Kinetics of flavour and aroma changes in thermally processed cupuaçu (*Theobroma grandiflorum*) pulp†

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Abstract: Changes in 'fresh' and 'cooked-notes' during thermal treatment of cupuaçu (*Theobroma grandiflorum*) pulp were evaluated and modelled. Isothermal experiments in the temperature range of 70–98 °C were carried out and a non-linear regression was performed to all data to estimate kinetic parameters. 'Fresh' and 'cooked-notes' change followed simple first-order ($Ea = 78–82\ kJ \cdot mol^{-1}$, $z = 30–31$ °C) and reversible first order ($Ea = 80–85\ kJ \cdot mol^{-1}$) kinetics, respectively. Although 'cooked-notes' were linearly correlated with 'fresh-notes' ($R^2 = 0.99$), the former was a better indicator for quality degradation. These results are useful to design pasteurisation processes while minimising sensory changes.

Keywords: flavour; aroma; cupuaçu; pasteurisation; kinetics

INTRODUCTION

Tropical/sub-tropical regions of the world are a rich source of highly aromatic fruits that are little known in the West.[1] These offer new possibilities for exotic new tastes.[2,3] Cupuaçu (*Theobroma grandiflorum*) is an Amazonian fruit very popular in Belém, Brazil, due to its unique flavour and aroma. It is added to dairy products, and used to make nectar, chocolate fillings and several desserts. Due to its low pH, approximately 3.4,[4] a pasteurisation process by hot filling was suggested by Silva and Silva[5] for preservation at ambient temperature. However, flavour and aroma are very sensitive to heat treatments. Several flavours and aromas unique to the fruit ('fresh-notes', FN) might be lost, and off-flavours ('cooked-notes', CN) might be formed during heat treatment. 'Fresh-notes' are associated to the original and natural organoleptic characteristics of the fruit.[6]

The determination of the kinetic parameters of flavour and aroma changes during thermal processing are needed to predict those changes,[7] and would therefore allow the optimisation of the operation conditions. To detect and quantify these organoleptic changes, the human nose is still more sensitive to certain odorous stimuli than the best instrumentation available at the present time, and has the advantage of being closer to those stimuli detected by the consumer.[8,9] Some authors have assumed first-order reaction and obtained z-values between 13 °C and 50 °C for flavour/odour attributes of several food products using sensory panels. The flavour of peas, corn and green beans had z values from 28 to 32 °C.[10] Ohlsson[11] determined z values in several food products: odour 13–29 °C, off-odour 18–22 °C, taste 17–34 °C and off-taste 18–29 °C. Finally, Argaiz and López-Malo[12] investigated the kinetics of change in flavour (z-value 16–19 °C) and cooked flavour development (z value 30–50 °C) using mango and papaya nectar and purees.

The main objective of this work was to determine the effects of thermal treatments on the changes of 'fresh' and 'cooked-notes' flavour and aroma of cupuaçu, and, to model and determine the kinetic parameters for destruction of 'fresh-notes' and formation of 'cooked-notes' using a sensory panel.

EXPERIMENTAL

Preparation and heat treatment of cupuaçu pulp

Cupuaçu fruit (cv Redondo) was purchased at a local

market in Belém, Brazil. The pulp was manually extracted, packed in plastic bags, frozen and stored at −20 °C. The frozen pulp was air-shipped in dry ice to Gainesville, Florida, and stored at −20 °C. Cupuaçu still in the plastic bag was thawed in tap water (≈25 °C) before thermal treatments.

Heavy duty freezer bags (brand Ziploc, 72 μm thick, 27 × 27.5 cm) were filled with 140 g of pulp for pasteurisation. The thickness of the bags containing the pulp was between 3 and 5 mm. Isothermal heating experiments were conducted at four different temperatures in a water bath (70, 80, 90 and 98 °C). The samples were removed from the bath at five different time intervals (between 2 and 120 minutes, Table 1), and cooled rapidly by immersion in ice slush. A total of 20 treatments × 2 replicates were evaluated by a sensory panel. All the sensory sessions were carried out during a period of 17 days and samples were stored frozen, and thawed on the day of sensory evaluation.

Sensory evaluation

The aroma 'fresh-notes' (FA), flavour 'fresh-notes' (FF), aroma 'cooked-notes' (CA), and flavour 'cooked-notes' (CF) attributes were rated on a 15-point scale, where the 1 corresponds to the low and 15 to the high FA, FF, CA and CF values of the scale. The evaluation was carried out by 15 trained panellists, consisting of graduate students and department staff, all with prior sensory experience. Three training sessions were conducted to familiarise the panellists with the flavour and aroma of cupuaçu, the scoring scales, and the scores for two reference samples to be used in all the sessions. Aroma and flavour were rated using pasteurised pulp and a sweetened nectar (25% pasteurised pulp, 15% sucrose and 60% water), respectively. The attributes agreed upon by panellists for the sensory evaluation were FA, CA, FF and CF. The reference C was a sample heated for 20 min at 98 °C and was agreed to be 4 for FA and FF, and 15 for CA and CF. The reference F was freshly thawed, non-heated pulp, and was decided to be 15 for FA and FF, and 1 for CA and CF. In the sensory sessions, five coded pulp samples, treated at the same temperature for different lengths of time, were presented to the panel together with the two references coded with the letters C and F. Panellists were asked to smell and rate them for FA and CA. Next, the same procedure was followed for the flavour, FF and CF, by tasting the nectar. Water and crackers were supplied to the panellists between samples and between aroma and flavour tests. All samples were coded using three digit random numbers, presented at room temperature in a random order and served in white cups on a white tray, in a sensory room with individual booths. Two replicate tests for each temperature treatment were made on different days. Each panellist evaluated a total of 80 samples (40 × 2), 10 by session, giving a total of eight sessions over a period of 17 days.

Table 1. Temperature-time combinations for the pasteurisation of cupuaçu pulp.

T(°C)	*Time (min)*				
70	7	15	30	60	120
80	5	11	22	45	90
90	3	6	12	25	50
98	2	4	6	10	15

Kinetics modelling and statistical analysis

The effect of panellist, time and temperature on the 'fresh-notes' and 'cooked-notes' attributes for flavour/aroma were analysed by MANOVA (multi-factor analysis of variance) using the Statistical Analysis System® [13] software. Significant differences among treatment means were determined using the least significance difference method. Outlying (most significantly different) panellists were removed and the data were re-analysed.

To model the thermal change kinetics of FA, FF, CA and CF, the treatment means of all the panellists and replicates were used. Goodness of fit criteria (residual plots, R^2) were used to decide which model best fitted each isothermal experiment data,[7] and then the temperature effect was included. The kinetic parameters were determined by a one-step non-linear regression[14,15,7] using Stata Version 3.0 [16] statistical software. This procedure narrowed the confidence intervals of the parameters estimated due to the increased degrees of freedom. Reference sample scores were also included in data modelling. The correlation of CF-FF and CA-FA was investigated using the treatment means.

RESULTS AND DISCUSSION

Effect of heating time and temperature

After an initial analysis of the data, three panellists (most significantly different) were removed, leaving 12 panellists for further analysis. A total of 12 panellists × 20 treatments × 2 replicates × 4 attributes (FA, CA, FF, CF) resulted in 1920 data points. With increasing temperature or time of pasteurisation, 'fresh-notes' (FN) decreased and 'cooked-notes' (CN) developed (Table 2). There was a better separation of FA-CA groups than those of FF-CF. This result was expected because in the flavour test a 1:4 (25% pulp) diluted nectar was evaluated. Heating time had a significant effect for each temperature and attribute. In general, panellists noticed greater differences in CN between samples than in FN, indicating that CN may have been a better indicator of thermal-induced quality degradation.

Regarding the temperature effect, only the samples processed during the same heating time could be compared. Once the heating times range was different for each temperature (Table 1), a rougher analysis had to be made. By comparing the means, this factor was found to have a significant effect on all attributes,

Table 2. Effects of heating time at different temperatures on fresh flavour (FF), cooked flavour (CF), fresh aroma (FA), and cooked aroma (CA)[1]

T (°C)	*Time (min)*	*FF*	*CF*	*FA*	*CA*
70	7	11.5a	4.8a	11.6a	4.3a
	15	11.8a	4.1a	12.1a	3.8a
	30	9.8b	6.8b	10.2b	6.0b
	60	9.9b	6.5b	8.8c	7.8c
	120	7.1c	9.8c	7.2d	10.2d
80	5	11.2a	5.2a	11.5a	4.4a
	11	10.3a	6.5a	10.8a	5.3a
	22	10.5a	6.0a	10.7a	5.3a
	45	7.8b	9.3b	7.0b	10.5b
	90	6.3c	10.8c	5.5c	12.5c
90	3	11.5a	4.9ab	12.2a	3.8a
	6	12.0a	4.0a	11.7a	4.5a
	12	9.8b	6.2b	9.2b	7.1b
	25	8.0c	8.4c	7.6c	9.5c
	50	5.6d	11.9d	4.4d	13.2d
98	2	10.8a	5.3a	12.3a	3.5a
	4	10.0ab	5.9a	11.6a	4.9a
	6	10.0ab	7.0ab	9.7b	6.9b
	10	8.8bc	8.5bc	9.4b	7.5b
	15	7.5c	10.0c	6.3c	11.4c

[1] Means within a temperature, and in a given column, followed by the same letter are not significantly different (LSD, $p = 0.05$).

especially for longer times. For short heating times, small differences were observed between temperatures. For example, at 5–7 min processing time only the temperature of 98 °C was significantly different from the others. After approximately 45–60 min, all the temperatures were significantly different from one another.

Finally, the 20 treatments were evaluated together to determine significant differences. The treatments of 90 °C-≤6 min, 70 °C-≤15 min, 80 °C-5 min and 98 °C-2 min had the lowest scores for CA-CF and the highest scores for FA-FF. Those treatments would likely give the highest sensory quality. The 80 °C-90 min and 90 °C-50 min were the heat treatments which gave the lowest sensory quality of cupuaçu and had the highest CA-CF and lowest FA-FF scores, as was expected.

Thermal kinetics modelling (FA, CA, FF, CF)

FN loss in aroma and flavour during heating followed a first-order kinetics:

$$\frac{FN}{FN_o} = e^{-kt} \tag{1}$$

where: FN_o-'fresh-notes' score of the non-heated sample, t - heating time (min), k - simple first-order rate constant (min^{-1}).

The kinetics of CN formation followed reversible first-order pattern, also called the fractional conversion model:[17]

$$\frac{CN - CN_f}{CN_o - CN_f} = e^{-kt} \tag{2}$$

where: CN_f-final equilibrium score for 'cooked-notes', CN_o– score of the non-heated sample.

The temperature dependence of k for both kinetic models was well described by the Arrhenius law:

$$k = k_{ref} e^{-[\frac{Ea}{R}(\frac{1}{T} - \frac{1}{T_{ref}})]} \tag{3}$$

where: k_{ref}-reaction rate at reference temperature (min^{-1}), T_{ref}-reference temperature (K), Ea-activation energy (J/mol), R - universal gas constant ($8.31434\,J \cdot mol^{-1} \cdot K^{-1}$).

The reaction kinetics obtained were expected since it is known that the decline of most food quality attributes follow zero or simple/reversible first-order kinetics during heating.[17] Table 3 shows the estimated values with the 95% confidence intervals for the parameters of the regression, and Fig 1 presents the predicted versus experimental scores obtained for FA, FF, CA and CF attributes. Good fits were obtained for all attributes (high R^2, small residuals range). Table 3 also shows the estimated z values and $D_{100\,°C}$ for FN using the thermal death time concept of Bigelow and Esty.[18] The same FN_o, R^2 and residuals ranges were obtained. The $D_{100\,°C}$ for FA (40.5 min) was slightly lower than for FF (45.4 min). This result was expected since the aroma is more sensitive to heating time than flavour. Fortunately, long times are needed to decrease the aroma/flavour properties by a factor of 10 because, overall, these D-values were high. The z-values of FA and FF were 31.3 °C ($Ea = 78.2\,kJ \cdot mol^{-1}$) and 29.8 °C ($Ea = 82.1\,kJ \cdot mol^{-1}$), respectively. Comparable results

Sensory attribute	*FA*	*FF*	*CA*	*CF*
Kinetics order	1		1 - reversible	
FN_o	13.7 ± 0.3	13.2 ± 0.4	–	–
CN_o	–	–	1.7 ± 0.4	2.3 ± 0.6
CN_f	–	–	15.3 ± 1.6	12.9 ± 1.6
$k_{100\,°C}$ (min^{-1})	0.055 ± 0.006	0.050 ± 0.007	0.090 ± 0.022	0.115 ± 0.042
$D_{100\,°C}$ (min)	40.5 ± 4.6	45.4 ± 6.8	–	–
Ea ($kJ \cdot mol^{-1}$)	78.24 ± 6.74	82.11 ± 9.29	79.67 ± 6.41	85.19 ± 10.75
z-value (°C)	31.3 ± 2.6	29.8 ± 3.3	–	–
R^2	0.99	0.99	0.98	0.97
Residuals range	−1.53 to +1.32	−1.65 to +1.81	−1.45 to +2.68	−1.77 to +3.56

Table 3. Estimated kinetic parameters with 95% confidence intervals for equations (1), (2) and (3), R^2 and residuals range.

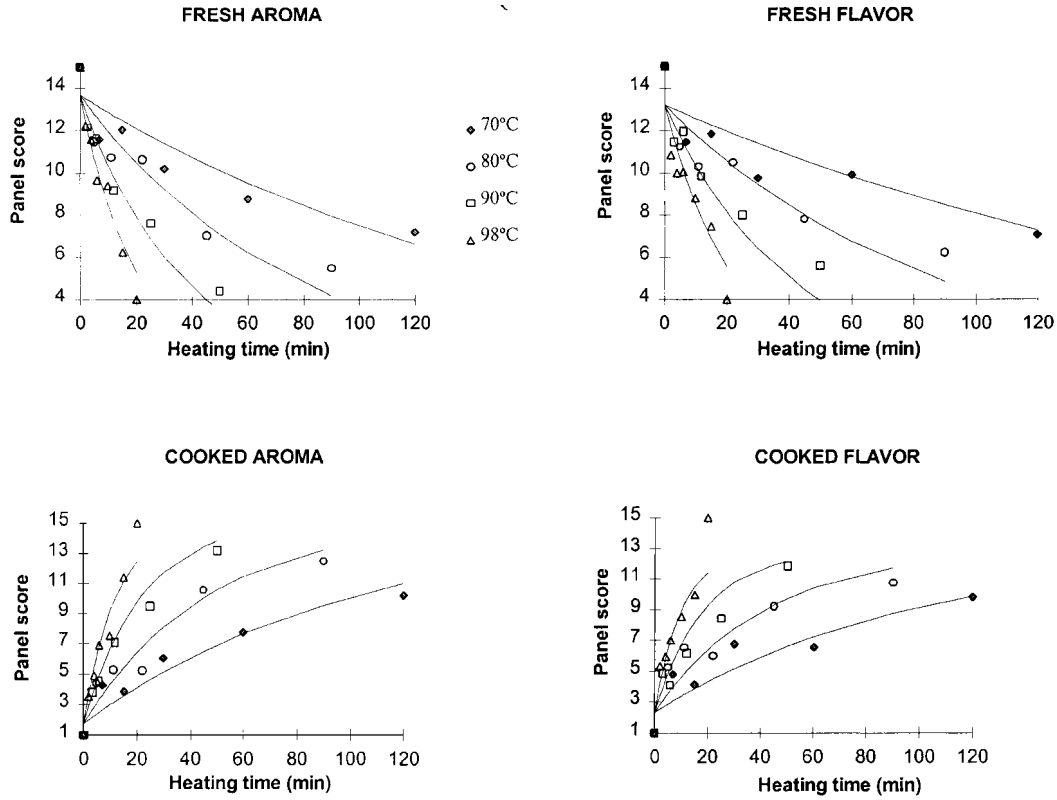

Figure 1. Effects of heating temperature and time on sensory panel scores for FA, FF, CA and CF: (◆○□△) experimental, (—) predicted.

were reported with the cooked flavour development in papaya puree with a $z = 29.5\,°C$,[12] the flavour of peas, corn and green beans with z-values ranging from 28.3 to 31.7 °C,[10] the odour of tomato sauce with a $z = 27\,°C$,[11] and colour, texture and flavour in several foods with Ea from 41.9 to 125.6 $kJ \cdot mol^{-1}$.[19]

'Cooked-notes' – 'fresh-notes' correlation

A linear regression was performed for CA-FA and CF-FF. The following equations were obtained:

$$CA = 18.9 - 1.23 \times FA \quad (4)$$

$$CF = 18.5 - 1.19 \times FF \quad (5)$$

An $R^2 = 0.99$ was obtained in both cases. This shows that the CN and FN were highly correlated and predictable for aroma and flavour within the rating scales, heating times and temperatures used. The residuals ranges were −0.71 to +1.23 for flavour, and −0.56 to 1.02 for aroma.

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