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Modelling the acidification curve of tropical fruits: cashew apple, coconut, kiwi, mango, papaya, red guava, watermelon and yellow melon

Santos, B. K., Juliano, G. M., Reis, R. M., Pereira, I. O., Turatti, M. A. and Augusto, P. E. D.

Technical School of Campinas (COTUCA), University of Campinas (UNICAMP), Campinas, SP, Brazil

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Abstract

The tropical/exotic fruits are important sources of nutrients, and its pleasant flavour and sensory profile results in a growing demand worldwide. Therefore there is a need for better understanding its processing and properties. The acidification is a unit operation widely used in vegetable processing, in special associated to pasteurization in order to guarantee the food preservation. Moreover, the acidification is widely used in pectin gels development, which is important for some fruit products processing and stability. However, although being extensively applied in fruit products processing, the acidification is slightly studied, in special its mathematical description. The present work evaluated two mathematical functions in order to modelling eight fruit pulps acidification curve. Both functions described well the experimental data and can be used for modelling the fruit pulp acidification curve. The obtained results can be directly used for processing design, being potentially useful for future studies on food properties and process design.

Introduction

The tropical fruits, also called exotic fruits, are important sources of vitamins, fibres and other nutritional components such as anti-oxidants. In addition to its health claim, the pleasant flavour and sensory profile increase the fruit demand worldwide. Therefore there is a need for better understanding its processing and properties (Augusto *et al*., 2012c; Oliveira *et al*., 2012). The health benefits and potential technological applications of exotic fruits could be better exploited if more information on their chemistry, biochemistry, nutritional properties, and microbiological, sensory, toxicological, technological and engineering aspects is available (Sant'Ana, 2011). Moreover, the native fruit commercialization plays an important role in social perspectives in developing countries like in Brazil (Ceva-Antunes *et al*., 2006; Furtado *et al*., 2010).

The food pH reduction allows the spores outgrowth inhibition, reduces microbial thermal resistance and decreases their growth rate or inhibit their growth (Derossi *et al*., 2011). Therefore, the acidification is a unit operation widely used in vegetable products processing, specially associated to pasteurization in order to guarantee the food safety and preservation. Moreover, the acidification is widely used in pectin gels development, which is important for some fruit products processing and stability.

The acidification was previously studied as a conservation method for some vegetable products as heart of palm (Berbari *et al*., 2008), cauliflower (Nogueira *et al*., 1993), garlic (Berbari *et al*., 2003), guava (Torrezan *et al*., 1999) and others (Silva *et al*., 2010). However, any of this works modelled the product acidification curve using mathematical functions, even though Derossi *et al*. (2011) highlighted the need for modelling the vegetable acidification process.

Therefore, although being extensively applied in fruit products processing, the acidification is slightly studied, in special its mathematical description. The acidification curve relates the acid addition to the sample with its pH. As the added acid amount is increased, the sample pH is decreased in an asymptotic non-linear shape. Modelling this curve is thus interesting for unit operations design, process optimization and high quality products assurance. The present work evaluated the acidification curve of eight tropical fruits (cashew apple (*Anacardium occidentale*), coconut (*Cocos nucifera*), kiwi (*Actinidia chinensis*), mango (*Mangifera indica*), papaya (*Carica papaya*),

*Corresponding author.
Email: *pedro@cotuca.unicamp.br*

red guava (*Psidium guajava*), watermelon (*Citrullus vulgaris*) and yellow melon (*Cucumis melon*)). Moreover, two mathematical models were used to describe this property.

Materials and Methods

Fruit pulps

The eight tropical fruits pulps evaluated (Table 1) were selected due to the importance of acidification in its processing. Moreover, acid (pH<4.5) and low-acid (pH>4.5) fruits were selected in order to represent both food groups.

Pasteurized frozen commercial pulps were used in order to guarantee the standardization and repeatability. After washing, the fruits are pulped, pasteurized, packaged in small plastic bags and then frozen, prior to commercialization.

Samples were thawed and carefully homogenized before evaluation. Its soluble solids content was determined by using a refractometer (digital refractometer r² mini, Reichert Analytical Inst., Japan), after filtering the samples in cotton. The pulps pHs were directly measured using a pHmeter (Tecnal, TEC-2, Brasil). Table 1 shows the soluble solid content and initial pH of the eight fruit pulps here evaluated.

Acidification

Due to its sensory properties and cost, the citric acid is the most used acid in food processing, justifying its selection for this work. The acidification curves were obtained by the pulps potentiometric titration (pHmeter Tecnal TEC-2, Brazil), using a citric acid solution of 15% (m/m; PA Ecibra, Brazil; concentration previously determined) and ~50 g of each pulp, until the equilibrium pH.

Mathematical modelling

The acidification curves were modelled using two mathematical functions (Equations 1 and 2), where [Ac] is the citric acid concentration added to the sample (g citric acid / 100 g of pulp). The Equation 1 is a logarithmic decay function described by only two parameters. The parameter A is a proportional factor, while the parameter B describes de sample pH changes due to the citric acid addition. The Equation 2 is an exponential decay function described by three parameters. The parameter pH_0 is the initial pH; the pH_E is the equilibrium pH and the parameter K describes the pulp pH changes due to the citric acid addition.

$$pH = A - B \cdot \ln[Ac] \quad \text{Equation 1}$$

$$pH = pH_E + (pH_0 - pH_E) \cdot e^{(-K[Ac])} \quad \text{Equation 2}$$

Table 1. The eight fruit pulps evaluated

Fruit pulp	pH	Soluble solids content (°Brix)
Cashew apple (*Anacardium occidentale*)	4.25	10.3
Coconut (*Cocos nucifera*)	6.20	5.7
Kiwi (*Actinidia chinensis*)	3.48	11.9
Mango (*Mangifera indica*)	4.01	13.7
Papaya (*Carica papaya*)	4.92	10.6
Red guava (*Psidium guajava*)	3.84	11.2
Watermelon (*Citrullus vulgaris*)	5.41	17.0
Yellow melon (*Cucumis melon*)	5.79	5.9

The parameters of each model were obtained by linear or non-linear regression using the software CurveExpert Professional v.1.2.0 using a significant probability level of 95%. The experiments were conducted in three replicate, and the regressions were obtained for each replicate.

The goodness of the models was evaluated by plotting the values of pH obtained by models (pH_{model}) as function of the experimental values ($pH_{experimental}$). The regression of those data to a linear function (Equation 3) results in three parameters that can be used to evaluated the description of the experimental values by the models, i.e. the linear slope (α; that must be as close as possible to the unit), the intercept (β; that must be as close as possible to zero) and the coefficient of determination (R^2; that must be as close as possible to the unit). It is a simple and efficient approach to evaluate the model fit (Augusto *et al*., 2012a; 2012b).

$$pH_{model} = \alpha \cdot pH_{experimental} + \beta \quad \text{(Equation 3)}$$

Results and Discussion

Figure 1 shows the typical shape of the acidification curves for yellow mellow and cashew apple pulps. The other pulps showed the same behaviour. As expected, the curve shape was a non-linear characteristic decay, initially with high pH decay and finishing with an asymptotic behaviour at the equilibrium pH. The acidification curves shape were close to those previously presented for other vegetables as heart of palm (Berbari *et al*., 2008), cauliflower (Nogueira *et al*., 1993), garlic (Berbari *et al*., 2003) and guava (Torrezan *et al*., 1999). Moreover, it shapes as an exponential-decay function, which confirms the mathematical models here evaluated. For all the evaluated fruit pulps, the equilibrium pH was close to 2.5, which is close to those necessary for the pectin gel formation (2.0-3.5; Bemiller and Whistler, 1996).

Table 2 shows the obtained values for the parameters of the logarithmic (Equation 1) and exponential (Equation 2) decay functions, considering the eight evaluated fruit pulps. The model regressions

Table 2. Parameters of the two evaluated models (mean of thee replicates ± standard deviation)

Fruit pulp	Equation 1			Equation 2			
	A	B ($[Ac]^{-1}$)	R^2 (minimum)	pH_0	pH_E	K ($[Ac]^{-1}$)	R^2 (minimum)
Cashew apple (*Anacardium occidentale*)	3.10 ± 0.03	0.35 ± 0.01	0.99	3.73 ± 0.04	2.30 ± 0.01	0.43 ± 0.01	0.96
Coconut (*Cocos nucifera*)	3.39 ± 0.03	0.54 ± 0.00	0.99	5.41 ± 0.04	2.41 ± 0.02	1.19 ± 0.01	0.92
Kiwi (*Actinidia chinensis*)	2.97 ± 0.02	0.26 ± 0.01	0.96	3.26 ± 0.03	2.28 ± 0.01	0.25 ± 0.00	0.99
Mango (*Mangifera indica*)	3.07 ± 0.02	0.33 ± 0.00	0.99	3.61 ± 0.03	2.36 ± 0.02	0.44 ± 0.03	0.98
Papaya (*Carica papaya*)	3.23 ± 0.03	0.43 ± 0.01	0.99	4.32 ± 0.09	2.44 ± 0.04	0.77 ± 0.05	0.95
Red guava (*Psidium guajava*)	2.98 ± 0.02	0.35 ± 0.01	0.95	3.77 ± 0.02	2.44 ± 0.03	0.80 ± 0.08	0.99
Watermelon (*Citrullus vulgaris*)	3.83 ± 0.02	0.56 ± 0.01	0.99	4.95 ± 0.07	2.64 ± 0.03	0.53 ± 0.03	0.97
Yellow melon (*Cucumis melon*)	3.35 ± 0.03	0.51 ± 0.00	0.97	5.19 ± 0.04	2.47 ± 0.01	1.24 ± 0.03	0.94

Table 3. Evaluation of the proposed models using Equation 4 (mean of thee replicates ± standard deviation): $pH_{model} = \alpha \cdot pH_{experimental} + \beta$

Fruit pulp	Equation 1			Equation 2		
	α	β	R^2 (minimum)	α	β	R^2 (minimum)
Cashew apple (*Anacardium occidentale*)	1.01±0.02	0.00±0.08	0.99	1.00±0.03	-0.03±0.06	0.97
Coconut (*Cocos nucifera*)	0.98±0.01	0.07±0.01	0.99	0.95±0.01	0.11±0.02	0.92
Kiwi (*Actinidia chinensis*)	0.97±0.04	0.08±0.12	0.96	1.00±0.03	0.00±0.08	0.99
Mango (*Mangifera indica*)	0.99±0.01	0.02±0.03	0.99	0.98±0.01	0.04±0.02	0.98
Papaya (*Carica papaya*)	1.00±0.02	0.00±0.07	0.99	0.95±0.03	0.13±0.07	0.95
Red guava (*Psidium guajava*)	0.96±0.02	0.11±0.05	0.95	1.00±0.02	0.00±0.04	0.99
Watermelon (*Citrullus vulgaris*)	1.00±0.01	0.00±0.01	0.99	0.97±0.01	0.09±0.02	0.97
Yellow melon (*Cucumis melon*)	0.99±0.01	0.03±0.01	0.99	0.94±0.02	0.16±0.03	0.95
General evaluation (the eight pulps together)	0.98	0.05	0.98	1.00	-0.01	0.96

showed high values for the coefficient of determination ($R^2 > 0.92$). Moreover, Table 3 shows the evaluation of both models by using Equation 3 (also shown on Figure 2). The values of α and R^2 were always close to 1.0, while the values of β were always close to 0.0. Therefore, both models can well describe the fruit pulps acidification curve.

The parameters B on the logarithmic function (Equation 1) and K on the exponential function (Equation 2) describe de sample pH decay proportion due to the citric acid addition. In fact, for most of the evaluated fruits, their values were close (Table 2). However, it is important to highlight that although representing the same issue, each one is related to a different mathematical function.

Therefore, it explains the reason for the difference in these values for some of the evaluated fruits (coconut, papaya, red guava and yellow melon). For these fruits, although both models showed good correlation with the experimental data (Tables 2 and 3; Figure 2), the acidification curve shape can be better described particularly by one of them, while for the other fruits, both models showed almost the same correlation (Table 3). Thus, for coconut and red guava, the logarithmic function (Equation 1) showed better correlation then the exponential function (Equation 2), while the opposite behaviour was seen for papaya and yellow melon. It highlights the importance to evaluate both models for each fruit, as well as to carry out the present explorative work, in order to better choose those one to describe the acidification behaviour.

Similarly, both parameters A on the logarithmic function (Equation 1) and pH_0 on the exponential function (Equation 2) are related to the sample initial pH. However, although the parameter pH_0 (Equation 2) is directly related to that, the A value on Equation 1 is indirectly related to the initial sample, as it is the pH value when the acid concentration is 1% (i.e., when $\ln[Ac] = 0$; Equation 1). Moreover, the logarithmic function is not defined in zero, and the initial pH value on Equation 1 can only be obtained by tending the [Ac] to zero. Thus, both parameters cannot be directly compared (only its magnitude).

The logarithmic decay function (Equation

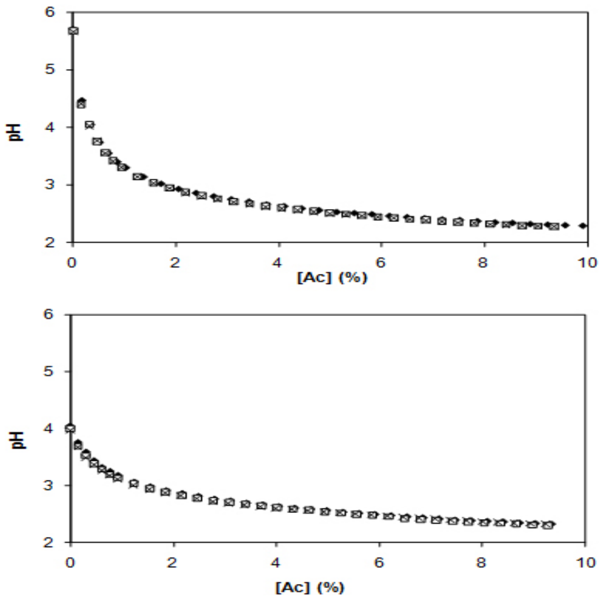

Figure 1. Example of the acidification curves: yellow mellow (up) and cashew apple (down). Markers are the replicates

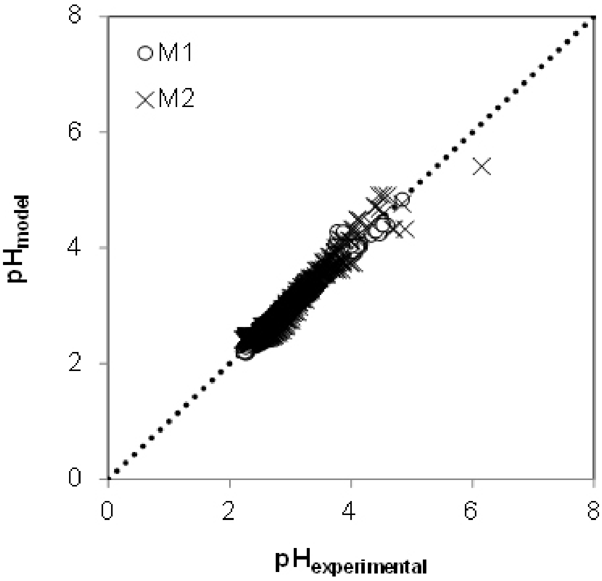

Figure 2. Evaluation of the proposed models using Equation 3. M1 is Equation 1 and M2 is Equation 2. The dots are the obtained data (model versus experimental) and the dashed line represents a regression with $\alpha = 1$, $\beta = 0$ and $R^2 = 1$

1) modelling can be carried out by simple linear regression, while the exponential decay function (Equation 2) modelling needs to be carried out by non-linear regression, using more complex softwares. In other hand, the use of Equation 2 is more intuitive, as its parameters directly represent the pH decay from an initial (pH_0) to an equilibrium (pH_E) value. Nevertheless both models can be used for the acidification curve modelling.

The acidification is a widely used unit operation during fruit processing, in special for the fruits here evaluated. It is essential in some sweet products processing, as jellies and jams. As an example, the guava preserve/jam is one of the most popular fruit products in Brazil (Peçanha *et al*., 2006). Moreover it is important in fruit pulps and juices preservation when associated with pasteurization processes.

The acidification curve shows a horizontal asymptotic behaviour after an initial accentuate pH decay, which difficult the final pH setting during processing. Thus, the mathematical description of this curve can reduce the amount of experiments in order to determine the acid concentration needed. Moreover, it can help researchers to describe and design acidification processes.

Derossi *et al*. (2011) reviewed the vegetable acidification process, highlighting the importance of mathematical modelling the process and parameters. By using the here evaluated functions, the fruit pulp acidification process can be better designed and evaluated in order to obtain an optimized product.

Conclusions

The present work evaluated two mathematical functions in order to modelling eight fruit pulps acidification curve. The first model was a logarithmic decay function, described by two parameters; the second was an exponential decay function, described by three parameters. Both functions described well the experimental data and can be used for modelling the fruit pulp acidification curve. The obtained results can be directly used for processing design, being potentially useful for future studies on food properties and process design.

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