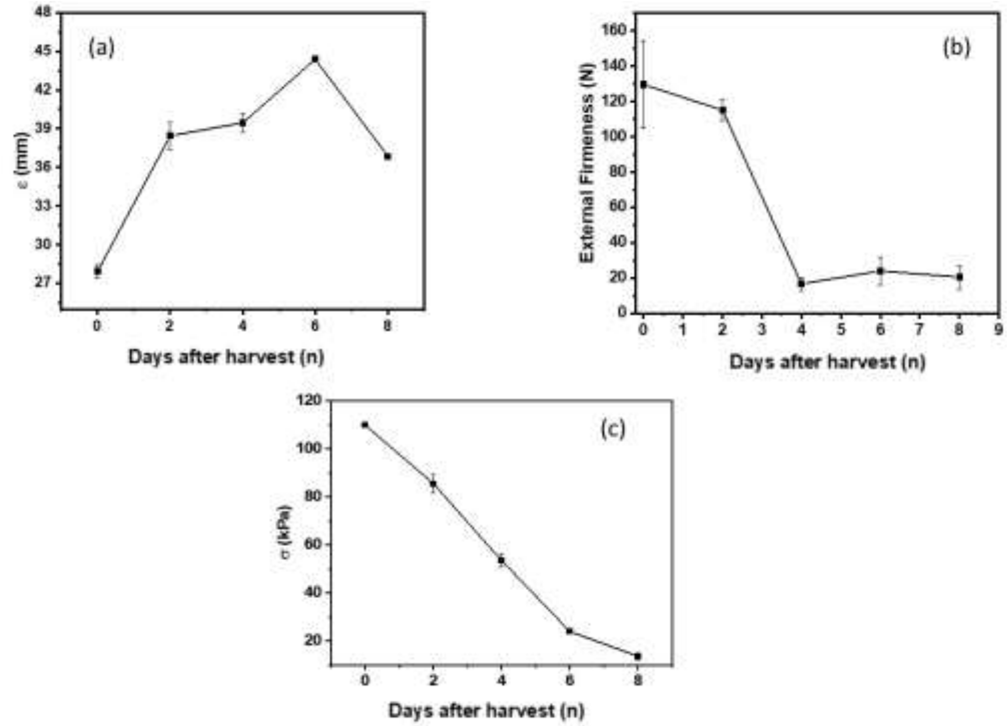

Figure 3. Mechanical assays of *Papayas* as a function of number of days after harvest: (a) external firmness, (b) deformation and (c) Henck tension. The error bar represents the deviation from medium value calculated from experiments in four different fruit per day.

kinetics of fruit degradation.

In order to evaluate the variation of different parameters in an independent manner with ripening stage, we plotted the behavior of firmness, elasticity and tension as a function of days of ripening (data shown in Figure 3). The external firmness of fruit (measured in N), shown in Figure 3a, presents a general decreasing trend in its value with strong variation between 2 d and 4 d after harvest, characterizing a typical plateau in which high level of firmness is observed for fresh fruit (t<2 d of harvest) followed by a low level of firmness (in order of 20 N) for t> 4 d from harvest. The result confirms the variation observed in TSS (with statistical significance) in the period of time between 2 d and 4 d, as a consequence of a more accelerated process of ripening and depreciation of the fruit that can be clearly identified in mechanical resistance data.

In association to this typical behavior for firmness, the mechanical elasticity and the Henck tension are two additional parameters with relevant information about properties of fruit (under ripening and in response of mechanical efforts). The deformation (a different measurement of elasticity of the fruit as shown in Figure 3b) increases with ripening degree in response to the decreasing firmness of the fruit. This process reaches a maximum after six days of harvest in which severe degradation tends to affect resistance of fruit.

As a consequence, the Henck tension tends to be strongly reduced (see Figure 3c) in the initial days of ripening decreasing firmness and increasing contact area as a result of elasticity of fruit with a reduced variation at severe condition of ripening.

Electrical characterization

The electrical response of *Papayas* was characterized by electrical impedance spectroscopy technique from direct measurement of bulky properties of fruit at high frequency range. In this case, it is possible to measure not only the interfacial mechanisms of transport and polarization (strongly affected by interaction of electrodes and the fruit peel) but more relevant bulky parameters - as previously reported for corresponding experimental systems (Figueiredo Neto et al., 2017). The mechanisms of ripening stage in *Papayas* is a function correlated to TSS and TA level which affects the transport mechanisms of current circulation in samples, as they are associated with the water content. As a consequence, the real part of impedance measured at high frequency range (1 MHz) was established as the most adequate parameter to characterize the bulky properties of

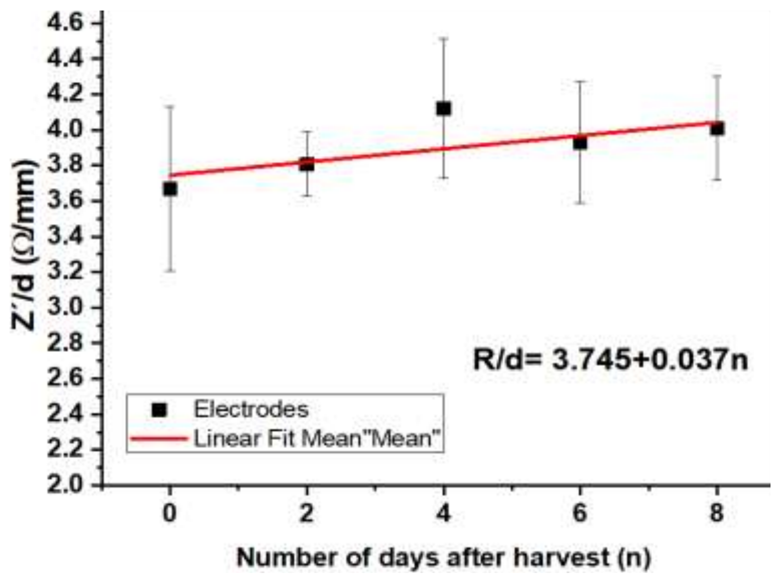

Figure 4. Dependence of real part of impedance of papaya (at 1 MHz) as a function of ripening degree. The error bar represents the deviation from medium value calculated from experiments in four different fruit per day.

transport mechanisms in *Papaya* since it helps to develop a single-point and non-invasive technique for identification of its ripening degree, minimal variation was observed in other range of frequencies due to variation in interfaces with degradation process.

Other important aspect to be addressed refers to the influence of the distance between electrodes on overall response of impedance. If considered the typical variation in the size of fruit, it is relevant to normalize the bulk resistance by diameter of fruit in order to evaluate a more intrinsic property from an electrical measurement.

Results in Figure 4 indicate a general trend, in which the normalized impedance increases with the days after harvesting of the *Papaya*. In spite of the low slope in the general behavior, an important aspect can be observed from this data, a small deviation of impedance at the fourth day of ripening. Despite the small displacement of curve from general slope (first order curve) it represents an elevation in normalized resistance that is in agreement with variation observed in corresponding parameters. Contrary to the mechanical data, the structural modification in the fourth day not affects the electrical property of material and initial variation that can be explored in the measurement of the ripening stage at severe condition.

If considered a more complex function to describe this data (than a simple first order function), it is possible to identify a stronger variation in the slope of curve that is in agreement with the corresponding variation in the firmness. Thus, this function can be considered as an important aspect in the kinetics of ripening.

The correlation between pairs of parameters explored from physico-chemical, mechanical and electrical properties were performed according to the first derivative of each parameter as a function of the number of days of ripening. The direct measurement of the slope variation per day can be explored in the determination of the overall kinetics of ripening. Figure 5 presents the variation of the slope for TSS (d(TSS)/dn) and the negative for TA (-d(TA)/dn): the signal is associated to the inverse variation of both parameters.

As we can see, the slope increases in the modulus of both parameters with the time, characterizing a strong variation in TSS and TA. An important aspect to be considered for the first derivative of the TSS refers to the inflexion point in the period between 2 d and 4 d, in which the slope remains with minimal variation.

Figure 6 shows the first derivative of firmness (dF/dn) and the negative of impedance (Z´/d) – d(Z/d)/dn as a function of time of harvest. The negative in derivative of impedance was established due to the reverse variation of both parameters contributing to the clearer visualization of both curves in the same plot.

As we can see, the first derivative of firmness with ripening (dF/dn) presents a strong variation in its value (the slope) at day two, in agreement with the corresponding value of firmness, strong reduction between 2 d and 4 d. After two days of ripening, the slope tends to lower values (plateau in the lower firmness values, severe ripening degree). In correspondence, the plot of -d(Z/d)/dn presents a similar variation with increasing the number of days after harvest as observed

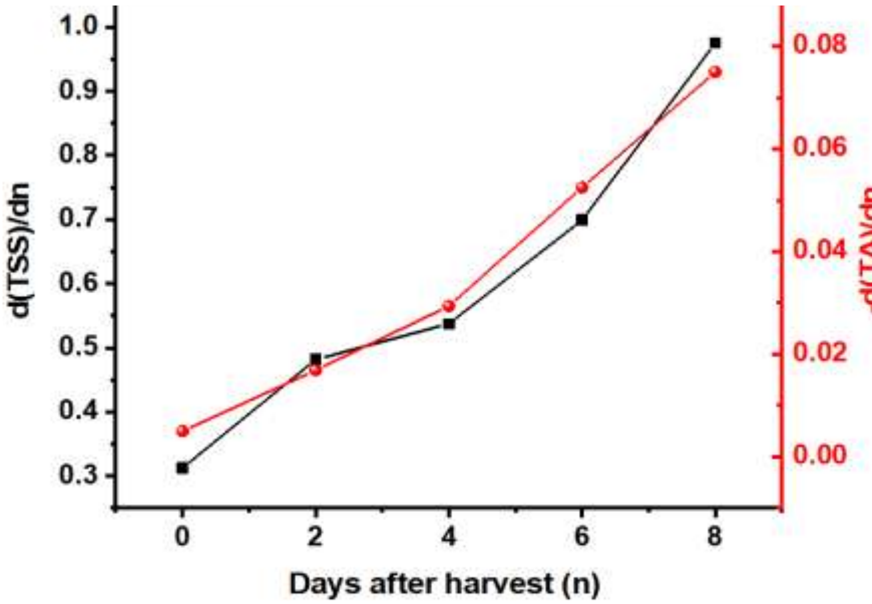

Figure 5. Comparison of first derivative of TSS and TA as a function of ripening degree.

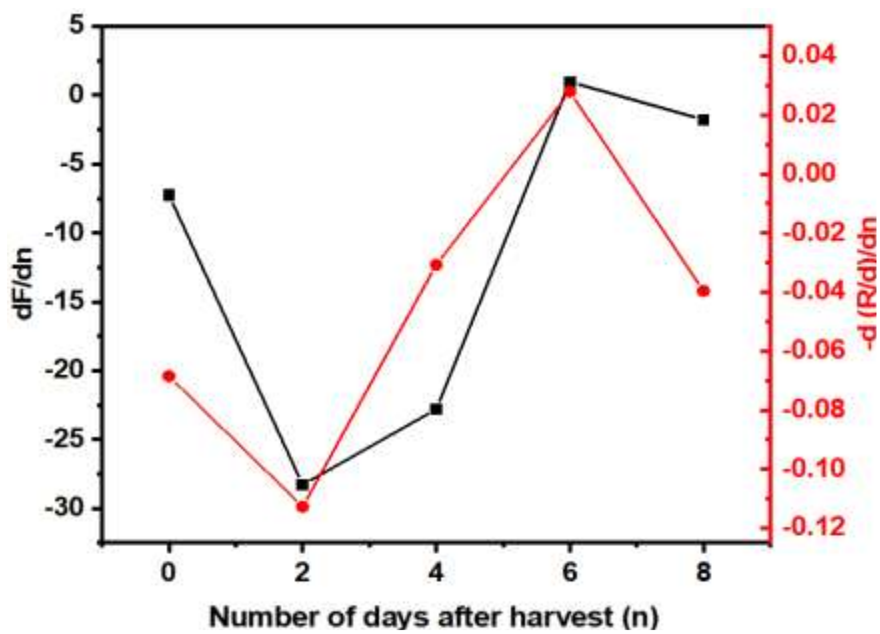

Figure 6. Comparison of first derivative of firmness and impedance as a function of ripening degree.

in the linear fitting, the medium in slope is in the order of 0.037 in the plot is possible to identify that at day two the slope presents a significant shift to a value in the order of 0.10. The correlation between these behaviors comparison of destructive (mechanical assay) and a non-invasive method (electrical impedance) confirms that the overall ripening process in terms of a detailed kinetics can be addressed by both techniques with the advantages of a non-invasive technique (the electrical impedance spectroscopy) that preserves the fruit and provides information relative to the degree of ripening and transitions detected by destructive assays beyond the limit of severe senescence of *Papaya*.

These results confirm that the direct measurement of ripening stage of *Papayas* by electrical impedance spectroscopy returns a reasonable level of sensitivity towards the physiological changes of fruit tissues. Different variation in the slope of the real part of impedance presented a strong correlation between intrinsic physico-chemical and mechanical parameters of fruit, such as lower variation in TSS and reduction in firmness of fruit. As a consequence, the development of a portable simple circuit that measures the impedance at 1 MHz can be explored as an interesting tool for identifying the ripening stage in *Papayas*. If we consider a calibration curve (control experiments), it is possible to associate the measured impedance with ripening degree in non-destructive and simple assays.

Conclusion

The kinetics of ripening in *Papaya* was performed using destructive and non-invasive techniques. The comparison of results revealed that all of properties were strongly affected after the fourth day of storage, characterizing this period of post-harvest as a transition between fresh condition, high firmness, low values of TSS and high TA to more severe conditions of ripening in which a strong variation in TSS and TA were followed by a lower firmness confirming the degradation of fruit. The use of EIS as an alternative technique for measuring the ripening stage of fruit confirmed all of those characteristics and introduced important advantages related to the development of a single point measurement of electrical properties in nondestructive assays.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

REFERENCES

AOAC – Association of Official Analytical Chemists (1992). Official methods of analysis of the association of official analytical chemistry. 11.ed. Washington: DC: AOAC, 1115p.

Chowdhury A, Bera TK, Ghoshal D, Chakraborty B (2015). Studying the electrical impedance variations in banana ripening using electrical impedance spectroscopy. Proceedings of the Third International Conference on Computer, Communication, Control and Information Technology (C3IT) DOI:10.1109/C3IT.2015.7060196

Dias TC, Mota WF, Otoni BS, Mizobutsi GP, Santos MGP (2011). Conservação pós-colheita de mamão formosa com filme de pvc e refrigeração. Revista Brasileira de Fruticultura (33-2):666-670.

El-Gewely MR (2008). Biotechnology Annual Review, Elsevier, first Edition, Hungary 14:474 p.

Figueiredo Neto A, Cárdenas Olivier N, Rabelo Cordeiro E, de Oliveira HP (2017). Determination of mango ripening degree by electrical impedance spectroscopy. Computers and Electronics in Agriculture 14:222–226.

Fonseca MJO, Cenci AS, Botrel N, Leal NR (2003). Uso de atmosfera controlada na conservação de frutos de mamoeiro 'Sunrise Solo'. Revista Brasileira de Armazenamento, Viçosa 28-2(17-22).

Grossi M, Bruno Riccò B (2017). Electrical impedance spectroscopy (EIS) for biological analysis and food characterization: a review. Journal of Sensors and Sensor Systems 6:303-325.

Harker FR, Forbes SK (1997). Ripening and development of chilling injury in persimmon fruit: an electrical impedance study. New Zealand Journal of Crop and Horticultural Science 25:149-157.

Islam M, Wahid K, Dinh A (2018). Assessment of Ripening Degree of Avocado by Electrical Impedance Spectroscopy and Support Vector Machine. Journal of Food Quality, pp. 1-15.

Jha SK, Sethi S, Srivastav M, Dubey AK, Sharma RR, Samuel DVK, Singh AK (2010). Firmness characteristics of mango hybrids under ambient storage. Journal of Food Engineering 97:208-212.

Khodabakhshian R, Emadi B (2011). Determination of the Modulus of Elasticity in Agricultural Seeds on the Basis of Elasticity Theory. Middle East. Journal of Scientific Research 7(3):367-373.

Martins DR, Barbosa NC, de Resende ED (2014). Respiration rate of Golden papaya stored under refrigeration and with different controlled atmospheres. Scientia Agricola 71:345-355.

Miloski K, Wallace K, Fenger A, Schneider E, Bendinskas K (2008). Comparison of biochemical and chemical digestion and detection methods for carbohydrates. American Journal of Undergraduate Research 7:48-52.

Noferini M, Fiori G, Farneti B, Costa G (2009). Impiego di um índice non distruttivo per determinare la correta época di Raccolta Del fruto di actinidia chinensis. In: MACFRUT.

Oliveira Jr LFG, Enilce M, Coelho EM Coelho FC (2006). Caracterização pós-colheita de mamão armazenado em atmosfera modificada. Revista Brasileira de Engenharia Agrícola e Ambiental 10-3:660-664.

Santos CEM, Couto FAD, Salomão LCC, Cecon PR, Wagner Júnior A, Bruckner CH (2008). Comportamento pós-colheita de mamões formosa 'Tainung 01' acondicionados em diferentes embalagens para o transporte. Revista Brasileira de Fruticultura 30-2:315-321.

Schwann HP (2002). Electrical properties of tissue and cell suspensions: mechanisms and models. Advances in Biological and Medical Physics 1:A70-A71.

Souza Junior FG, Silva AM, Oliveira GE, Costa RM, Fernandes ER, Pereira ED (2015). Conducting and magnetic mango fibers. Indust. Crops Product 68:97-104.