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# Ultrasound assisted acidification of model foods: Kinetics and impact on structure and viscoelastic properties

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## ABSTRACT

This work aimed to describe the acidification process of two specific model foods using the ultrasound technology, as well as to evaluate the changes on its viscoelasticity properties. For that, two types of model food were used, with similar composition but different structures: natural melon cylinders and restructured melon-agar cylinders. The acidification process was performed using a citric acid solution (0.2% w/w) assisted with and without ultrasound (40 W/L of volumetric power and 20 kHz of frequency) at constant temperature (25 °C). In addition, the stress relaxation analysis was performed on the cylinders in order to evaluate the changes on the viscoelastic properties. As a result, both ultrasound processing and the different structural conformation of the model foods affected the acidification kinetics, being improved by ultrasound. Further, the acidification process with and without ultrasound affected the mechanical properties of both products, reducing their elasticity. The relaxation data could be described by a Maxwell model with two bodies and a residual spring, providing a possible explanation of the association between the mechanical model parameters and the microstructural conformation of both studied cases.

## 1. Introduction

The acidification process is a mass transfer unit operation consisting of incorporating $H^+$ protons in the food to decrease its pH. By decreasing the food pH, less severe thermal processing can be performed to assure safety and quality (Derossi, De Pilli, & Severini, 2013). Consequently, the acidification is frequently used in combination with pasteurization in vegetable processing.

The acidification is a specific mass transfer unit operation, as solution equilibria (a weak acid is partially dissociated in solution) and reactions (acid/base, neutralization) take place, complicating the phenomenon description. For instance, the cell membranes do not let charged molecules to cross it; thus, only the non-dissociated acid molecules enters the cells, being then partially dissociated in the cytoplasm, decreasing its pH (Stratford & Rose, 1986). Further, the cell buffer effect can delay the acidification process (A. Derossi, A. Fiore, T. De Pilli, & C. Severini, 2011) since the cells activate mechanisms to avoid the pH variation and its effect on biochemical reactions. For that reason, this process in not as simple as it seems.

In fact, although widely used, there are few studies about the acidification kinetics in food. For example, there are studies with model gels (Giannakopoulos & Guilbert, 1986), potato slices (Zhao, Shehzad, Yan, Li, & Wang, 2017), zucchini slices (A. Derossi, T. De Pilli, M. La Penna, & C. Severini, 2011), green beans (Zareifard, Savard, Marcotte, Lecompte, & Grabowski, 2015), carrots (Tola & Ramaswamy, 2013), different solid food cubes (Marcotte, Grabowski, Karimi, & Nijland, 2012) and mushrooms (Derossi et al., 2013). Any of those studies used ultrasound to enhance the process, which it would be desirable.

The use of ultrasound (acoustic waves with frequencies higher than 20 kHz) has demonstrated excellent result improving mass transfer processes such as in drying (Gamboa-Santos, Montilla, Cárcel, Villamiel, & Garcia-Perez, 2014), hydration (Miano, Pereira, Castanha, Júnior, & Augusto, 2016), extraction (Vinatoru, 2015) osmotic dehydration (Dehghannya, Gorbani, & Ghanbarzadeh, 2015) and desalting (Ozuna, Puig, Garcia-Perez, & Cárcel, 2014). As described, the use of this technology to assist the acidification process was still not evaluated.

The mass transfer improvement by the ultrasound technology has been attributed to diverse mechanisms that can enhance the external resistance to mass transfer (acoustic cavitation, acoustic streaming, acoustic jets (Ojha, Keenan, Bright, Kerry, & Tiwari, 2016; Yasui, 2015)) and/or the internal resistance to mass transfer (direct effects, as sponge effect and inertial flow, and indirect effects, as micro channel formation (Miano, Ibarz, & Augusto, 2016)). The micro channel formation affects the structure of the food, since the acoustic cavitation cause the matrix (cells and/or tissues) disruption. Therefore, the food

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mechanical properties can be affected, being important studying these properties.

Texture is an important food property since is and indicator of quality and acceptability. There are several analyses to measure textural properties. As foods have mechanical behaviors similar to both liquids and solids, its rheology must be evaluated through the viscoelastic properties. The stress relaxation analysis is a simply way to understand the viscoelastic properties of food. It consists of an instantaneous deformation to a sample, maintaining the strain constant and evaluating the related stress. Then the way by how the sample attempts to alleviate the imposed stress can be correlated with mechanical models (Rao & Steffe, 1992). As ultrasound modified the food structure, the textural properties can estimate how severe were the changes on samples by this emerging technology.

For those reasons, this work aimed to describe the ultrasound assisted acidification process of a model food, as well as how its viscoelastic properties change. This work used model foods in order to study the mechanisms by how ultrasound enhances the acidification process and to explain how the mechanical properties are changed by the process.

## 2. Materials and methods

### 2.1. Samples preparation

This work was conducted using cylinders of *in natura* melon and restructured melon, with 1.5 cm of diameter and 4 cm of height.

The cylinders were obtained from yellow/canary melon (*Cucumis melo inodorus*) with 88.5 ± 0.6% w.b. of moisture, 11.7 ± 0.9°Brix and 6.3 ± 0.1 of pH, using a stainless-steel corer (special cylindrical knife, Fig. 1).

In addition, to study the effect of the structure on the acidification process, the restructured cylinders were obtained by gelling the triturated melon pulp with agar (Fig. 1). This allowed the evaluation of cylinders with almost the same composition, also maintaining the same buffer capacity, but with specific structure. For that, agar (2% w/w) was dispersed in melon pulp (obtained using a blender), being heated until 80 °C for 30 s and then cooled at 5 °C in a refrigerator. After 24 h of storage, the gel was cut using the same stainless-steel corer, thus obtaining the cylinders.

### 2.2. Acidification process

The acidification with and without ultrasound was performed in a citric acid solution (0.2%) at 25 ± 1 °C.

For conventional acidification process, fifteen cylinders (melon cylinders or agar-melon cylinders) were placed in a beaker with 4 L of solution (to assure that the variation on the solution concentration was negligible), controlling the temperature using a water bath (Dubnoff MA 095 MARCONI, Brazil).

For the ultrasound assisted acidification process, fifteen cylinders (melon cylinders or agar-melon cylinders) were placed at the bottom of an ultrasonic bath (Q13/25, Ultronique Brazil; frequency of 25 kHz and a volumetric power of 41 W/L) with 4 L of acid solution. In this case, the temperature was controlled using a heat exchanger inside the ultrasonic bath to maintain the temperature at 25 ± 1 °C during the entire process. The location of the samples inside the ultrasonic bath was decided to take into account the good practices described by Vinatoru (2015) to assure the highest ultrasonic intensity.

For studying the acidification kinetics of all treatments, the pH of the samples along the process time was recorded. One of the fifteen cylinders was removed from the acid solution at 5, 10, 15, 20, 30, 45, 60 and 80 min, superficially dried with paper towel and triturated using a mortar and a pestle in order to measure its pH with a pH-meter (Tecnal, Brazil). All the experiments were performed in quintuplicated.

According the obtained behavior, a first order kinetic equation considering the driving force the pH difference ($\mathrm{pH_t} - \mathrm{pH_\infty}$) was used to describe the data:

$$\mathrm{pH_t} = \mathrm{pH_\infty} + (\mathrm{pH_0} - \mathrm{pH_\infty})\bullet e^{-k\bullet t} \quad (1)$$

### 2.3. Stress relaxation analysis

For evaluating the effect of the acidification process and the use of ultrasound on the cylinder texture, the stress relaxation analysis was performed. For that, the cylinders (with and without processing) were cut to have 1.5 cm of height and 1.5 cm of diameter discarding the edges. This test was performed using a Texture Analyzer (TA.XT Plus, Stable Micro Systems Ltd., Surrey, UK) with a load cell of 5 kg-f (49,03 N) and a 35 mm cylindrical probe (P/35). The cylinders were firstly compressed until 2 mm of deformation at 0.2 $\mathrm{mm\cdot s^{-1}}$. Then, the deformation was maintained constant for 30 s, being the data of force (N) versus time (s) recorded to plot and to analyze the relaxation curves (Fig. 2).

The data was fitted using the generalized Maxwell model (Maxwell, 1851; Rao & Steffe, 1992) with a residual spring element (Eq. (2)), which relate the modulus of elasticity (Eq. (3)) as a function of time (see the Nomenclature section for clarity). By combining a series of Hookean springs (representing the solid behavior) and Newtonian dashpots (representing the fluid behavior), organized in series and parallel, the generalized Maxwell model can describe the viscoelastic properties of foods.

$$E_t = E_1\bullet e^{-t/\tau_1} + E_2\bullet e^{-t/\tau_2} + \ldots + E_n\bullet e^{-t/\tau_n} + E_{n+1} \quad (2)$$

$$E = \frac{F/A}{dL/L} \quad (3)$$

$$\eta_n = \tau_n\bullet E_n \quad (4)$$

### 2.4. Optical microscopy

Slices of ~10 μm were obtained using a manual micrometer (Ancap, Brazil). The slices were placed in glass slides and observed under an optical microscope (Olympus system microscopy model BX41, Japan) equipped with a digital color camera (Q-Color 3 OLYMPUS America INC, including the SQ Capture 2.90.1 Ver. 2.0.6 Software, Canada) and a 4 × objective. The images were captured at least in quintuplicate for each sample, after guaranteeing a representative field.

### 2.5. Statistical analysis

Statistical analysis was performed to the treatments equation parameters through analysis of variance (ANOVA) and Tukey's test ($P \leq 0.05$). The data nonlinear regression to Eqs. (1) and (2) was performed with a confidence level of 95% using the Levenberg-Marquardt algorithm. Both analysis were performed using Statistica 13.0 (StatSoft, USA) software.

## 3. Results and discussion

### 3.1. Acidification process

Fig. 3 shows the acidification kinetics of both natural melon cylinders and restructured melon-agar cylinders. For both, ultrasound has enhanced the acidification process by reducing the final pH (equilibrium pH). In addition, the data successfully fit Eq. (1), as presented on Table 1 and Fig. 3.

Further, the variance analysis stated that the parameter $k$ was affected by the structure (natural and restructured cylinder; $p < 0.05$), and slightly by ultrasound ($p < 0.2$), probably due to the high deviations, and it was not affected by the interaction. On the other hand, the