Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 106 (2008) 172–179
Food Chemistry
www.elsevier.com/locate/foodchem

Non-enzymatic browning in clarified cashew apple juice during thermal treatment: Kinetics and process control

Leandro F. Damasceno [a], Fabiano A.N. Fernandes [b,*], Margarida M.A. Magalhães [a], Edy S. Brito [c]

[a] Universidade Federal do Rio Grande do Norte, Departamento de Engenharia Química, Campus Universitario, Natal – RN, Brazil
[b] Universidade Federal do Ceara, Departamento de Engenharia Química, Campus do Pici, Bloco 709, 60455-760 Fortaleza – CE, Brazil
[c] Embrapa Agroindústria Tropical, R. Dra. Sara Mesquita, 2270, Pici, 60511-110 Fortaleza – CE, Brazil

Received 26 January 2007; received in revised form 27 March 2007; accepted 24 May 2007

Abstract

The effect of thermal treatment on clarified cashew apple juice was studied at temperatures from 88 to 121 °C. Changes in colour measured with colorimetric parameters (reflectance spectra, colour difference and CIELAB), and the variation in ascorbic acid, 5-hydroxymethylfurfural (5-HMF) and sugar content were used to evaluate non-enzymatic browning. Kinetic models were applied to the changes in reflectance spectra, ascorbic acid and 5-HMF. The effect of temperature on kinetic constants was described by an Arrhenius type equation. The sugar content remained constant during thermal treatment and did not affect non-enzymatic browning, which was mainly affected by degradation of ascorbic acid. The kinetic models were used to optimise and control the thermal treatment for clarified cashew apple juice.

Keywords: Cashew apple juice; Non-enzymatic browning; Thermal treatment; Optimization

1. Introduction

Food products from the cashew tree (*Anacardium occidentale* L.) can be divided into two groups, one from the cashew nut, the real fruit, and other from the fruit peduncle from which juice, candies and other products can be produced. Cashew apple juice has a pleasant flavour and is rich in vitamin C, but it has limited acceptance due to its astringency. Clarified cashew apple juice, however, has greater acceptance due to its low astringency.

Thermal treatments are used in the preservation of fruit derivatives and in their manufacturing process. The negative effects of thermal treatments include non-enzymatic browning, nutrient loss and formation of undesirable products such as 5-hydroxymethylfurfural (5-HMF). Browning due to thermal treatment is the result of several reactions known as the Maillard reactions, which include condensation between reducing sugars and amino-acids, caramellisation, ascorbic acid degradation and pigment destruction (Beveridge, Franz, & Harrison, 1986; Cornwell & Wrolstad, 1981). Non-enzymatic browning reactions mainly cause colour change, sugar and vitamin C loss and 5-HMF formation, affecting the quality of fruit juices (Ibarz, Pagán, & Garza, 1999).

To minimise the browning preserving quality of the juice, the reactions that cause non-enzymatic browning need to be studied and the main factor involved needs to be identified. For process design and process condition optimisation adequate kinetic models of the reactions are required.

The objective of this study was to discover the main reaction that causes non-enzymatic browning on clarified cashew apple juice, submitted to thermal treatment at high temperatures. Studies to obtain suitable kinetic models for

* Corresponding author. Tel.: +55 85 33669611; fax: +55 85 33669610.
E-mail addresses: fabiano@efftech.eng.br (F.A.N. Fernandes), edy@cnpat.embrapa.br (E.S. Brito).

0308-8146/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2007.05.063

Nomenclature

a^*	redness	k_{AA}	ascorbic acid degradation kinetic rate constant (min^{-1})
A_{420}	absorbance at 420 nm	k_{CA}	colour appearance kinetic rate constant (min^{-1})
A^0_{420}	initial absorbance at 420 nm (at $t = 0$)	k_{HMF}	5-HMF formation first order kinetic rate constant (first kinetic stage) (min^{-1})
AA	ascorbic acid concentration (mg/L)	$k_{HMF,2}$	5-HMF formation zero order kinetic rate constant (second kinetic stage) (min^{-1})
AA^0	initial ascorbic acid concentration (at $t = 0$) (mg/L)	k_{PD}	pigment destruction kinetic rate constant (min^{-1})
b^*	yellowness	R	concentration of reducing sugars (g/L)
C	process variable	R_0	initial concentration of reducing sugars (g/L)
C_0	initial value of the process variable	S	concentration of total sugars (g/L)
HMF	concentration of 5-HMF (mg/L)	S_0	initial concentration of total sugars (g/L)
HMF^0	initial concentration of 5-HMF (at $t = 0$) (mg/L)	t	time (min)
HMF^0_2	initial concentration of 5-HMF at the beginning of the second kinetic stage (mg/L)	t_{TR}	transition time between the first and second kinetic mechanisms of 5-HMF formation (min)
L^*	lightness	T	temperature (K)
k_0	process variable zero order kinetic rate constant	ΔE^*	colour difference
k_1	process variable first order kinetic rate constant		
k_{420}	absorbance kinetic rate constant (min^{-1})		

the reactions were carried out on different colorimetric parameters and on the evolution of sugar and ascorbic acid (vitamin C) contents, as well as, on 5-HMF formation. The kinetic models were used to optimise the thermal treatment of clarified cashew apple juice.

2. Materials and methods

2.1. Cashew apple juice

Cashew apples were collected at the Embrapa Experimental Station (Pacajus – CE, Brazil). The cashew apples were washed in running water and pressed, to obtain the juice in an expeller press (Incomap 300) operating at 300 psi (2068 kPa). Clarification of the cashew apple juice was carried out with the addition of 50 ml of food grade gelatin 10% solution per litre of cashew apple juice (Rebiere, São Paulo – Brazil) followed by filtration, where the juice was allowed to flow through the filter medium (felt) by gravity. After clarification the juice was bottled in 200 ml green PET bottles.

2.2. Thermal treatment

The thermal treatment was carried out on clarified cashew juice samples at four different temperatures 88, 100, 111 and 121 °C. The experiments at 88 and 100 °C were carried out in thermal water bath equipment (Fanem model 147) and the experiments at 111 and 121 °C were carried out in an autoclave (Quimis model Q-190-24). Every 30 min, for 5 h, a new bottle was opened and aliquots were extracted and immediately brought to room temperature in an ice-water bath. The opened bottle was discarded after taking the aliquots. Chemical and colorimetric determinations were performed for each aliquot. Experiments and analyses were carried out in triplicate.

2.3. Physical and chemical analyses

Glucose, fructose, sucrose and 5-HMF contents were determined by HPLC using a Varian ProStar. For sugar analysis, water was used as the mobile phase and a refractive index detector with a Varian Metacarb 87P (300 mm × 7.8 mm) column was used. The flow rate was set at 0.6 ml/min and the temperature at 60 °C. Calibration was carried out using standard solutions and five calibration points between 50 and 500 mg/l were used to obtain the calibration curve. For the analysis of 5-HMF content, a mixture of acetonitrile:water (20:80) was used as the mobile phase and a UV–VIS detector, fixed at 285 nm wavelength with a Varian Microsorb C-18 (250 mm × 4.6 mm) column, was used. The flow rate was set at 0.7 ml/min and the temperature at 30 °C. Calibration was carried out using standard solutions and five calibration points between 2.0 and 20.0 mg/l were used to obtain the calibration curve. The solvents used in the HPLC analysis were bought from Vetec (São Paulo, Brazil) and the standards were bought from Sigma–Aldrich.

Vitamin C was measured by the (2,6-dichloro-phenyl)-phenyl-indole method according to Strohecker and Henning (1967) using a Cary50conc UV–VIS spectrophotometer at 520 nm. The soluble solid content was determined with an Atago PR-101 refractometer.

2.4. Colorimetric parameters

Absorbance variation at 420 nm (A_{420}) was measured using a Cary50conc UV–VIS spectrophotometer. The

CIELAB parameters and colour difference ΔE^* in samples were determined by a Minolta CR300 photocolorimeter, measuring their reflectance spectra using a D_{65} light source, large viewing area and the observer at 10°. Colour difference was calculated from the a^* (redness), b^* (yellowness) and L^* (lightness) parameters using the Hunter–Scotfield equation

$$\Delta E^* = \left[(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2\right]^{0.5} \quad (1)$$

2.5. Mathematical modeling

Non-enzymatic browning reactions present an initial induction period that corresponds to the stage of coloured-compound formation. After this induction period, which can be fast, the colour of the product can increase linearly with time (zero order kinetics) or can increase exponentially with time (first order kinetics) (Garza, Ibarz, Pagán, & Giner, 1999; Labuza, 1972; Toribio & Lozano, 1984).

$$C = C_0 + k_0 \cdot t \quad \text{(Zero order kinetics)} \quad (2)$$

$$C = C_0 \cdot \exp(k_1 \cdot t) \quad \text{(First order kinetics)} \quad (3)$$

Production of coloured-compounds requires the reaction and hence consumption of key components of the juice such as sugars, amino-acids and ascorbic acid. The consumption of these compounds can also follow zero order or first order kinetics and were also modeled with Eqs. (2) and (3). Regression analysis (curve fitting) and the calculation of kinetic rate constants were performed using the Microcal Origin v.6.0 software. Statistical analysis of the regressions and level of fit were performed using the Statistica v5.0 software. All statistical analyses were carried out at a 95% level of confidence.

3. Results and discussion

Table 1 shows the results of the physicochemical characterisation obtained for the clarified cashew apple juice prior to thermal treatment.

Non-enzymatic browning has several causes such as reducing sugars reaction with amino-acids, sugar caramellisation, vitamin C decomposition and pigment destruction. Different juices have different main causes that lead to browning, so it is important to find out which factor most affects browning in cashew apple juice.

Table 1
Physicochemical characteristic of clarified cashew apple juice

Absorbance at 420 nm	0.0111 ± 0.0003
Soluble solids content (°Brix)	12.2 ± 0.1
Reducing sugars (g/100 g)	9.8 ± 0.1
Total sugars (g/100 g)	9.9 ± 0.1
pH	4.4 ± 0.0
Ascorbic acid (mg/L)	180 ± 5.2
5-HMF (mg/L)	0.00 ± 0.02

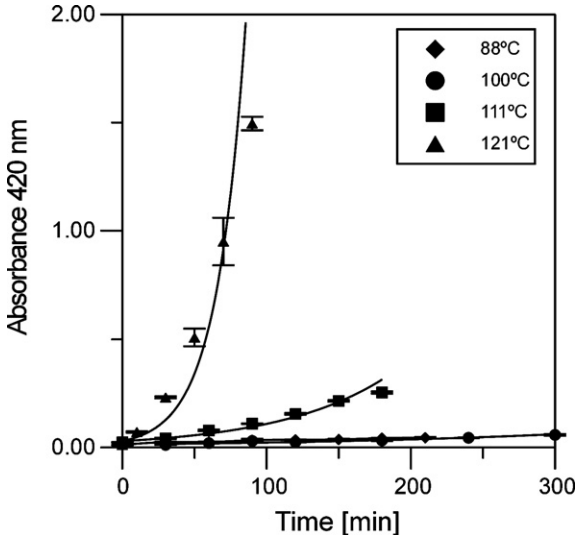

Fig. 1. Evolution of the absorbance at 420 nm of clarified cashew apple juice during thermal treatment at different temperatures.

The changes in absorbance at 420 nm (A_{420}) were studied with the time of treatment. Results showed that increasing processing times increased the absorbance at 420 nm (Fig. 1). Increasing temperatures also showed to increase browning rate measured by A_{420}. The A_{420} variation was adequately described by a first order kinetic model and the kinetic rate constant followed the Arrhenius equation:

$$\frac{dA_{420}}{dt} = +k_{420} \cdot A_{420} \quad (4)$$

$$A_{420} = A^0_{420} \cdot \exp(k_{420} \cdot t) \quad (5)$$

$$k_{420} = 6.978 \times 10^{29} \cdot \exp\left(\frac{-28752}{T}\right) \quad (6)$$

Measurement of the absorbance at 420 nm showed that at zero time an initial reading was already registered ($A^0_{420} = 0.0111$), which was due to inherent compounds in the juice.

The concentration of reducing sugars, fructose and total sugars as well as soluble solids content did not change with time and the variation among data points was within the standard error (Fig. 2). Hexoses (fructose and glucose) have direct participation in browning reactions as well as sucrose, which can hydrolyse into glucose and fructose during thermal treatment. The results obtained for total sugars and reducing sugar content did not show any definite tendency at any temperature. The steady concentration of sugars during thermal treatment showed that they did not react with amino-acids and consequently did not influence browning, not even at high temperatures. In the thermal treatment of fruits that are affected by the reaction of sugars with amino-acids, the changes in total sugar after 300 min are significant and the reduction observed in sugar concentration can be higher than 50%. Ibarz et al. (1999) have studied the thermal treatment of pear puree and observed a decrease by 63% in total sugar content due to the reaction with amino-acids after 300 min at 98 °C. For

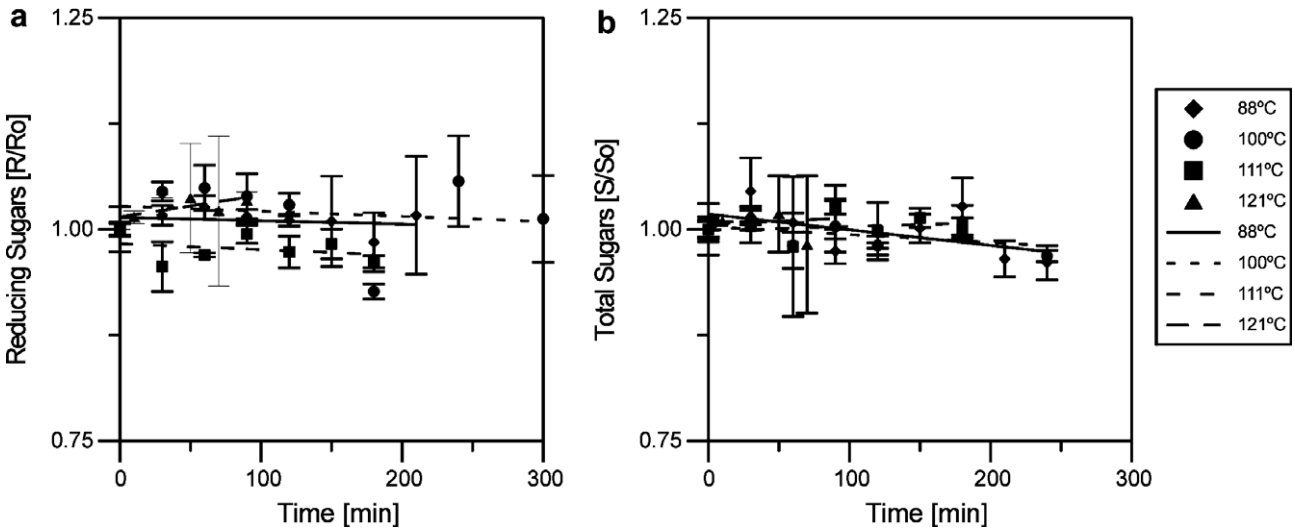

Fig. 2. Evolution of the reducing sugars (a) and total sugars (b) of clarified cashew apple juice during thermal treatment at different temperatures. Data was normalised based on the initial concentration of reducing (a) and total (b) sugars of the clarified cashew apple juice.

cashew apple juice the lowest value for total and reducing sugar concentration, observed after the thermal treatment, was less than 4% lower than the initial sugar concentration, denoting that the reaction of sugars with amino-acids was not present or was not significant for the browning process.

Increasing the processing times and temperatures had a significant effect on ascorbic acid decomposition (Fig. 3). The ascorbic acid variation was adequately described by a first order kinetic model and the kinetic rate constant followed the Arrhenius equation:

$$\frac{dAA}{dt} = -k_{AA} \cdot AA \quad (7)$$

$$AA = AA^0 \cdot \exp(-k_{AA} \cdot t) \quad (8)$$

$$k_{AA} = 2.134 \times 10^{12} \cdot \exp\left(\frac{-13081}{T}\right) \quad (9)$$

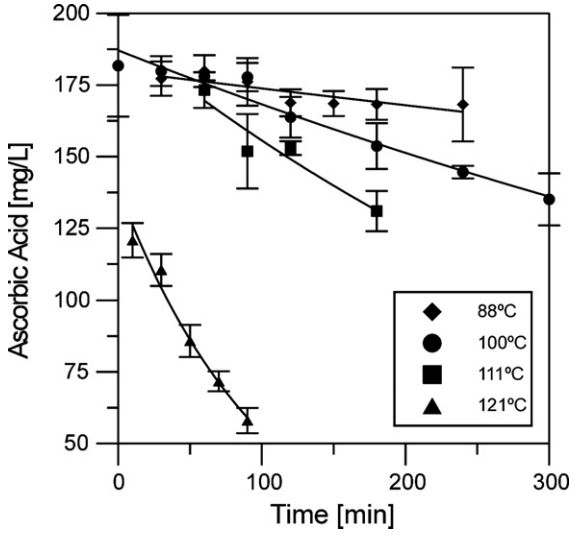

Fig. 3. Evolution of ascorbic acid contents of clarified cashew apple juice during thermal treatment at different temperatures.

Correlation of the change in absorbance at 420 nm with the loss of ascorbic acid showed an inverse relationship, indicating that ascorbic acid may be the main factor that causes browning in cashew apple juice. This is in accordance with several proposed theories implicating ascorbic acid loss with the formation of browning products such as furan-type compounds, lactones, acids, 3-hydroxy-2-pyrone, furaldehyde and 5-hydroxymethylfuraldehyde (Clegg, 1964; Clegg & Morton, 1965; Kanner, Harel, Fishbein, & Shalom, 1981; Robertson & Samaniego, 1986; Tatum, Shaw, & Berry, 1969). A number of these compounds, identified as non-enzymatic browning products, were already found in fruit juices (Roig, Bello, Rivera, & Kennedy, 1999). Oxidation of ascorbic acid produces reactive carbonyls compounds, such as α,β-unsaturated carbonyls, which are potent browning agents (Clegg & Morton, 1965; Flink, 1983; Wedzicha, 1981). These degradation products of ascorbic acid can react with amino compounds forming brown pigments. Furaldehyde and 5-HMF result from the decomposition of ascorbic acid as shown by several studies (Huelin, 1953; Kanner et al., 1981; Robertson & Samaniego, 1986). Since these compounds are related to quality loss in juices, the 5-HMF indexing has been recommended as a basis for quality control (Berry & Tatum, 1965; Robertson & Samaniego, 1986).

The concentration of 5-HMF was influenced by processing time and temperature and showed two distinct kinetic periods, a first order kinetic rate period at the beginning of the thermal treatment followed by a zero order kinetic rate period (Fig. 4). The transition between the first order and the zero order kinetic rate periods was also temperature dependent. The first kinetic period of 5-HMF was related to the high decomposition rate of ascorbic acid and the reaction of its degradation products, producing 5-HMF. The effect of ascorbic acid decomposition on the formation of 5-HMF decreased as the concentration of ascorbic acid decreased and when the concentration of

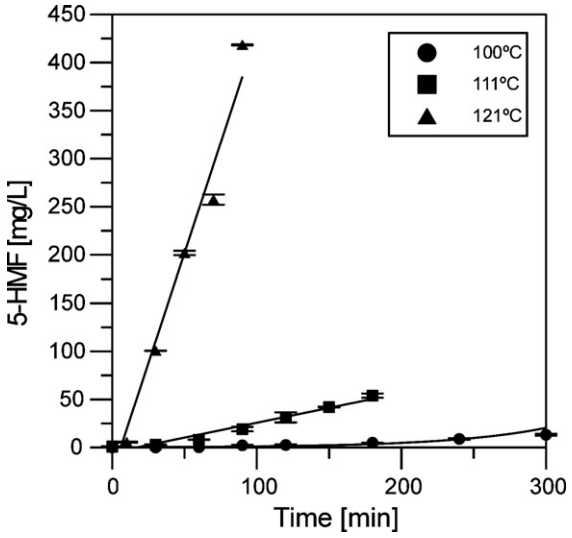

Fig. 4. Evolution of 5-hydroxymethylfurfural (5-HMF) contents of clarified cashew apple juice during thermal treatment at different temperatures.

ascorbic acid became lower than 120 mg/l, the second kinetic period started. The second kinetic period started after 420 min at 100 °C, 150 min after 111 °C and after 15 min at 121 °C. The second kinetic period was influenced by the slower decomposition rate of ascorbic acid and by slow chain reactions, that continue to form 5-HMF even after the reduction in the concentration of ascorbic acid (Flink, 1983).

The first kinetic period was adequately described by a first order kinetic model and the kinetic rate constant followed the Arrhenius equation:

$$\frac{\mathrm{dHMF}}{\mathrm{d}t} = +k_{\mathrm{HMF}} \cdot \mathrm{HMF} \tag{10}$$

$$\mathrm{HMF} = \mathrm{HMF}^0 \cdot \exp(k_{\mathrm{HMF}} \cdot t) \tag{11}$$

$$k_{\mathrm{HMF}} = 8.874 \times 10^{25} \cdot \exp\left(\frac{-24274}{T}\right) \tag{12}$$

$$\mathrm{HMF}^0 = 1.139 + 2.170 \times 10^{-39} \cdot \exp\left(\frac{33105}{T}\right) \tag{13}$$

The second kinetic period was described by a zero order kinetic model. The kinetic rate constant showed a linear relationship with temperature

$$\frac{\mathrm{dHMF}}{\mathrm{d}t} = +k_{\mathrm{HMF},2} \tag{14}$$

$$\mathrm{HMF} = \mathrm{HMF}_2^0 + k_{\mathrm{HMF},2} \cdot t \tag{15}$$

$$k_{\mathrm{HMF},2} = -178.40 + 0.4655 \cdot T \tag{16}$$

$$\mathrm{HMF}_2^0 = 1647.82 - 4.328 \cdot T \tag{17}$$

The transition period was observed in the thermal treatments at 111 and 121 °C and the transition time could be adequately shown by the equation

$$t_{\mathrm{TR}} = 30 + 5.320 \times 10^{34} \cdot \exp\left(\frac{T}{5.051}\right) \tag{18}$$

The results showed that the thermal treatment temperature was the major factor influencing browning and 5-HMF formation. At low temperatures (⩽100 °C) the thermal treatment can be carried out for 180 min without reaching the recommended 5-HMF concentration limit of 5 mg/L. On the other hand, thermal treatment time was significantly reduced when higher temperatures were employed (Fig. 4). For instance, the recommended 5-HMF limit was achieved in 50 min at 111 °C and in 9 min at 121 °C limiting the possible techniques and industrial treatment equipment that can be used.

The kinetic equations (5), (8) and (11) obtained for absorbance at 420 nm, of ascorbic acid and 5-HMF can be manipulated mathematically to create new equations correlating directly the amount of ascorbic acid and 5-HMF with the absorbance at 420 nm. First the variable time has to be isolated in Eqs. (5), (8) and (11), then the equations can be equated and finally the desired variable (5-HMF or ascorbic acid) can be isolated. Eqs. (19)–(21) show the empirical correlations obtained among 5-HMF, ascorbic acid and absorbance at 420 nm.

$$\mathrm{AA} = \mathrm{AA}^0 \cdot \left(\frac{A_{420}}{A_{420}^0}\right)^{-3.058 \cdot 10^{-18} \cdot \exp(15671/T)} \tag{19}$$

$$\mathrm{HMF} = \mathrm{HMF}^0 \cdot \left(\frac{A_{420}}{A_{420}^0}\right)^{1.272 \cdot 10^{-4} \cdot \exp(4478/T)} \tag{20}$$

$$\mathrm{HMF} = \mathrm{HMF}^0 \cdot \left(\frac{\mathrm{AA}}{\mathrm{AA}^0}\right)^{-4.158 \cdot 10^{13} \cdot \exp(-11192/T)} \tag{21}$$

3.1. Colour parameters

The CIELAB colorimetric space was also used to characterise the change in colour during the thermal treatment. An increase in temperature and time caused a darkening of the cashew apple juice which was reflected in the degree of lightness (L^*). Fig. 5 shows the variation of lightness for the thermal treatment. The results confirmed that non-enzymatic browning was favoured by the increase in operating temperature.

The trend in the plane a^*–b^* showed an increase in the b^* values with treatment time that was accentuated at increasing temperatures. The a^* values showed a tendency to increase when treatment temperature increased, while at low treatment temperatures (88 °C) the a^* value showed a tendency to decrease (Fig. 6). At temperatures above 100 °C the colour variation showed a clear tendency shifting from light yellow to a dark brown hue which became pronounced with increasing treatment temperature.

The colour difference (ΔE^*) increased with time and treatment temperature as shown in Fig. 7. From 88 °C to 100 °C the colour difference increased slightly, whereas a more rapid increase was observed at higher temperatures. The colour difference can be expressed by Eq. (22) which

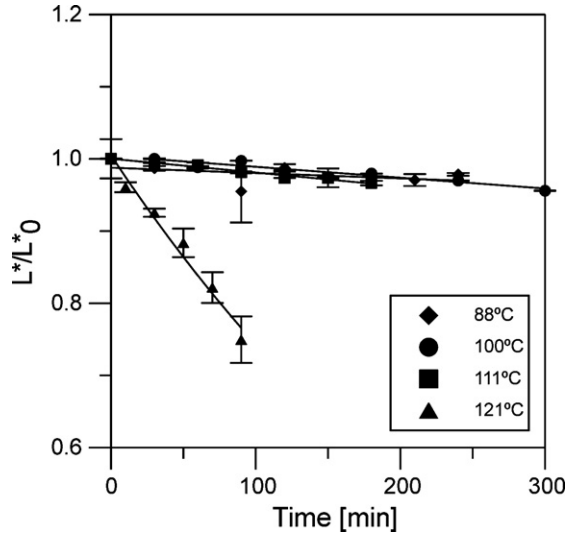

Fig. 5. Evolution of the CIELAB L^* parameter of clarified cashew apple juice during thermal treatment at different temperatures.

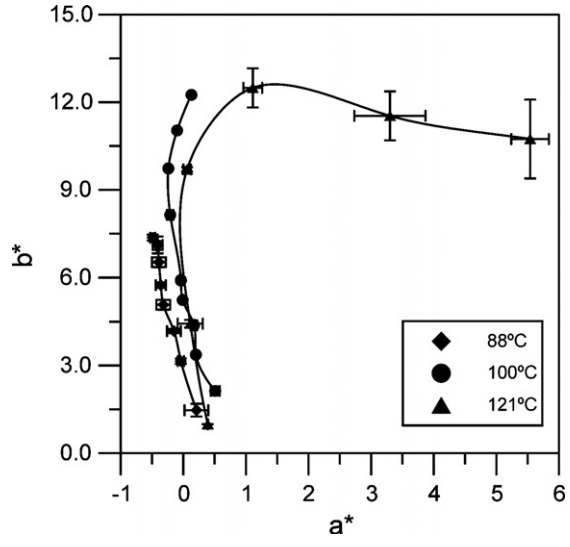

Fig. 6. Change in CIELAB b^* versus a^* parameters of clarified cashew apple juice during thermal treatment at different temperatures.

was proposed by Lozano and Ibarz (1997) to study the colour variation in fruit derivates

$$\Delta E^* = K - K \cdot \exp(-k_{PD} \cdot t) \quad (22)$$

In the equation, the value of K expresses the maximum colour difference (ΔE^*) obtained for long treatment times. According to the proposed kinetic model, the K value would represent the relation between kinetic constants k_{CA} (colour appearance) and k_{PD} (pigments destruction). K values greater than 1.0 indicates that the Maillard reaction predominates over pigment destruction (Lozano & Ibarz, 1997).

During the thermal processing of clarified cashew apple juice the K values increased with temperature going from 6.016 ± 0.384 at 88 °C to 13.967 ± 0.451 at 121 °C. In consequence, an increase in the temperature implies a higher

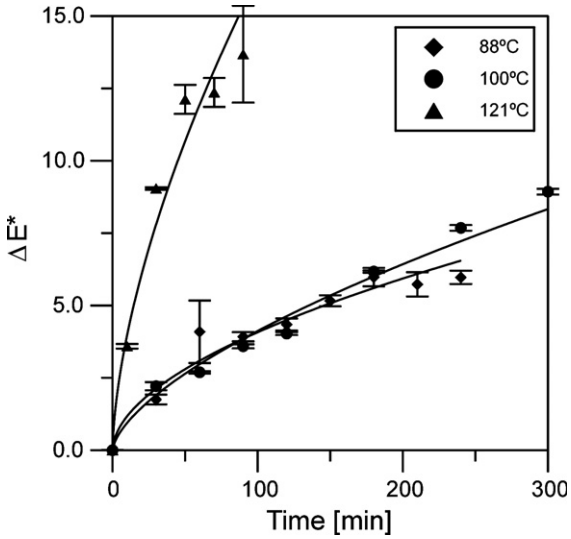

Fig. 7. Evolution of the ΔE^* of clarified cashew apple juice during thermal treatment at different temperatures.

increase in colour. Moreover, the higher the temperature, the higher the value of K was, thus favoring the colour formation stage. The K values were higher than 1.0 indicating the predominance of the Maillard reaction over pigment destruction. The pigment destruction kinetic parameter (k_1) increased from 0.014 ± 0.001 at 88 °C to 0.037 ± 0.002 at 121 °C.

3.2. Process control

Process control and optimisation requires understanding the consumers' desires, who prefer a clear juice with light brown-yellow colour and a high vitamin C content (higher nutritional value). To meet consumers expectations the thermal treatment should not increase, too much, the clarified juice absorbance at 420 nm, which can increase by 20%. It is more preferable to increase only by 10%. These values were defined based on sensorial evaluation carried out by Brito (2005). Thus, absorbance at 420 nm acts as a constraint to process optimisation, which will have two degrees of freedom: time and temperature. Two degrees of freedom means that the process can have multiple optimum operating conditions represented by time–temperature sets as shown in Fig. 8a.

Additional constraints can be used to find a single optimum operating condition. According to the International Federation of Fruit Juice Producers (IFFJP, 1985) the recommended maximum 5-HMF content in juices is 5 mg/L and this limit can be set as a constraint to decide a single optimum operating condition to the process.

Fig. 8b shows the 5-HMF content (dashed line) as a function of temperature calculated at the optimum processing time for that temperature. The concentration of 5-HMF did not exceed the maximum recommended concentration, for any thermal treatment temperature, and decreased as the treatment temperature increased. Higher

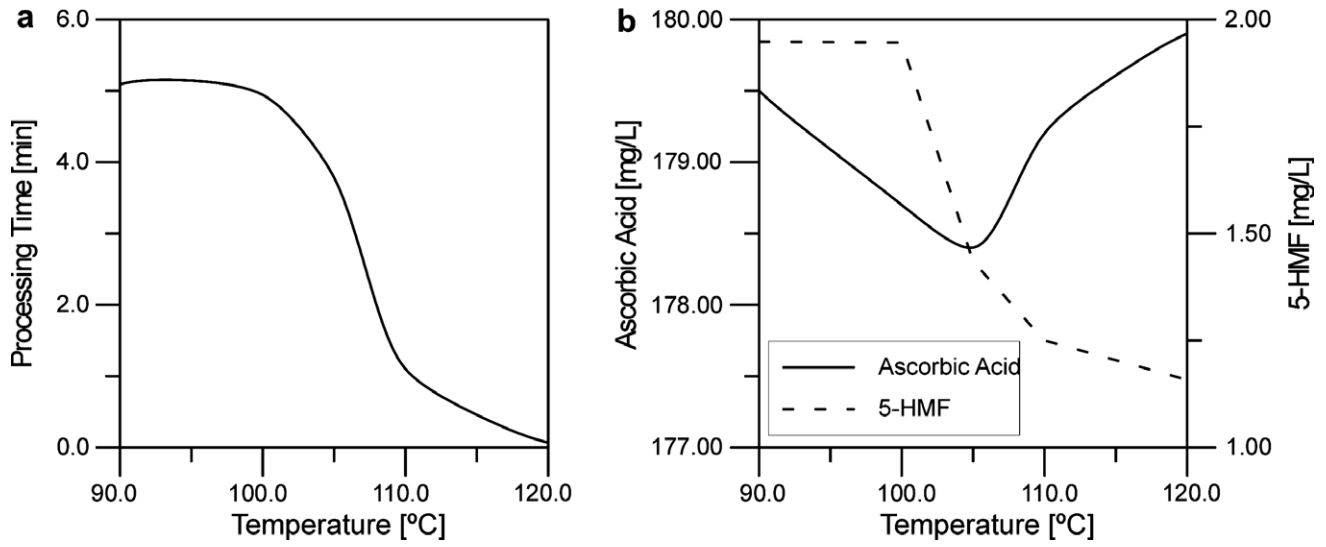

Fig. 8. (a) Possible optimal time–temperature processing conditions to achieve an absorbance at 420 nm 10% higher than the juice's initial absorbance at 420 nm and (b) ascorbic acid and 5-HMF concentrations found at the optimal operating time for different processing temperatures.

temperatures lead to higher 5-HMF formation rates but the significantly lower processing time required at higher processing temperatures has greater influence in the process of decreasing the 5-HMF concentration. Based on 5-HMF concentration, the best thermal treatment would be carried out at 120 °C, treatment which leads to the lowest 5-HMF concentration. At 120 °C the processing time is 0.07 min (4.2 s) which can only be achieved using a plate heat exchanger with high turbulence and heat exchange coefficient.

If the process is applied at small producers using a water bath under atmospheric pressure, then a maximum temperature of 100 °C can be achieved and in this case the process time should be of 4.9 min. The optimum time of 4.9 min may be short for some industrial thermal treatment technologies. If bottles of 350 mL, with an average diameter of 0.055 m, are immersed in a water bath a minimum time is required to achieve total homogenisation of the temperature inside the bottle. Cashew apple juice has thermal conductivity of 0.533 $W\,m^{-1}\,K^{-1}$ and thermal diffusivity of $1.396.10^{-7}\,m^2\,s^{-1}$ (Azoubel, Cipriani, El-Aouar, Antonio, & Murr, 2005). If a bottle is immersed in a water bath at 100 °C, heat conduction and homogenisation of the temperature inside the bottle will take 4.5 min if good agitation is applied in the water bath (based on a Reynolds number of 31400) and 17.9 min if mild agitation is applied (based on a Reynolds number of 3100). Handling of the bottles is also time consuming and 4.9 min of processing would require automated bottle handling and good agitation of the water bath.

If a 20% increase from the initial product absorbance, at 420 nm, is allowed during thermal treatment, the optimal time for the thermal treatment will increase. Based on the 5-HMF concentration, the best thermal treatment would still be carried out at 120 °C, treatment which leads to the lowest 5-HMF concentration. If the process is applied at small producers using water bath at 100 °C under atmospheric pressure then the process time would be 10.4 min and if the bottles are handled manually the time needed to remove all bottles from the water bath would not implicate in significant additional browning.

Vitamin C content can also act as an additional constraint to find a single optimum operating condition. In this case there is not a recommended value for vitamin C concentration in juices but it would be desired to lose as little vitamin C as possible. Fig. 8b shows the ascorbic acid content (full lines) as a function of temperature calculated at the optimum processing time for that temperature. The concentration of ascorbic acid is very dependent on processing time and process temperature and as temperature increases the vitamin C content diminishes until a temperature (about 105 °C), where the optimal processing time becomes so short that the degradation of ascorbic acid is low. So, based on vitamin C concentration, the best thermal treatment should be carried out at 120 °C, treatment which leads to the highest vitamin C concentration in the clarified cashew apple juice.

This is different from when the 5-HMF concentration acts as a constraint, if the thermal treatment is carried out in water bath the best thermal treatment should be carried out at 90 °C, a temperature that would maintain a high concentration of vitamin C in the juice.

4. Conclusion

Browning of clarified cashew apple juice was caused by the degradation of ascorbic acid. Changes in the absorbance at 420 nm and the ascorbic acid levels during thermal treatment of clarified cashew apple juice were described by first order kinetics, showing the correlation

between ascorbic acid loss and colour formation (browning). Two kinetic periods were observed for the formation of 5-HMF, where the first stage followed a first order kinetic in direct association with ascorbic acid loss.

The kinetic rate constants obtained for ascorbic acid concentration, 5-HMF concentration and absorbance at 420 nm allowed the optimisation of the thermal treatment. To produce a juice with high Vitamin C content and low 5-HMF content the thermal treatment should be carried out at 120 °C with low residence times in plate heat exchangers or similar heat-transfer equipment. If a water bath is used as the thermal treatment equipment then the process should be carried out at 90 °C, conditions that causes low degradation of ascorbic acid but at the expense of higher 5-HMF content.

Acknowledgements

The authors thank Banco do Nordeste for the financial support of this work and CAPES for the award of a scholarship.

References

Azoubel, P. M., Cipriani, D. C., El-Aouar, A. A., Antonio, G. C., & Murr, F. E. X. (2005). Effect of concentration on the physical properties of cashew juice. *Journal of Food Engineering, 66*, 413–417.

Berry, R. E., & Tatum, J. H. (1965). Comparison of orange concentrate and foammat powders by chromatographic procedures. *Journal of Agricultural and Food Chemistry, 13*, 588.

Beveridge, T., Franz, K. Y., & Harrison, J. E. (1986). Clarified natural apple juice: production and storage stability of juice and concentrate. *Journal of Food Science, 51*, 411–414.

Brito, E. S. (2005). Avaliação das cajuínas fabricadas no Ceará. Relatório Técnico da Embrapa, Fortaleza.

Clegg, K. M. (1964). Nonenzymatic browning of lemon juice. *Journal of the Science of Food and Agriculture, 15*, 878.

Clegg, K. M., & Morton, A. D. (1965). Carbonyl compounds and the nonenzymic browning of lemon juice. *Journal of the Science of Food and Agriculture, 16*, 191.

Cornwell, C. J., & Wrolstad, R. E. (1981). Causes of browning in pear juice concentrate during storage. *Journal of Food Science, 46*, 515–518.

Flink, J. M. (1983). Nonenzymatic browning of freeze-dried sucrose. *Journal of Food Science, 48*, 539.

Garza, S., Ibarz, A., Pagán, J., & Giner, J. (1999). Non-enzymatic browning in peach puree during heating. *Food Research International, 32*, 335–343.

Huelin, F. E. (1953). Volatile products of apples (III) identification of aldehydes and ketones. *Food Research, 18*, 633.

Ibarz, A., Pagán, J., & Garza, S. (1999). Kinetic models for colour changes in pear puree during heating at relatively high temperatures. *Journal of Food Engineering, 39*, 415–422.

IFFJP (1985). International Federation of Fruit Juice Producers Methods, Analysen-analyses. *Zug. Swizerland: Fruit-Union Suisse Assoc. Suizzera Frutta, 12*, 1–2.

Kanner, J., Harel, S., Fishbein, Y., & Shalom, P. (1981). Furfural accumulation in stored orange juice concentrates. *Journal of Agricultural and Food Chemistry, 29*, 948–949.

Labuza, T. P. (1972). Nutrient losses during drying and storage of dehydrated foods. *CRC Critical Review in Food Technology, 3*, 217–223.

Lozano, J. E., & Ibarz, A. (1997). Colour changes in concentrated fruit pulps during heating at high temperatures. *Journal of Food Engineering, 34*, 365–373.

Robertson, G. L., & Samaniego, C. M. L. (1986). Effect of initial dissolved oxygen levels on the degradation of ascorbic acid and the browning of lemon juice during storage. *Journal of Food Science, 51*, 184–187.

Roig, M. G., Bello, J. F., Rivera, Z. S., & Kennedy, J. F. (1999). Studies on the occurrence of non-enzymatic browning during storage of citrus juice. *Food Research International, 32*, 609–619.

Strohecker, R., & Henning, H. M. (1967). *Analisis de vitaminas: métodos comprobados*. Madrid: Paz Montalvo, 428p.

Tatum, J. H., Shaw, P. E., & Berry, R. E. (1969). Degradation products from ascorbic acid. *Journal of Agricultural and Food Chemistry, 17*, 38–40.

Toribio, J. L., & Lozano, J. E. (1984). Non-enzymatic browning in apple juice concentrate during storage. *Journal of Food Science, 49*, 889–892.

Wedzicha, B. L. (1981). Sulfur dioxide: The reaction of sulfite species with food components. *Nutrition and Food Science, 11/12*, 14.