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Unripe Banana Flour Produced by Air-Drying Assisted with Ultrasound – Description of the Mechanisms Involved to Enhance the Mass Transfer in Two Approaches

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Abstract:
In this research the application of ultrasound, prior to air-drying, describing the phenomena in two approaches: unripe banana slices immersed in water (hydrated) and vacuum packaged (non-hydrated) were investigated. The results showed two falling rate periods during the air-drying. For the second rate period, an increase of water effective diffusivity due to the "sponge effect" (direct effect of ultrasound) and the microscopic channels formation (indirect effect) was observed. Scanning electron microscopy images showed that untreated dried slices were less porous, characterized by small cavities and high density, while ultrasound pretreated slices resulted in a porous structure with more free volume between cells. An increase in porosity decreased the resistance for diffusion, influencing positively the water effective diffusivity. Moreover, ultrasound produced partial disorder of the crystalline structure within the starch granules, reducing the amount of energy required for gelatinization. Moreover, reduction of resistant starch content was not observed.

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1 Introduction

Several fruits and vegetables are produced in large quantities mostly for export, especially in tropical countries (banana, pineapple, orange, melon, mango, among others). Drying can be applied to reduce post-harvest loss, and the dehydrated fruit can be used in foodstuffs formulations, providing an extension of shelf life, lighter weight for transportation, and less space required for storage [1]. Drying is the most common method of food preservation, which involves simultaneous heat and mass transfer, accompanied by phase change [1, 2]. Pretreatment to air-drying process can be used to reduce the initial water content or to modify the fruit tissue structure in order to improve the air-drying process [3].

The use of ultrasound (US) in the food industry has been growing for many years. Up to a few years ago, most applications of US in the food industry were related to non-invasive monitoring of the processes or food quality. In recent years, many applications of ultrasonic energy have been investigated concerning the use of US directly affecting the process or product [1, 4].

High-intensity US considers the use of frequencies from 20 kHz to 1 MHz and power intensity > than 1 W/cm^2, the goal of these applications is to improve mass and heat transport [5]. Therefore, high-intensity US may represent an attractive alternative to intensify dehydration and dewatering in gas-solid and liquid-solid systems, affecting both internal and external resistances to mass transfer [6]. Thus, resulting in shorter time for the air-drying process, it results in a significant reduction of energy consumption. Moreover, because of US effects are mainly mechanical, it does not induce any significant material heating and, therefore, the product quality could be maintained [5].

The improvement of the mass transfer by the US has been attributed to direct and indirect effects [7]. The indirect effect is related to the formation of micro-channels in the product, due to the mechanical stresses associated with wave transmission. The direct effect is related to the "sponge effect" produced by the ultrasonic

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waves traveling through the product. As a consequence, a rapid series of alternative compressions and expansions occur, which are compared with a sponge squeezed and released repeatedly [8]. Moreover, the "sponge effect" helps to keep the micro-channels free for moisture movement promoting moisture migration in the solid [8, 9].

The effects produced by the US when applied in a medium are diverse, and their relative importance depends on the characteristics of ultrasonic waves, the amount of energy transmitted and, the characteristics of the media itself: viscosity, density, surface tension or agitation. All these variables could improve or make difficult to transmit vibration and, therefore, to extend the US effects, when operating under identical conditions [5]. Hence, a good understanding of the role of each variable is very important to achieve desirable results. This work presents the study of US application as a pretreatment in two approaches: unripe banana slices immersed in water (hydrated) and vacuum packaged (non-hydrated) in order to distinguish the microstructural changes attributed to the US from the water intake resulted from immersing the unripe banana slices in water. Studies concerning the application of US, in these different approaches, in unripe banana slices, were not related in the literature yet. The effects of US on the quality of the final product, unripe banana flour (UBF), were also studied.

2 Materials and methods

2.1 Raw material

Unripe bananas (*Musa cavendishii*), variety Nanicão from Vale do Ribeira region (São Paulo, Brazil), were purchased from the local market. As soon as the fruits arrived at the laboratory, they were characterized according to the following parameters: soluble solids and firmness and processed immediately. For this cultivar, to confirm the first stage of maturation, the mean values of soluble solids should be close to (3.5 ± 0.8) ºBrix and firmness (25.8 ± 2.4) N [10].

Soluble solids were determined by a refractometer and corrected for acidity and temperature values [11]. A texture analyzer TA-XT2i*plus* was used to evaluate the firmness with a flat probe of 6 mm diameter, at penetration velocity of 1 mm/s until 20 mm of deep. Initial moisture content was determined by the gravimetric method at 70°C under vacuum pressure (≤20 kPa) until constant weight [11]. Soluble solids, firmness, and initial moisture content were performed before processing, in triplicate.

2.2 US pretreatment

Because the effects of US are directly related to the ultrasonic field applied, its characterization is fundamental; only then it is possible to evaluate the influence of US application and to establish the relationships between US parameters and observed effects [5]. Acoustic energy could be different from the electrical consumption, and its direct measurement is difficult; however, some methods based on the measurement of physical or chemical changes produced by the US could represent great results. In the case of liquid applications, the calorimetric method results remarkable [5]. Ultrasonic volumetric power was calculated by eq. (1), considering the heating power as a consequence of the energy delivered by the US waves:

$$P_{US} = \left(mC_P \frac{dT}{dt} \right) \frac{1}{V} \tag{1}$$

The experiments were conducted in a bath (UNIQUE, model USC-1850, Brazil), 154 W and 25 kHz, without mechanical agitation. The ultrasonic bath was insulated to minimize heat transfer through the surroundings. In order to avoid the return of the ultrasonic waves to the transducer and to guarantee perfectly absorption in water, the equipment was tilted 30° and the walls and the bottom of the water bath were covered with aluminum paper [12, 13]. The equipment was filled with 2 L of distilled water at a temperature of 26°C and turned on for 5 min (300 s) while the water temperature was monitored with a thermocouple. Ultrasonic volumetric power was determined in quintuplicate.

The bananas were peeled and cut into slices of 5 mm thickness. With the purpose of study the direct and indirect effects of US and water incorporation during it, two different pretreatments were performed:

Pretreatment 1: Consisted in immersing unripe banana slices in distilled water in the US bath (hydrated slices) with the application of US for 20 min. The water fruit ratio was maintained at 4:1 (weight basis). After US pretreatment, the slices were drained to remove the excess of water.

Pretreatment 2: Unripe banana slices were previously packed in polypropylene plastic bags (REGISTRON, Brazil) with a vacuum sealer (SELOVAC, model 200S, Brazil) (non-hydrated slices) and then immersed in the same ultrasonic bath, for 20 min, without simultaneous hydration. The pack was placed at the bottom of the US bath to receive the ultrasonic waves with more efficiency.

All the experiments were carried out at ambient temperature, in duplicate. Before and after pretreatment, weight and moisture content were determined to calculate the Water Gain (*WG*) according to eq. (2). Moisture content was determined in triplicate by the gravimetric method at 70°C under vacuum pressure (≤ 20 kPa) until constant weight [11]:

$$WG = \left(\frac{m_{us} x_{us} - m_0 x_0}{m_0} \right) \times 100 \tag{2}$$

2.3 Air-drying process

Batches of 1 kg of banana slices untreated and pretreated with the US, according to the conditions above described, were submitted to air-drying process. Figure 1 presents a schematic diagram of the vacuum-convective drier (LABMAQ, model L.M.ES-20, Brazil), with capacity of 4 kg distributed in four perforated trays, in each of them, it is coupled a load cell sensor for monitoring real-time weight (data acquisition rate: 1 point per min). The equipment control system registers the loss of weight, air velocity, temperature and relative humidity (*RH*). For all the experiments, the air velocity was maintained at 4 m/s, temperature of 50 °C and *RH* of 10 %. Experiments were performed until reaching $a_w < 0.6$, which is the condition to maintain the UBF microbiological stable [14].

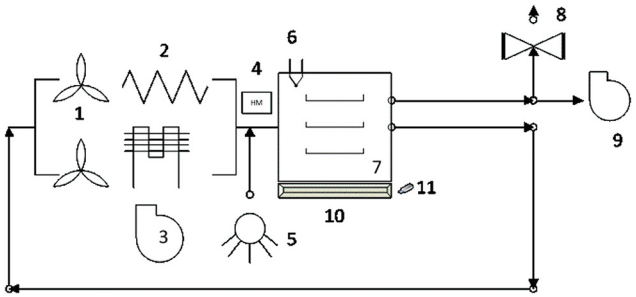

Figure 1: Schematic diagram of the vacuum-convective drier: (1) fans, (2) resistance, (3) refrigeration unit, (4) hygrometer, (5) atomizer, (6) temperature sensor (PT 100), (7) drying chamber, (8) solenoid valve and (9) vacuum pump, (10) equipment control system and (11) USB port.

2.3.1 *Determination of water effective diffusivity (D_{eff})*

Moisture ratio (*MR*) was calculated from experimental drying curves according to eq. (3). For X_e, the values already reported for the unripe banana at 50 °C and 10 % of *RH* were considered [15].

$$MR = \frac{X - X_e}{X_0 - X_e} \tag{3}$$

Water effective diffusivity (D_{eff}) for the falling-rate period was calculated according to Ficks second law of diffusion as presented in eq. (4).

$$\frac{\partial X}{\partial t} = \nabla \left(D_{eff} \nabla X \right) \tag{4}$$

Crank in 1975 gave the analytical solutions for eq. (4) for various regularly shaped bodies such as rectangular, cylindrical and spherical [16]. Considering banana slices as a plane sheet and applying the following boundary conditions:

– Uniform initial moisture content: $X(z,0) = X_0$

– Symmetry of moisture: $\frac{\partial y}{\partial x}|_{z=0} = 0$

– Equilibrium moisture at surface: $X(L,t) = X_e$

The solution for the water effective diffusivity at the falling-rate period is eq. (5).

$$\frac{X - X_e}{X_0 - X_e} = \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left[-(2i+1)^2 \pi^2 \frac{D_{eff}}{4L^2} t\right] \tag{5}$$

For long drying time eq. (5) can be simplified to the first term by setting $i = 0$:

$$\frac{X - X_e}{X_0 - X_e} = \frac{8}{\pi^2} \exp\left[-\pi^2 \frac{D_{eff}}{4L^2} t\right] \tag{6}$$

The water effective diffusivity was calculated applying the method of slopes [2, 17]. The resulting drying curves were fitted to the logarithmic model [18] presented in eq. (7) and the model proposed by Midilli [19] presented in eq. (8)

$$MR = a \exp(-kt) + c \tag{7}$$

$$MR = a \exp(-kt^n) + bt \tag{8}$$

The models were selected among several typical drying models including Newton, Page, Henderson and Pabis by the quality of fit determined with the coefficient of determination (r^2), root mean square error (RMSE) and reduced chi-square (χ^2), according to the following equations:

$$\text{RMSE} = \left[\frac{1}{N} \sum_{i=0}^{N} \left(MR_{\text{model}\,i} - MR_{\text{exp}i}\right)^2\right]^{1/2} \tag{9}$$

$$\chi^2 = \frac{\sum_{i=0}^{N} \left(MR_{\text{model}i} - MR_{\text{exp}i}\right)^2}{N - n} \tag{10}$$

wherein: $MR_{\text{model},i}$ is the predicted moisture ratio, $MR_{\text{exp},i}$ is the experimental moisture ratio, N the number of observations and n the number of constants.

After drying, the unripe bananas slices were ground in a mill (IKA, model A10, USA) to 250 μm. The UBF was portioned and packaged in aluminum zip-lock bags and stored in a room at 21 °C for further analyses.

2.4 UBF characteristics

With the aim of verifying the influence of US effects, the moisture content, water activity, gelatinization temperature and enthalpy, resistant starch content, solubility and microstructure analysis were performed for UBF produced under different treatments.

The moisture content was determined, in triplicate, by gravimetric method at 70°C under vacuum pressure (≤20 kPa) until constant weight [11].

The water activity was determined using the Vapor Sorption Analyzer (DECAGON, model Aqualab-VSA, USA) at 25°C, in triplicate.

The gelatinization temperature and enthalpy were determined in triplicate by a differential scanning calorimetry (DSC) (TA Instruments, model Q-Serie, USA). Approximately 2 mg of sample was placed in a hermetic aluminum pan with 7 mL of deionized water and kept still for about 60 min, at room temperature, before the assay [20]. Samples were submitted to a heating program from (20 to 100)°C, at a heating rate of 10°C/min, in triplicate. Peak temperature (T_p) and enthalpy (ΔH) were obtained from curves by TA Instruments program.

The resistant starch (RS) content was determined, in triplicate, according to the A.O.A.C.2002.02 method [21].

The solubility of UBF was determined in triplicate, according to the following method. Suspensions of 0.1 g of UBF in 10 mL of distilled water were prepared in centrifugal tubes and heated in a water bath at temperatures of (25, 40, 50 and 60)°C for 30 min, under agitation. After heating, samples were cooled to ambient temperature

and centrifuged (3000 rpm for 15 min). The supernatant was separated with a micropipette and dried at 105°C for 24 h [22, 23]. Thus, the solubility (S) was calculated according to eq. (11):

$$S = \frac{\text{dry weight}}{\text{sample weight}} \times 100 \tag{11}$$

The microstructure of the unripe banana slices and the UBF were analyzed by scanning electron microscopy (SEM) images. For better visualization, the cross-section images from unripe banana slices and UBF were coated with platinum in a high-vacuum coating system (BAL-TEC, model MED020, Switzerland). The examinations were performed by a high-resolution SEM (FEI, model Quanta 600FEG, Netherlands) under vacuum at 10 kV and magnification range from 600x, for unripe banana slices, to 5000x for UBF.

2.5 Statistical analyses

Data was analyzed by analysis of variance (ANOVA) applying Tukey's test at 95 % of confidence level as a post-hoc test through Statgraphics Centurion XV software (StatPoint, Inc., USA).

3 Results and discussion

Unripe bananas presented values of initial moisture content of (3.09 ± 0.15) g H_2O/g in dry basis (d.b.), (2.1 ± 0.2) ºBrix and firmness of (32.1 ± 2.7) N ratifying that they were in the first stage of maturation.

3.1 US pretreatment

The determined value of ultrasonic volumetric power was 9.38 ± 0.60 W/L. As shown in Table 1, ANOVA revealed a statistical difference for different pretreatments ($p < 0.05$). *WG* when applying the US in a liquid-solid system was already reported for different fruits and for different application time [1, 24, 25]. Nevertheless, in none of these studies is it explained if *WG* resulted due to the application of the US, or the hydration, consequence of immersing the unripe banana slices into water. Moreover, these slices gained water in the range of value already reported in the literature for ripe banana pretreated at the same conditions [3, 24]. As can be seen in Table 1, vacuum packaged slices (non-hydrated) gained a much less amount of water than those submitted to US immersed in water (hydrated). As expected, the *WG* was due to the immersion in water and not US application. The effect of US on the microstructure of slices can be observed by SEM micrographs (Figure 2). The resistant starch granules presented in the raw material are preserved by the amyloplast, where it is possible to see smaller cavities and high density (Figure 2A). Tissue for pretreated unripe bananas slices shows damaged cells with larger intercellular spaces. Moreover, amyloplast was broken in some regions of the sample (Figure 2B and Figure 2). Nevertheless, it was not possible to distinguished differences in the structure for US pretreatment in hydrated or non-hydrated unripe banana slices. The formation of micro-channels due to the application of US was already observed in fruits such as melon [1], apple [26], and passion fruit [27], among others.

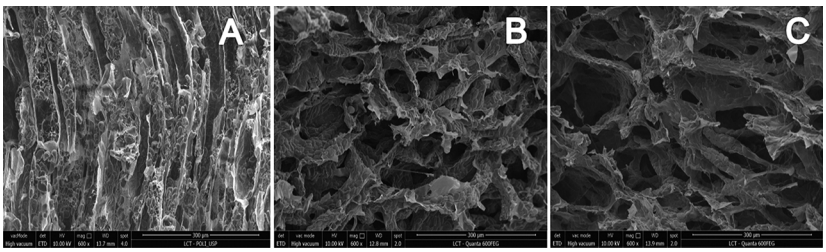

Figure 2: SEM micrographs of unripe banana slices pretreated with US: raw material (A); vacuum packaged (non-hydrated) unripe banana slices (B); immersed (hydrated) unripe banana slices (C).

Table 1: Water gain (*WG*) and water effective diffusivity (D_{eff}) of unripe banana slices untreated, vacuum packaged (non-hydrated) and immersed (hydrated) slices pretreated with US, and submitted to air-drying process.

Condition	*WG* (g/100g)	D_{eff} x 10^{-9} (m^2/s) 1st falling rate	2nd falling rate
Untreated	0.0[a]	10.02 ± 0.09[a]	5.24 ± 0.18[a]
Non-hydrated	0.83 ± 0.03[b]	11.71 ± 0.65[a]	8.05 ± 0.20[b]
Hydrated	7.60 ± 0.05[c]	10.02 ± 0.50[a]	7.30 ± 0.40[b]
HSD	0.22	2.77	1.57

Mean value and standard deviation (SD) respectively.
Mean with same letters in the same column are not significantly different ($p > 0.05$).
HSD, honestly significant difference.

3.2 Drying kinetics

The water effective diffusivity (D_{eff}) was calculated for the first and the second falling rates applying the method of slopes (Table 1). The increase of the D_{eff} due to US pretreatment was already reported in the literature [1, 24, 25]. For the first falling rate period, ANOVA revealed no statistical difference among the pretreatments. Although, during the second falling rate period, in which the moisture diffusion depends only on the material structure [28], there was an improvement of the water effective diffusivity. The same effect was observed in the air-drying of red bell pepper and was attributed to the changes in the structure and "sponge effect" caused by the US pretreatment [17]. Therefore, in this period, ANOVA revealed statistical difference ($p < 0.05$) between slices pretreated with the US and untreated slices. Whereas, no statistical difference was observed between hydrated or non-hydrated unripe banana slices. The increase in the value of water effective diffusivity found for non-hydrated slices was around 50 % in comparison with the value obtained from slices dried without pretreatment. As can be observed in Figure 4, pretreated slices resulted in higher rates of water removal, more visible at the final stages of the air-drying process. Thus, higher values of water effective diffusivity were observed during this period (Table 1). Besides, as shown in Figure 3, it can be seen that immersed and vacuum packaged pretreated unripe banana slices presented greater values of drying rates, in comparison with untreated banana slices. These two approaches were performed to distinguish the microstructural changes attributed to the US from the water intake resulted from immersing the unripe banana slices in water. Although the difference in water intake between the unripe banana slices pretreatments, in both cases, the indirect effect of the US related to the formation of micro-channels, was evident, resulting in higher drying rates (Figures 3 and 4) and higher values of water effective diffusivity (Table 1).

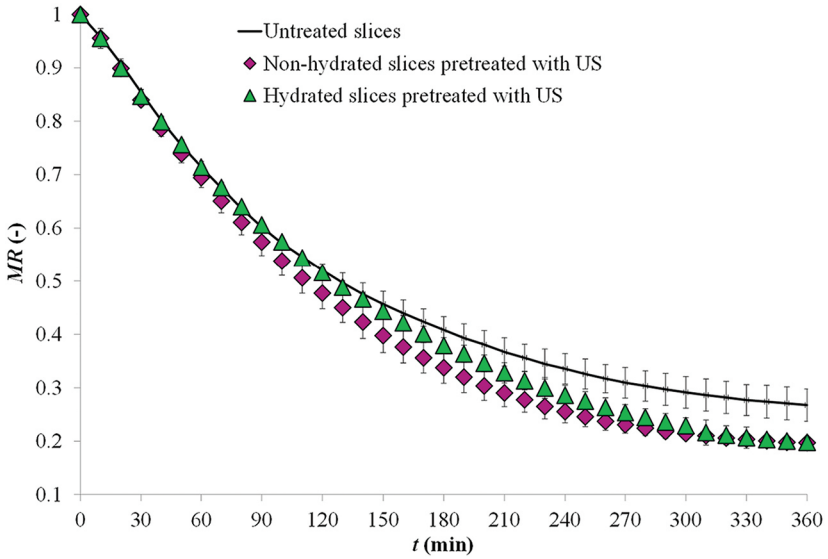

Figure 3: Drying curves of vacuum packaged (non-hydrated) and immersed (hydrated) unripe banana slices pretreated with US and submitted to air-drying at 50 °C, 10 % of *RH* and 4 m/s, in comparison with untreated slices.

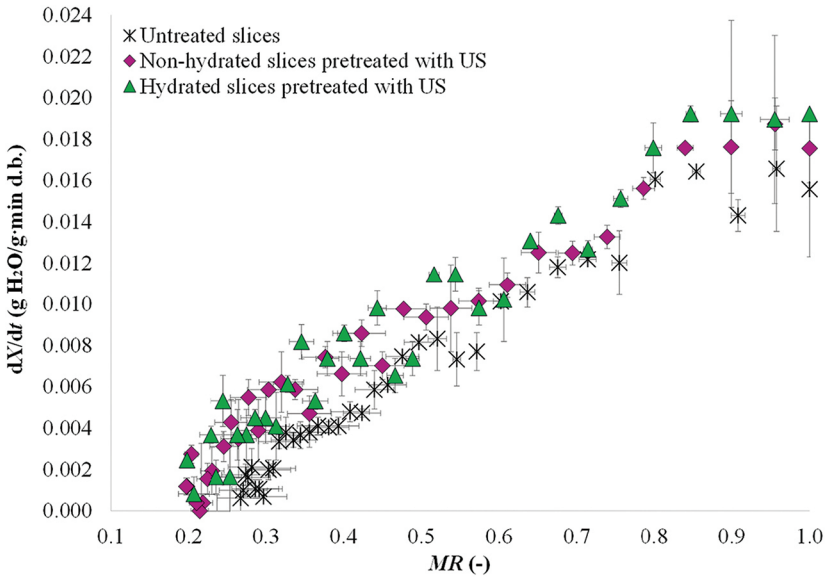

Figure 4: Drying rate curves of vacuum packaged (non-hydrated) and immersed (hydrated) unripe banana slices pretreated with US and submitted to air-drying at 50 °C, 10 % of *RH* and 4 m/s, in comparison with untreated slices.

The effect of US on sorghum grains with higher water activity (0.985 ± 0.003) immersed in water and vacuum packaged was investigated [7]. Improvement in the hydration process was observed due to the US, in comparison with untreated samples. The authors conclude that enhancement of mass transfer by the US was due to the direct effects ("sponge effect") and the indirect effects (micro-channels formation), and these effects were observed independent of whether sorghum grains were vacuum packaged or immersed in water during the pretreatment with US [7]. Nonetheless, for carrots dried at 40 °C, it was observed that in vacuum packaged carrots pretreated with the US, the rate of water removal during air-drying was less effective, in comparison with, carrots untreated and pretreated with the US immersed in water [29]. Not only the micro-channels formation but also the water gain were the mechanisms that enhance the drying process of carrots. For unripe banana slices, it was observed that the increase of the drying rate was dependent on US direct and indirect effects and independent of the water intake during the pretreatment like occurred with the sorghum grains. This result was important because encourages the application of US pretreatment in vacuum packaged unripe banana slices, promoting not only the reduction of energy consumption related to US technology [5] but also the reduction in waste of water. Therefore, an innovative environmentally-friendly technology for UBF industrial production is presented.

It is possible to observe that, dried slices pretreated (Figure 5B and Figure 5C) resulted in a porous structure with a more free volume between cells, in comparison with, dried slices untreated (Figure 5A), which presented a microstructure with small cavities and high density. An increase in porosity increases the void spaces and decreases resistance for diffusion, directly influencing the D_{eff} [1]. The cell walls act as a semi-permeable membrane inferring resistance for diffusion of water and solids [1]. Moreover, the application of US in a liquid-solid system can affect the solute transport, reducing the internal resistance to mass transfer. That influence comes from the "sponge effect" or the creation of micro-channels, which can make the movement of solutes inside the solid easier [30]. As illustrated in Figure 5B and Figure 5C, due to the porous microstructure observed in the dried slices pretreated, higher values of water effective diffusivity were obtained (Table 1). However, it was not possible to see structural differences between immersed (hydrated) and vacuum packaged (non-hydrated) unripe banana slices.

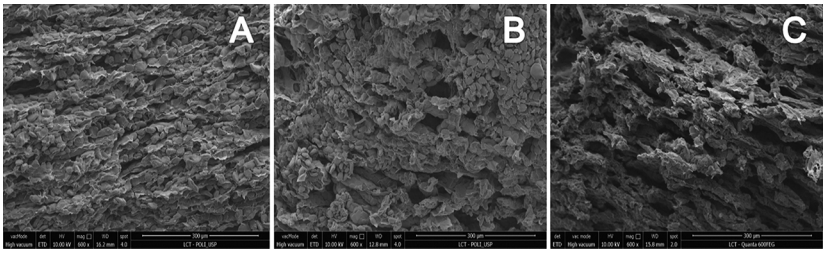

Figure 5: SEM micrographs of dried unripe banana slices pretreated with US: untreated (A); vacuum packaged (non-hydrated) unripe banana slices (B); immersed (hydrated) unripe banana slices (C).

The parameters for the mathematical modeling are shown in Table 2. As can be seen the three-term logarithmic model resulted in a good fit with r^2 value > 0.9989, RMSE < 0.0080 and χ^2 < 0.00007. Also, Midilli's model with four terms resulted in a good fit with r^2 value > 0.9996, RMSE < 0.0094 and χ^2 < 0.00010. Good fit applying Midilli's model was already reported for foodstuffs pretreated with US, such as apple and red bell pepper [17, 31]. According to the results, a three-term model could satisfactorily describe the air-drying of unripe banana slices pretreated with US.

Table 2: Constants and statistical parameters for the mathematical fit according to logarithmic and Midilli's model.

Condition	Model	*a* (-)	*b* (1/min)	*k* (1/min)	*c* (-)	*n* (-)	r^2	RMSE	$\chi^2 \times 10^{-5}$
Untreated	Logarithmic	0.7955		0.0081	0.2214		0.9996	0.0040	1.7695
	Midilli	1.0116	0.0005	0.0067		0.9896	0.9996	0.0094	9.8765
Non-hydrated	Logarithmic	0.8939		0.0080	0.1306		0.9989	0.0080	6.8833
	Midilli	1.0028	0.0004	0.0047		1.0827	0.9999	0.0085	8.0636
Hydrated	Logarithmic	0.9067		0.0065	0.1017		0.9998	0.0038	1.6070
	Midilli	1.0030	0.0002	0.0056		1.0160	0.9999	0.0077	6.6804

3.3 UBF characteristics

In this study, unripe banana slices were dried until reaching what is considered as a microbial stable condition, water activity < 0.6 and moisture content close to 0.15 (g H_2O/g d.b.), to avoid unnecessary power consumption [14]. As it can be seen in Table 3, UBF obtained from different conditions met these requirements. ANOVA revealed no statistical differences in water activity and moisture content of UBF produced from different pretreatments ($p > 0.05$).

Table 3: Moisture content (X_f), water activity (a_w), peak temperature (T_p), enthalpy (ΔH) of gelatinization and resistant starch content (*RS*) of unripe banana flour produced at different conditions.

Condition	X_f (g H_2O/g d.b.)	a_w (-)	T_p (°C)	ΔH (J/g)	*RS* (g/100g d.b.)
Untreated	0.08 ± 0.01[a]	0.48 ± 0.09[a]	75.39 ± 0.81[a]	2.75 ± 0.37[a]	52.73 ± 0.31[a]
Non-hydrated	0.10 ± 0.01[a]	0.54 ± 0.05[a]	74.45 ± 0. 56[a]	1.83 ± 0.22[ab]	49.61 ± 1.22[a]
Hydrated	0.08 ± 0.01[a]	0.46 ± 0.05[a]	72.48 ± 0.29[b]	1.59 ± 0.31[b]	50.09 ± 0.23[a]
HSD	0.06	0.17	1.83	1.14	4.37

Mean value and standard deviation (SD) respectively.
Mean with same letters in the same column are not significantly different ($p > 0.05$).
HSD, honestly significant difference.

Resistant starch (*RS*) has attracted interest because of its positive effect on human health and banana when unripe have high *RS* content. Nowadays, a lot of effort is being done in order to increase this product as a potential functional ingredient in foodstuffs [32]. Bananas, when unripe have high *RS* content (47–57) g/100 g in dry basis (d.b.) [33]. In this study, the resistant starch content for raw material reached a value of 59.55 g/100 g d.b. Moreover, its flour may present (40–59) g/100 g d.b. [10, 34]. The resistant starch content of UBF obtained in this study was similar to those reported in the literature [10, 34]. Partial disorganization of the crystalline granule structure of corn starch due to the application of the US pretreatment was already reported in the literature [35]. The crystalline region of starch distorts during the US, prior to reversible hydration of the amorphous phase, which results in the destruction of granular structure [35]. Moreover, cavitation disrupts starch granules, and the diffusion of water leads to breaking the crystal structure [35]. However, as shown in Table 3, for UBF produced from slices untreated and pretreated with US at different conditions ANOVA revealed no statistical difference ($p > 0.05$). This achievement is important, because as mentioned previously, an increase in water effective diffusivity was reached, without significant reduction in resistant starch content.

The DSC curves for UBF produced with unripe banana slices untreated and pretreated with the US are presented in Figure 6. The curves revealed that UBF showed a single endothermic transition. The gelatinization temperature was defined as the peak temperature (T_p), and the energy required for the transition was con-

sidered the gelatinization enthalpy (ΔH). As shown in Table 3, gelatinization temperatures for UBF appeared between 72.48 and 75.39°C, values similar those reported in other studies for unripe banana [20, 22, 23]. Reduction of T_p and ΔH due to the application of US was already reported in the literature for corn starch [35] and unripe banana [22]. The reduction is a consequence of the differences between the bonding forces of the double helix forming the amylopectin structure, which results in different alignments of the hydrogen bonds within the starch molecules, resulting in lower values of T_p and ΔH [35]. As shown in Table 3, ANOVA revealed that T_p and ΔH of UBF produced from slices pretreated with US immersed in water decreased significantly ($p < 0.05$) as described in the literature. Thus, less energy is required for gelatinization. Even though, as pointed out before, reduction of the resistant starch content, which is the principal characteristic to preserved, was no statistically significant ($p > 0.05$) for UBF produced from slices untreated and pretreated with US at different conditions.

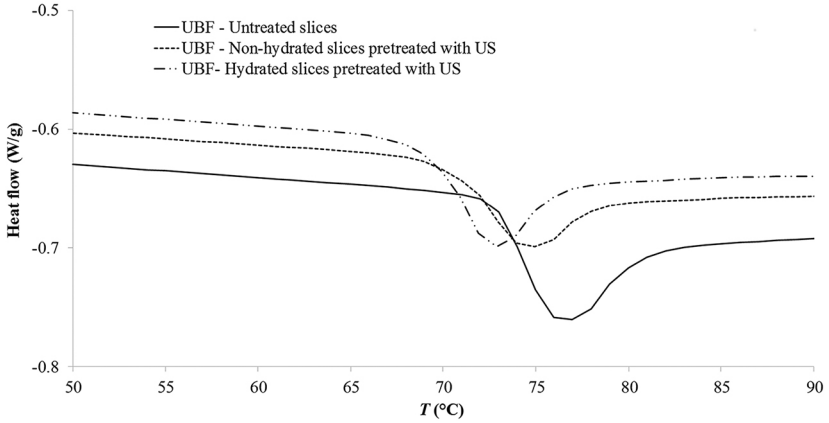

Figure 6: Gelatinization parameters for UBF produced from vacuum packaged (non-hydrated) and immersed (hydrated) unripe banana slices pretreated with US, in comparison with UBF produced from untreated slices obtained by differential scanning calorimetry.

Furthermore, the solubility is another good parameter to evaluate the integrity of the starch granule. It is related to the amount of soluble solids in the dry sample enabling the application of treatments, which depend on gelatinization, dextrinization and the following solubilization of starch [36]. In general, UBF present a low dispersability and solubility [10, 20]. In fact, agglomeration process to increase the dispersability and wettability was studied [20]. Moreover, the dispersion at higher temperatures should be avoided due to the thermosensibility of *RS* at temperatures above its gelatinization temperature (>68 °C) [10, 20]. Therefore, as expected, at the range of temperatures studied in this work, UBF showed low solubility, even though the increase of this parameter was directly related to temperature (Figure 7). Increase in this parameter due to higher temperatures occurs since hydrogen bonds are broken, the water molecules bound to hydroxyl group release and the granule expands, and amylose is exuded [36]. The molecular arrangement, which depends on the amount of amylose and amylopectin, allows an estimation of the kind of organization occurring in the interior of the granule. Increase of solubility in UBF due to higher temperatures was already observed [36]. Moreover, the higher facility for water entrance in a corn starch granule due to US disruption was reported [35]. The cavitation forces cause the major impact on starch granule disintegration. Then, the sudden collapse of cavitation bubbles induces high-pressure gradients and high local velocities of liquid layers in their vicinity breaking the chains of polymers. Thus, the crystalline molecular structure is broken, which could cause an increase in solubility [35]. As shown in Figure 7, ANOVA revealed no statistical differences among UBF at (25 and 40) °C ($p > 0.05$). However, at 50 and 60°C UBF produced from slices pretreated with US non-hydrated resulted in higher solubility as described in the literature [35].

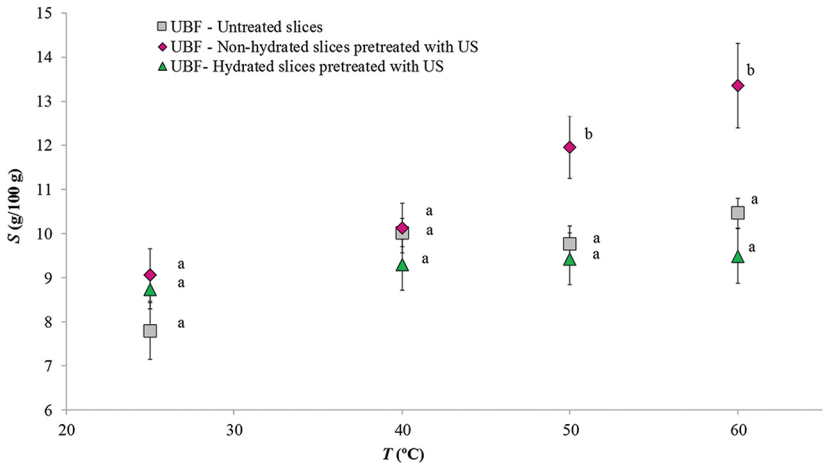

Figure 7: Solubility at (25, 40, 50 and 60) °C for UBF produced from vacuum packaged (non-hydrated) and immersed (hydrated) unripe banana slices pretreated with US, in comparison with UBF produced from untreated slices. Same letters, at the same temperature, are not significantly different ($p > 0.05$).

As shown in Figure 8 US did not affect the size of starch granules, ranging between 37.88 and 52.81 µm, as related in the literature [37]. However, UBF produced from untreated slices resulted in starch granules with less damages (Figure 8**A** and Figure 8**B**). The collapse of cavitation bubbles during the US induces high-pressure gradients and high local velocities of liquid layers, which causes shear forces that are capable of breaking the chains of polymers and damaging granules [35], as shown in Figure 8**C** to **8F**. No difference was observed between the starch granules of UBF from hydrated and non-hydrated unripe banana slices pretreated with the US.

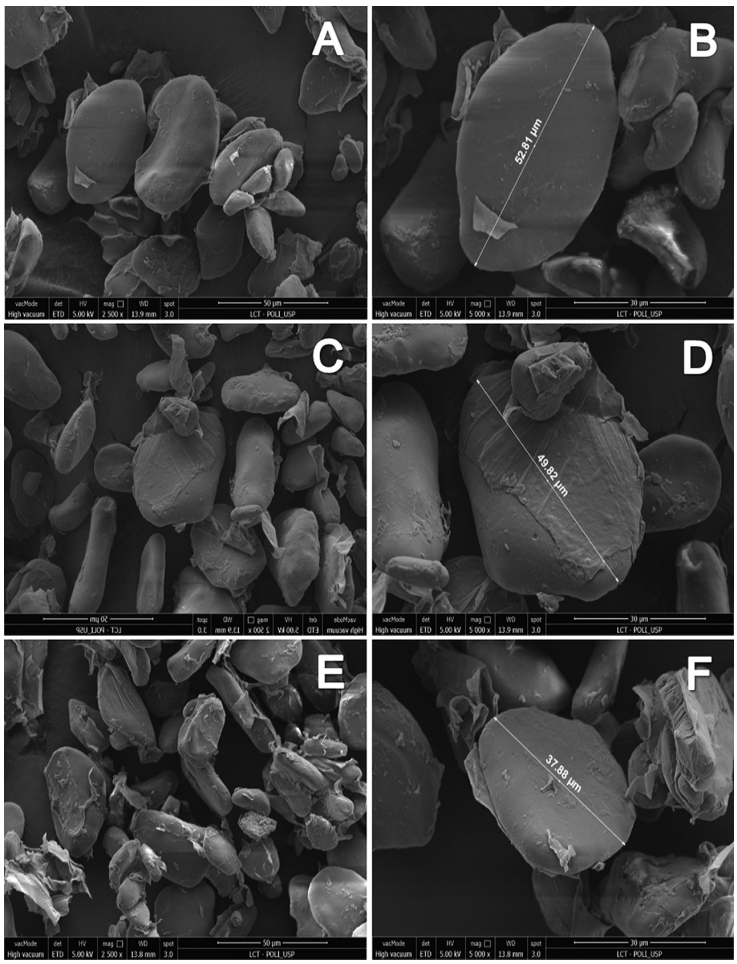

Figure 8: SEM micrographs of UBF produced from untreated unripe banana slices (**A** and **B**); vacuum packaged (non-hydrated) unripe banana slices pretreated with US (**C** and **D**); and immersed (hydrated) unripe banana slices pretreated with US (**E** and **F**).

4 Conclusions

The application of US enhanced the water effective diffusivity in the air-drying process of unripe banana slices. The formation of micro-channels was observed, and pretreated dried slices resulted in being more porous with more free volume than the untreated unripe banana. Moreover, US produced a partial disorder of the crystalline structure within the granules, reducing the amount of energy required for gelatinization and higher solubility was observed. Nevertheless, reduction in resistant starch content was not significant for all the UBF produced. The microstructural changes attributed to US were evident independent of whether the unripe banana slices were immersed in water (hydrated) or vacuum packaged (non-hydrated). Thus, an innovative technology for UBF production could be applied in order to promote energy consumption and reduction in waste of water.

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Nomenclature

a constant of Logarithmic and Midilli's models (-)

a_w water activity (-)

b constant of Midilli's model (1/min)

c constant of Logarithmic model (-)

C_p specific heat (J/g K)

D_{eff} water effective diffusivity (m^2/s)

k drying kinetic parameter of Logarithmic and Midilli's models (1/min)

L sample half-thickness (m)

m mass (g)

MR moisture ratio (-)

n constant of Midilli's model (-)

P_{US} ultrasonic volumetric power (W/L)

RH relative humidity (%)

RS resistant starch content (g /100 g d.b.)

S solubility (g/100 g)

t time (min)

T temperature (°C)

V volume (L)

x moisture content on wet basis (g H_2O/g)

X moisture content on dry basis (g H_2O/g)

WG water gain (g/100 g)

Subscripts

0 Initial
e Equilibrium
f Flour
p Peak
US ultrasound

Greek letter

ΔH gelatinization enthalpy (J/g)

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