EFFECT OF POWER ULTRASOUND APPLICATION ON THE DRYING KINETICS AND THE ORGANIC ACIDS CONTENT OF PINEAPPLE

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The effect of the power ultrasound (US) application (23.2 W/L) previous to drying on the drying kinetics and the organic acid contents (citric and malic) of pineapple (*A. cosmosus v. Perola*) has been studied. US application was carried out at 30 °C during 10-30 min using distilled water (DW) and pineapple juice (PJ). Drying was carried out at 60 °C and 0.5 m/s. The effective diffusion coefficient during drying was higher when US was applied and DW was used as soaking media. Citric and malic acid contents were measured in untreated and treated samples (with and without US application) before and after drying. The US application promoted an average reduction of the citric acid content of 9.2±0.7% (DW) and 28.4±0.8% (PJ); however; an average increment of malic acid of 8.5±3.7% (DW) and 8.0±2.4% (PJ) was observed. In general, when US was applied, treated-dried samples exhibited higher contents of citric and malic acid than the untreated-dried sample.

Keywords: **Ultrasound, Drying, Citric acid, Malic acid, Pineapple**

1. Introduction

Fruits are an important part of the human diet. They are a major source of vitamins, minerals and health promoting antioxidants (Paz et al., 2014). Over the past few years, food technologists have focused their interest on the development of new processing methods which preserve not only the nutritional and sensorial characteristics of the fruits but also the bioactivity and availability of certain constituents (Soria & Villamiel, 2010). A commonly used preservation method is convective drying, because it removes water from the food and reduces water activity that prevents the growth of spoilage microorganisms and slows down enzymatic reactions during storage (Silva, Garcia, Amado, & Mauro, 2015). Despite of multiple benefits of this method, during drying, mass and heat transfer takes place and the phase transition occurs. It results in high-energy consumption and hence, the high costs of operation (Fijalkowska, Nowacka, Wiktor, Sledz, & Witrowa-Rajchert, 2015). Besides, drying can promote vitamin degradation, antioxidant activity reduction, and undesirable changes of color, texture and flavor of the fresh product (Mandala, Anagnostaras, & Oikonomou, 2005).

Taking into account the increasing demand of food with a high nutritional quality, food technologists have directed their research on the application of new methods to intensify the drying process in terms of kinetics and quality of the final product (Chemat, Zill, & Khan, 2011). Acoustic assistance has been widely used as a technology able to promote an intensification of the water removal process, either when ultrasound have been applied previously (as a treatment) or during the drying process (Cárcel, García-Pérez, Benedito, & Mulet, 2012).

Power ultrasound has been considered as a technology to accelerate the removal of water during the drying process when it is applied pre-treatment (Rodríguez, Llabrés, Simal, Femenia, & Rosselló, 2015). Ultrasonic baths have been widely used to carry out the intensification of the drying process in different fruits like melon (Fernandes, Gallão, & Rodrigues, 2008); pineapple (Fernandes, Linhares Jr, & Rodrigues, 2008); strawberry (Garcia-Noguera et al., 2010); guava (Kek, Chin, & Yusof, 2013), apple (Nowacka, Wiktor, Śledź, Jurek, & Witrowa-Rajchert, 2012). Usually, the acoustic assistance has been performed by using distilled water, sucrose solutions, acidified solutions, and the juice of the own fruit as immersion liquids at temperatures ranging from 25 to 30 °C during 10 to 60 min. The ultrasonic frequency used varied from 25 to 40 kHz, being the ultrasonic nominal power in some cases of 4870 W/m^2.

Pineapple (*A. cosmosus*) is a tropical fruit with attractive sensorial properties and nutritional characteristics (Ramallo & Mascheroni, 2012). It has been considered as a rich source of vitamins A, B and C, besides several minerals such as calcium, phosphorus and iron (Mhatre, Tilak-Jain, De, & Devasagayam, 2009). Two organic acids, citric and malic, are dominant in pineapple, and understanding the elaboration of acidity requires studying the mechanisms involved in the change of both as a consequence of processing (Lobit, Genard, Soing, & Habib, 2006). Therefore, the aim of this study is to analyze the effect of the ultrasound application (exposition time and soaking medium) on citric and malic acid contents of pineapples before and after a convective drying process.

2. Materials and Methods

2.1. Sample preparation

Pineapples (*A.cosmosus var. pérola*) were purchased in a local market in Fortaleza, Brazil. Fruits were washed and peeled. Coreless fruits were shaped into cubes (0.01 m edge). After cutting, samples were immediately processed. The initial average moisture content (W_0) of untreated samples obtained by using the AOAC method Nº. 934.06 (AOAC, 2006) was 4.97±0.06 g water/g dm. The total soluble solids content of pineapples, measured as °Brix using a HI 96801 refractometer (Hanna, Romania) was of 12.15±0.25% and the pH figure measured using a PHS 25 CW pH/Vm meter (Lida, China) was of 3.44±0.11.

2.2. Power ultrasound application

Treatments were carried out without (NUS) and with acoustic assistance (US). Acoustic assistance was carried out in an ultrasonic bath USC-2850A (Unique, Brazil) with a frequency of 25 kHz and an acoustic density of 23.2 W/L. Experiments were carried out at a temperature of 30 C, during 10, 20 and 30 min, by the immersion of ca. 30 g of pineapple cubic samples on 200 mL of distilled water (DW) or pineapple juice (PJ) prepared at the laboratory by squeezing chopped pineapples and using a juice maker Master Suco (Fun Kitchen, Brazil).

2.3. Drying experiments

After the application of power ultrasound, treated samples were kept during 24 h at 4 °C to ensure a homogenous water distribution within the sample. Drying experiments were carried out in a forced circulating air-drying oven TE-394/I (Tecnal, Brazil) previously described by Fernandes et al. (2008). The experiments were carried out at a constant air temperature of 60 °C (relative humidity of ca. 18 %) and air velocity of 0.5 m/s. The moisture content of the sample during the air-drying period was measured by weighting the sample every 15 min for the first 2h of drying and then every 30 min until a constant weight was reached (8 h).

2.4. Organic acids determination

The HPLC determination of the organic acids was carried out following the method previously reported by Chinnici et al. (2005). Samples before injection (methanolic extracts) were filtered through a C18 cartridge and a 0.45 uM HA membrane cellulose ester (13 mm in diameter, white, smoth). The injection volume was of 20 µL. A 1260 Infinity Quaternary LC System (Agilet technologies, USA) was used. Organic acids were analyzed onto an Aminex HPX-87H column (300 × 7.8 mm) (Bio-Rad, USA) and kept at 50 °C. The isocratic elution was performed with 0.01M sulfuric acid in deionized water as mobile phase for 30 min (flow rate 0.6 mL/min). In order to quantify the citric acid (retention time: 8.0 min) and malic acid (retention time: 9.6 min), calibration curves were obtained by mixing these acids at different concentrations: 0.1 - 1.0 g/L and 0.2-2.0 g/L, respectively.

2.5. Statistical analysis

The data used were the average of three replicates and were reported as mean ± standard deviations. An analysis of variance was applied to analyze the attained results in order to determine whether the effect of both, the duration of the acoustic treatment and the soaking medium used were significant. Means were compared by Tukey's test at $p<0.05$ using Matlab 2012a® (The Mathworks, Inc., USA).

3. Results and discussion

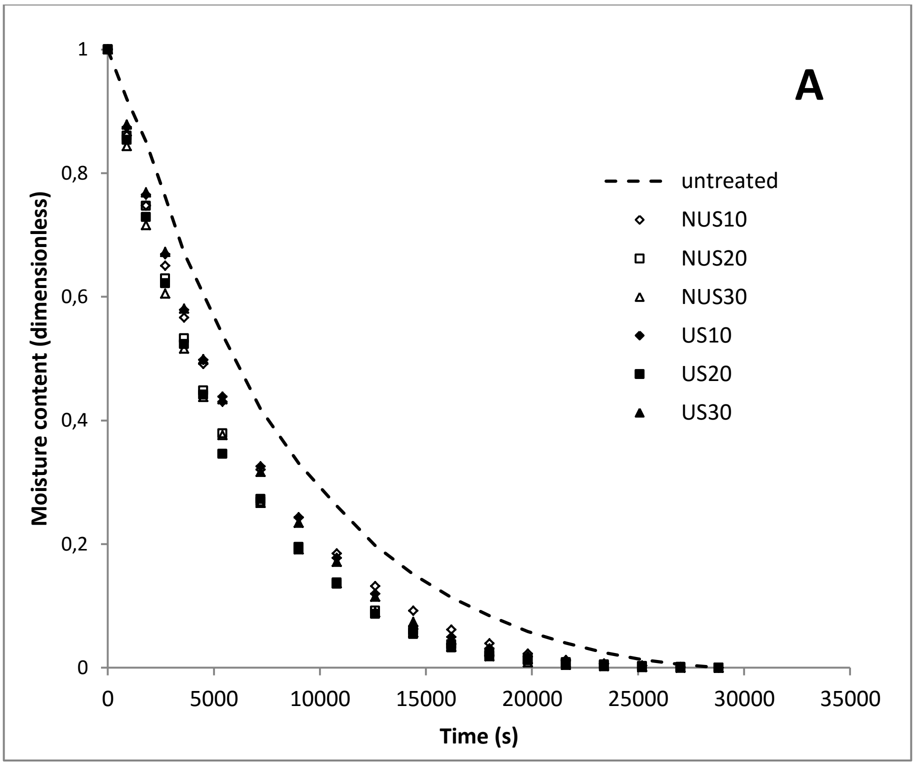
All analyses determinations were carried out in triplicate, and results were expressed as gain/loss of quality attribute using the untreated sample as reference (d.m), as presented in Eq. 1.

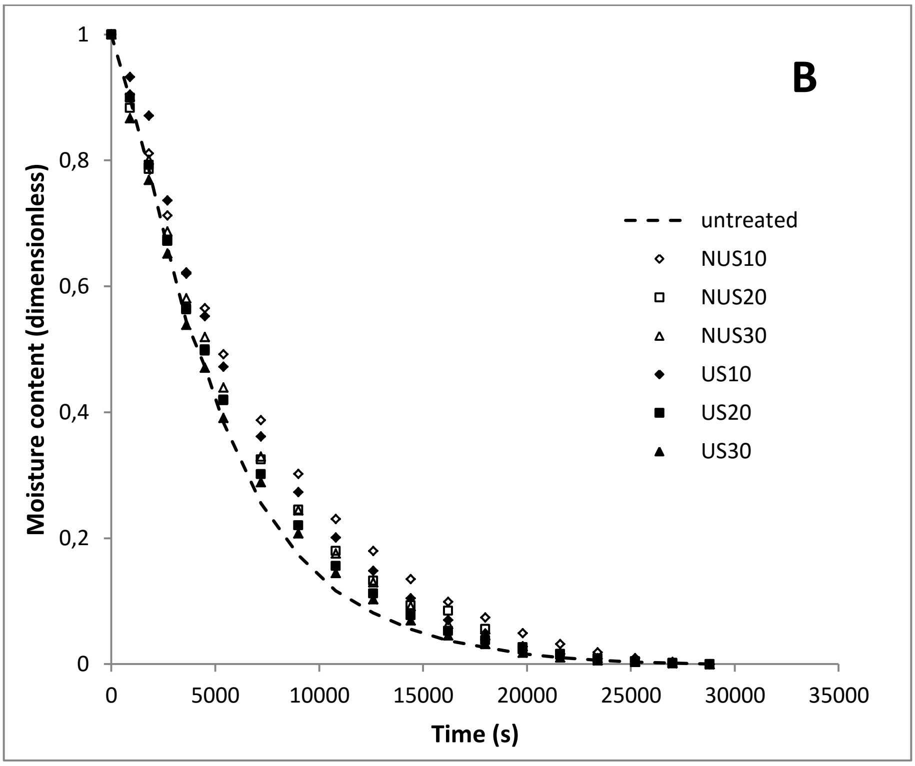
$$Relative\ amount\ (\%) = \left(\frac{ABS_{sample}}{ABS_{untreated}}\right) \times 100 \qquad \text{Eq.1}$$

3.1. Drying kinetics

To compare the drying kinetics, the dimensionless moisture content (MR) was calculated. Figure 1 shows the experimental drying curves (MR vs. time) of treated pineapples without (NUS) and with (US) power ultrasound using DW (1A) and PJ (1B) as soaking medium, together with the untreated sample. The acoustic assistance promoted a faster water removal when DW was used as soaking media. As an example, the drying time needed to reach a moisture content of 1.0 g water/g d.m was of 3.43 h for the untreated sample, and 3.12 h, 3.04 h, and 3.00 for US10, US20, US30 samples. The reduction of the drying time could be related to the alternative compressions and expansions of the sample provoked by the acoustic waves in a liquid medium (sponge effect) (Cárcel, Benedito, Rosselló, & Mulet, 2007). Similar results were observed by Rodríguez et al. (2015) reported that the acoustic assistance (12.9 W/cm^2) applied to apples cubes soaked in DW during 5 min allowed a reduction of the drying time (50 °C) of 46.4% compared with the untreated sample. Kek et al (2013) observed that the acoustic assistance (1.75 kW, 60 min) using DW as soaking medium promoted a reduction of the drying time (70 °C) of guava slices of 11.1%. When treatment was carried out using PJ as soaking medium, the improvement in the drying kinetics was less notorious; being the drying time need to reach a moisture content of 1.0 g water/g d.m was of 3.97 h, 3.27 h and 3.12 h for US10, US20, and US30 samples, respectively.

Figure 1. Experimental drying curves of treated pineapples with (US) and without (NUS) acoustic assistance using DW (6A) and PJ (6B) as soaking medium, together with the untreated sample.





With the aim of obtaining a mathematical model representative of the moisture transport during the drying process, Fick's second law was combined with the microscopic mass transfer balance, and the process was considered to be isothermal. The governing equation for a differential element of cubic shape was formulated (Eq. 2) liquid diffusion being considered the main transport mechanism.

$$D_e\left(\frac{\partial^2 W}{\partial_x{}^2}+\frac{\partial^2 W}{\partial_y{}^2}+\frac{\partial^2 W}{\partial_z{}^2}\right)=\frac{\partial W}{\partial_t} \qquad \text{Eq.2}$$

The governing equation (Eq. 2) can be solved by considering that the moisture distribution inside the solid was uniform at the beginning of the process. The boundary conditions considered were those related to the moisture distribution symmetry, and the external resistance to the mass transfer (Ó Rodríguez et al., 2014). The effect of solid shrinkage on the transfer process was taken into account according to the equation proposed by Yan et al. (2008). In addition, the sorption isotherms reported by Simal et al. (2007) and the psychometric data were considered to complete the model. The identified D_e for the untreated pineapple was of 3.07 x 10^{-10} m^2/s. This figure is the range of the one reported by Fernandes et al. (2008) (8.41 x 10^{-9} m^2/s), and by Ramallo & Mascheroni (2013) (3.18 x 10^{-10} m^2/s), both for pineapple dried at 60 °C. The identified D_e figures for treated pineapples without (NUS) and with (US) acoustic assistance, using DW and PJ as soaking medium are shown in table 1. As it can be seen, the effect of the acoustic assistance is more evident samples were soaked in DW than in PJ. The highest increments of the D_e were of 286.3% and 187.9% were observed in US30 samples soaked in DW and PJ, respectively. In addition, the longer the treatment the higher D_e figure identified for both soaked medium.

Table 1. Initial moisture content W_0 and the effective water diffusion coefficient D_e during convective drying (60 °C, 0.5 m/s) of untreated and treated pineapples without (NUS) and with (US) acoustic assistance using distilled water and pineapple juice as soaking medium.

Soaking medium	Sample	W_0 (g water/g d.m)	D_e x 10^{10} (m^2/s)
Distilled water (DW)	NUS10	5.67±0.28	5.80±0.61
	NUS20	6.07±0.36	6.61±0.54
	NUS30	6.22±0.25	7.75±0.66
	US10	6.36±0.38	6,26±0.61
	US20	7.09±0.49	8,28±0.91
	US30	7.55±0.52	8,79±0.91
Pineapple juice (PJ)	NUS10	5.01±0.51	3,82±0.33
	NUS20	5.27±0.41	5,10±0.51
	NUS30	5.31±0.52	5,49±0.48
	US10	5.17±0.51	3,89±0.41
	US20	5.37±0.62	5,63±0.40
	US30	5.47±0.60	5,77±039

3.2. Organic acids

The citric and malic acid contents of untreated pineapple (var. Perola) were of 4.32±0.27 g/100 g d.m and 1.92±0.16 g/100 g d.m, respectively. Drying promoted a reduction of the organic acid contents of the untreated sample, being the relative amount of citric and malic acids of 58.4±3.1% and 66.6±4.5%, respectively. Da Silva et al.(2013) found a reduction of the citric acid content in pineapple pulp during a drying process from 6.72 g/100 g d.m to 0.39 g/100 g (46 °C, 1.0 m/s) and to 0.67 g/100 g (60 °C, 1.5 m/s).

Table 2 and 3 shows the relative amount of citric and malic acids of treated pineapples respectively, without (NUS) and with ultrasound (US) using distilled water (DW) and pineapple juice (PJ) as soaking medium, before (BD) and after drying (AD). Regarding the citric acid content, all treated samples exhibited a reduction of this parameter, but higher figures were obtained in NUS samples soaked in DW (90.8±2.8%), and lower ones in US samples soaked in

PJ (58.3±7.5%). Drying promoted a major reduction of the citric acid content of treated samples; however, higher figures were obtained US samples, being the average relative amount of 73.2±2.4% and 58.9±8.4% when DW and PJ were used, respectively. A different trend was observed regarding the malic acid content. All treated samples exhibited slightly higher figures of this parameter (109.6±7.1%), however no significant differences ($p < 0.05$) were observed among samples soaked in DW or PJ. Drying promoted a reduction of the malic acid content. A minor reduction was observed in samples soaked in DW (98.6±5.9%); while this effect was more notorious in samples soaked in PJ, the lowest figures were obtained in NUS samples (62.9±7.0).

Table 2. Relative amount of citric acid (%) of treated pineapples without (NUS) and with (US) acoustic assistance using distilled water (A) and pineapple juice (B) as soaking media, before (BD) and after drying (AD). Means for treatments with different letters show significant differences according to Tukey's test with $p<0.05$. Uppercase for BD samples, lowercase for AD samples.

Soaking medium	Sample	Before drying (BD)	After Drying (AD)
Distilled water (DW)	NUS10	91,68	61,19
	NUS20	90,37	63,36
	NUS30	90,41	65,09
	US10	79,04	72,60
	US20	81,97	74,14
	US30	85,20	72,77
Pineapple juice (PJ)	NUS10	72,26	66,63
	NUS20	70,74	54,15
	NUS30	71,75	43,44
	US10	67,85	68,60
	US20	54,91	58,78
	US30	52,15	49,46
Untreated		100	58.39

Table 3. Relative amount of malic acid (%) of treated pineapples without (NUS) and with (US) acoustic assistance using distilled water (A) and pineapple juice (B) as soaking media, before (BD) and after drying (AD). Means for treatments with different letters show significant differences according to Tukey's test with $p<0.05$. Uppercase for BD samples, lowercase for AD samples.

Soaking medium	Sample	Before drying (BD)	After Drying (AD)
Distilled water (DW)	NUS10	104,22	100,22
	NUS20	110,94	102,89
	NUS30	110,24	99,66
	US10	111,76	98,05
	US20	115,03	99,06
	US30	110,78	91,56
Pineapple juice (PJ)	NUS10	110,54	68,67
	NUS20	105,67	64,73
	NUS30	107,65	55,38
	US10	106,17	80,45
	US20	106,97	85,75
	US30	115,08	82,66
Untreated		100	84,31

Conclusions

The acoustic assistance applied during a treatment affected in different ways the compounds of pineapple samples. On one hand, it promoted and increment of the malic acid; on the other hand, the citric acid content was reduced by the acoustic assistance during the treatment. However, in general, after drying, acoustically treated samples exhibited higher figures of all these compounds in comparison to the untreated dried sample. In addition, water removal during the drying process accelerated by application of acoustic energy (higher effective diffusion coefficients were identified in treated samples). These facts enhance the use of acoustic energy before a drying process not only for energy saving purposes but also to improve the quality of the dried product.

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