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**Monitoring and modelling of physicochemical properties of papaya chips during
vacuum frying to control their sensory attributes and nutritional value**

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17 **Abbreviations**

18

19	a_w	water activity (dimensionless)
20	all- <i>E</i> , <i>Z</i>	carotenoid isomer forms
21	BC, BC ₀	β-carotene, and initial β-carotene content (mg·kg ⁻¹ NF-DW)
22	BCX, BCX ₀	β-cryptoxanthin, and initial β-cryptoxanthin content (mg·kg ⁻¹ NF-
23		DW)
24	BI, BI ₀	browning index, and initial browning index (dimensionless)
25	b_{aw} , b_{BI} , b_{suc}	time to reach the sigmoid's midpoint for a_w , browning index and
26		sucrose (min)
27	DW	dry weight
28	E_a	activation energy (J·mol ⁻¹)
29	Exp	experimental data
30	FW	fresh weight
31	k_{aw} , k_{BI} , k_{suc}	rate constant of a_w , browning index, and sucrose (min ⁻¹)
32	k_{BCX} , k_{ref}	β-cryptoxanthin degradation rate constant, and rate constant at
33		reference temperature (kg·mg ⁻¹ ·min ⁻¹)
34	k_M	rate of water loss (min ⁻¹)
35	k_O	rate of oil uptake (min ⁻¹)
36	L^* , a^* , b^*	CIELAB color space parameters (dimensionless)
37	L_{aw} , L_{BI} ,	curve's maximum of a_w , and browning index (dimensionless)
38	L_{suc}	curve's maximum of sucrose (g·100 g ⁻¹ NF-DW)
39	LYC, LYC ₀	lycopene, and initial lycopene content (mg·kg ⁻¹ NF-DW)
40	M, M ₀	moisture content, and initial moisture content (g·g ⁻¹ DW)

41	NF-DW	non-fat dry weight
42	O, O _e	oil content, and oil content at infinite time (g·g ⁻¹ DW)
43	p	probability
44	r	correlation coefficient
45	R	gas constant (8.314 J·mol ⁻¹ ·K ⁻¹)
46	R ²	coefficient of determination
47	RAE	retinol activity equivalent
48	RDI	reference daily intake
49	t	time, min
50	T	temperature (°C or K)
51	T _{ref}	reference temperature (°C or K)
52	ΔE	color difference

Abstract

Vacuum frying is an alternative technology to obtain fruit snacks with higher sensory and nutritional quality compared to traditional fried snacks. Vacuum frying of a carotenoid-rich fruit (red-fleshed papaya) was performed at 25 kPa, using soybean oil at 100, 120, and 140°C from 0 to 14 min. The study aimed to monitor and model physicochemical changes that chips undergo during vacuum frying, which are related to their sensory and nutritional attributes. Moisture content, a_w , oil uptake, sugar content, browning index (BI) and carotenoid contents were monitored. Water loss and oil uptake followed first-order kinetics while the decrease in a_w followed a logistic trend. Glucose and fructose followed the same degradation pattern while BI and sucrose content increased as a function of frying time and oil temperature. β -cryptoxanthin (BCX) loss followed second-order kinetics and retention was 60 and 40% after 14 min at 120 and 140 °C, respectively. Contents of lycopene and β -carotene were increased suggesting an improvement in availability of these compounds to extraction. Optimal vacuum frying conditions for processing papaya fruit comprise a combination of temperatures (107-120 °C) and frying times (9-14 min) to produce quality papaya chips with a_w ranging from 0.1 to 0.3, low color degradation and BCX loss ≤ 30 %.

Keywords

Kinetics; Browning index; Sugars; β -cryptoxanthin; β -carotene; Lycopene

1. Introduction

The consumer trends towards healthier foods require alternative strategies to the consumption of traditional fried snacks, which are rich in simple sugars, saturated lipids, and salt (Da Silva, & Moreira, 2008). The manufacturing of fried chips based on fruits

77 having good nutritional and sensory properties represents such an alternative. Vacuum
78 frying is a unit operation in which the food is under pressure below atmospheric level.
79 Thus, decreasing the boiling point of the water in the product and consequently the frying
80 medium. The lower temperatures (from 90 to 140 °C) compared to atmospheric frying, and
81 the absence of oxygen during the process minimize some undesirable chemical reactions,
82 including the degradation of natural pigments and Maillard and caramelization reactions,
83 thus preserving the natural color and nutrients in fried foods (Dueik & Bouchon, 2011). In
84 addition, this technology allows the use of unsaturated vegetable oils as frying medium due
85 to the process conditions that reduce oil deterioration (Andrés-Bello et al., 2011). For these
86 reasons, vacuum frying is currently used for making healthy and attractive snacks from
87 fruits (Andrés-Bello et al., 2011; Da Silva & Moreira, 2008; Dueik & Bouchon, 2011).

88 Several factors influence the quality attributes of vacuum-fried fruits such as vacuum frying
89 equipment, properties of the raw fruit (composition of fruit matrix), pre- and post-
90 treatments, and processing conditions. Oil temperature and frying time influence color,
91 texture, nutrients, and content of oil and sugars of fried fruits (Ayustaningwarno et
92 al., 2020a; Dueik, & Bouchon, 2010; Mariscal, & Bouchon, 2008; Troncoso, & Pedreschi,
93 2009).

94 Different physicochemical changes occur in foods during frying affecting their sensory and
95 nutritional attributes. During frying, the food product loses water rapidly and gains oil,
96 specially at the food's surface (Fan et al., 2010). Moisture content in dehydrated foods
97 (those with a_w in the range of 0.1 to 0.4) is of utmost importance to obtain a product with
98 adequate mechanical properties, such as crispness. Likewise, during frying, some
99 compounds (e.g., sugars, vitamins, and pigments) undergo reactions in the fried food that
100 may significantly impair the product quality (Moreira, 2012). For instance, the color

variation of fruit fried products is due to pigment degradation (e.g., carotenoids) or the presence of brown compounds formed from Maillard and caramelization reactions (e.g., hydroxymethylfurfural, HMF) (Dueik & Bouchon, 2011). Degradation of sugars is involved in Maillard and caramelization reactions causing the formation of volatile molecules and browning in foods processed at high temperatures (Martins et al., 2000). The degree of browning is considered one of the most important sensory parameters in the definition of the quality of fried foods (Pathare et al., 2013).

In this study, papaya fruit (*Carica papaya* L.) was selected as a model fruit because it is a valuable source of lycopene and pro-vitamin A carotenoids (β -carotene and β -cryptoxanthin) (Schwiggert et al., 2011; USDA, 2020). Carotenoids are well known to be natural antioxidants with beneficial health effects such as provitamin A activity; in addition, they enhance the immune system functions and lower the risk of developing chronic diseases (e.g., macular degeneration, type 2 diabetes, and cardiovascular diseases) (Kopeck, & Failla, 2018; Kulczynski et al., 2017). Besides its nutritional value, papaya fruit is consumed worldwide, representing a world production of about 13 million tons in 2017 (FAO, 2020). Thus, vacuum-fried papaya chips could represent a novel and healthy fried food compared to traditional snacks due to their high carotenoid content (Soto et al., 2021).

In this context, this study first proposes to monitor and model different physicochemical properties (water content, aw, oil uptake, sugar content, carotenoid degradation, and browning index) of papaya chips during vacuum frying. The selected physicochemical properties are related to the sensory attributes and nutritional value of the final fried product, such as color, texture, and provitamin A content. Finally, the study proposes to define the best conditions of the vacuum frying process to optimize the quality of papaya chips taking into account the most relevant physicochemical characteristics for this type of

product. The information generated from this study will be of great interest for manufacturers of fried products who try to obtain attractive and healthy snacks.

2. Materials and methods

2.1. Materials

Red-fleshed papaya fruits (*Carica papaya* L.) from hermaphrodite plants of the commercial Costa Rican hybrid Pococí were acquired from Orofrut (Orotina, Alajuela, Costa Rica) in October 2019 at ripening stage 4 (41-55% of skin yellowing). Commercial soybean frying oil Clover® (Grupo NUMAR, Costa Rica) was used as frying medium.

2.2. Chemicals

The following chemicals were used: SigmaUltra standards for glucose, fructose, and sucrose from Sigma-Aldrich (St. Louis, MO, USA); β -carotene, β -cryptoxanthin and lycopene standards from Sigma-Aldrich (St. Louis, MO, USA). Other analytical grade chemicals and HPLC grade solvents were purchased from JT Baker Inc. (Phillipsburg, NJ, USA).

2.3. Sample preparation

Papaya fruits were selected and then washed and peeled manually. Each fruit was vertically cut into 4 pieces and the seeds were removed. The pre-cut pieces were sliced, firstly into 4-mm thick pieces using a food processor (FP-100 Hobart, CA, USA) and then into discs (diameter 30.0 ± 0.2 mm) using a circle-shaped cookie cutter.

2.4. Vacuum frying

The papaya chips were obtained using a vacuum frying system (Auriol, Marmande, France) as previously described by Soto et al. (2021). Briefly, this system consists of a stainless-steel vessel (capacity of 80 L), with a lid equipped with a rotary axis coupled to a piston, a stainless-steel basket, electric heat resistors to heat the oil, a temperature transducer, a filter, a heat exchanger to condense the water vapor generated during the process, a condensate vessel and a liquid ring vacuum pump. The frying vessel was filled with 55 L (~50 kg) of soybean oil which was heated to the target temperature. Once the temperature was reached, the papaya discs (100 ± 1 g) were placed into the basket, then the lid was closed, and the vessel depressurized. When the pressure in the vessel achieved the vacuum (25 kPa), the basket was immersed into the oil for the set time to obtain the chips. Once the papaya discs were fried, the basket was raised, and the centrifuging system was applied at 300 rpm ($16.6 \times g$) for 2 min in order to remove excess oil. Finally, the vessel was pressurized, and the papaya chips were removed from the fryer and left to cool down at ambient temperature prior to packaging.

2.5. Study design

Papaya discs were fried at three different oil temperatures (100, 120 and 140 °C) for seven frying times (0, 2, 4, 6, 8, 10 and 14 min) to obtain the papaya chips. For each frying experiment a product/oil ratio of 1/500 was performed to avoid a decrease in the oil temperature during the vacuum frying trials (to maintain isothermal conditions) (supplementary material 1) and to keep the vacuum pressure stable during process (supplementary material 2). Three frying trials or repetitions were conducted for each frying condition (combination of temperature/time). After each trial extra oil was added to

the vessel to keep the same product/oil ratio. The soybean oil was filtered after every three trials and was replaced after 12 trials to keep the oil fresh. After vacuum frying, samples were packaged in metallized PET/PE bags (Multivac, France) and stored at -80 °C prior to analyses. Different physicochemical properties were measured in the papaya chips: moisture, a_w , oil content, sugar content, color parameters (L^* , a^* , b^*) and carotenoid content. In addition, the browning index was measured in aqueous extracts obtained from papaya chips.

2.6. Physicochemical analyses

2.6.1 Moisture content, oil content, a_w , protein content and pH

Moisture was determined using AOAC standard method 920.151 (AOAC, 2015). Lipid content was determined by the method described by Carpenter et al. (1993). Water activity of the samples were determined at 25 °C using a water activity meter (Aqualab, model CX-2, Decagon Devices, Inc., Pullman, WA).

In addition, protein content and pH value were determined in fresh papaya. Protein content was measured by standard AOAC method 920.152 (AOAC, 2015) using a nitrogen conversion factor of 6.25. To measure pH, a digital pH-meter (Metrohm 827 pH lab meter, Metrohm Ion Analysis, Switzerland) was used.

2.6.2. Sugar content

Briefly, samples were ground and then defatted with petroleum ether (b.p. 40-60 °C) using a fat extraction unit E-812 (Büchi, Fawil, Switzerland). This was done to avoid any interference of lipids. Defatted samples were weighed (300-1000 mg) in 40 mL centrifuge

tubes. Then 5 mL of distilled H₂O was added and mixed using an IKA® Ultra-Turrax® (Merck KGaA, Darmstadt, Germany) for 5 min. The mixture was incubated for 30 min in a water bath at 70 °C. After incubation, the tubes were cooled in an ice bath and centrifuged at 1400 x g (Allegra 21 Centrifuge, Beckman Coulter, Switzerland) for 10 min at 15 °C. The supernatant was membrane filtered (0.45 µm) prior to sugar analysis.

Sugars (sucrose, glucose, and fructose) were determined by the Shimadzu HPLC system (Shimadzu Manufacturing, Inc., Canby, Oregon, USA) equipped with a RID-10A refractive index detector, a DGU-20A5 degasser, a SIL-20AHT autosampler, a CTO-20A column oven and a LC-20AT binary gradient pump. Sugars were separated using a Zorbax carbohydrate column (250 mm x 4.6 mm i.d., 5 µm) (Agilent, CA, USA) with a guard column. The mobile phase was acetonitrile/H₂O (80/20). The operation temperature was set at 30 °C. The flow rate was set at 1mL/min and the injection volume was 10 µL. Isocratic conditions were programmed with a run time of 15 min. Quantification was performed after obtaining linear calibration curves of glucose, fructose, and sucrose. In order to keep the same basis among samples, the results were expressed as non-fat dry weight.

2.6.3. Color analysis in papaya chips

Color was measured in the papaya chips with a spectrophotometer (ColorFlex, HunterLab, Virginia, USA). Color parameters were expressed in CIELab units L^* , a^* and b^* using illuminant D65 and a 10 ° observer angle.

2.6.4. Color analysis in aqueous extracts from papaya chips

Aqueous extracts were obtained from papaya chips that had been previously defatted and dehydrated, to express results on the same basis. Briefly, samples were ground and then defatted with petroleum ether (b.p. 40-60 °C) using a fat extractor unit E-812 (Büchi, Fawil, Switzerland). To avoid undesirable color change, defatted samples were then dehydrated at 25 °C in desiccators containing saturated solution of CaCl₂ (*a_w* at equilibrium of 0.280). It was considered that samples reached the equilibrium point when they showed a constant weight during three consecutive readings. Then defatted and dehydrated samples were weighed (300 mg) in 40 mL centrifuge tubes. Then 5 mL of distilled H₂O was added and mixed using an IKA® Ultra-Turrax® (Merck KGaA, Darmstadt, Germany) for 5 min. The tubes were incubated for 30 min in a water bath at 70 °C. After incubation, the tubes were cooled in an ice bath and centrifuged at 1400 x g (Allegra 21 Centrifuge, Beckman Coulter, Switzerland) during 10 min at 15 °C. The supernatant constituted by the hydrosoluble compounds was membrane filtered (0.45 µm) prior to color analysis. Color of the extracts was measured using the same protocol as previously mentioned with the papaya chips. Then, the browning index (*BI*) was calculated using *L**, *a** and *b** values as follow:

$$BI = 100 \times \left[\frac{\left(\frac{a^* + 1.75L^*}{5.645L^* + a^* - 3.012b^*} \right) - 0.31}{0.17} \right] \quad [1]$$

where *L**, *a** and *b** represented the values of aqueous extracts from papaya chips after vacuum frying. *BI* represents the purity of brown color and is considered to be an important parameter associated with browning in food products containing sugar (Pathare et al., 2013). *BI* at each frying time was represented with respect to its initial value (*BI*₀).

2.6.5. Carotenoid content

Procedures and conditions for carotenoid extraction of papaya chips were described previously by Soto et al. (2020). Briefly, samples were weighed (200-500 mg) in 20 mL tubes. Then, 2 mL of an ethanol solution containing 1 % pyrogallol was added. The mixture was homogenized using a Vortex mixer and incubated for 2 min in the dark in a water bath at 70 °C. Then after cooling, saponification of the samples was performed for 30 min in a water bath at 70 °C by adding 1.5 mL of saturated KOH (12 N). After incubation, the tubes were cooled in an ice bath and 2 mL of distilled water and 5 mL of hexane were added. Then, after mixing and decantation, the organic phase was recovered, and the aqueous phase was extracted two more times with 5 mL of hexane. The organic phases were mixed and evaporated under nitrogen at 30 °C until dryness. Finally, the residue was re-dissolved in 500 µL of methyl tert-butyl ether (MTBE)/methanol (80/20) and placed in an amber vial prior to HPLC analysis.

Carotenoid identification was performed by HPLC using an Agilent 1100HPLC-DAD system (Massy, France). Carotenoids were separated using a C30 column (150 mm x 4.6 mm i.d., 3 µm) (YMC EUROP GmbH, Germany) with a guard column, and the mobile phase was methanol as eluent A and MTBE as eluent B. Operation temperature was set at 30 °C. The flow rate was set at 0.6 mL/min and the injection volume was 10 µL. The gradient program is described by Soto et al. (2021). All-E-β-cryptoxanthin, all-E-β-carotene and their isomers were detected at 450 nm, and all-E-lycopene and their isomers were detected at 470 nm (Soto et al., 2020). The contents of Z-β-carotene and Z-lycopene were expressed as the sum of all their Z-isomers, respectively. In order to maintain the same basis among samples, the results were expressed on a non-fat dry weight basis.

2.6.6. Vitamin A activity

Vitamin A activity was expressed as Retinol Activity Equivalent (RAE). RAE estimate was calculated for a bioconversion ratio (carotenoid:retinol) of 12:1 for all-E- β -carotene, and 24:1 for all-E- β -cryptoxanthin and Z- β -carotene (US IOM, 2000).

2.7. Kinetic modelling

2.7.1. Moisture content

An exponential model was chosen to describe the moisture content in papaya chips during the frying process as shown in Eq. 2 (Krokida et al., 2000; Manjunatha et al., 2014; Ayustaningwarno et al., 2020b). It is based on the following assumptions: 1) the oil temperature is constant during frying, 2) initial water content ($t=0$) in papaya chips is uniform, 3) the moisture content at an infinite process time ($t=\infty$) is negligible.

$$M = M_0 * \exp(-k_M * t) \quad [2]$$

where M is the moisture content at time t ($\text{g} \cdot \text{g}^{-1}$ dry weight, DW); M_0 is the initial moisture content ($\text{g} \cdot \text{g}^{-1}$ dry weight, DW); k_M represents the specific rate of water loss for this model (min^{-1}); t is the frying time (min).

2.7.2. Oil content

A first-order kinetic model was chosen to describe the moisture content in papaya chips during the frying process as shown in Eq. 3 (Krokida et al., 2000). This model assumes that the oil temperature is constant during frying. The initial oil content ($t=0$) in papaya chips was negligible.

287

288 $O = O_e * (1 - \exp^{(-k_o*t)})$ [3]

289 where O is the oil content at time t ($\text{g} \cdot \text{g}^{-1}$ DW); O_e is the oil content at infinite time ($t=\infty$);
290 ($\text{g} \cdot \text{g}^{-1}$ DW); k_o represents the specific rate of oil uptake for this model (min^{-1}); t is the
291 frying time (min).

292

293 *2.7.3. Water activity (a_w), sucrose content, and browning index (BI)*

294 A logistic model of three parameters was used to describe a_w , and sucrose content in papaya
295 chips and BI in aqueous extracts from papaya chips during vacuum frying as shown in Eq.
296 4 (Nambi et al., 2016; Vaikousi et al., 2008).

297

298 $P_i = \frac{L_i}{1 + e^{-k_i*(t-b_i)}}$ [4]

299 where P_i is the parameter measured at time t : a_w (dimensionless), sucrose content (expressed
300 as $\text{g} \cdot 100 \text{ g}^{-1}$ non-fat dry weight, NF-DW), and BI (represented in the dimensionless form
301 BI/BI_0); L_i is the curve's maximum of the variable (dimensionless for a_w and BI/BI_0 ; for
302 sucrose in $\text{g} \cdot 100 \text{ g}^{-1}$ NF-DW); b_i represents the time to reach the sigmoid's midpoint (min);
303 k_i represents the rate constant (min^{-1}); t is the frying time (min).

304

305 *2.7.4. β -cryptoxanthin*

306 A second-order kinetic model was used to describe the degradation of β -cryptoxanthin
307 (BCX) during vacuum frying as described by Eq. 5 (Soto et al., 2020). BCX degradation
308 was presented in the dimensionless form BCX/BCX_0 .

309

$$BCX = \frac{1}{((1/BCX_0) + k_{BCX} * t)} \quad [5]$$

where BCX represents the carotenoid concentration at time t and BCX_0 is the initial concentration ($t=0$) ($\text{mg} \cdot \text{kg}^{-1}$ non-fat dry weight); k_{BCX} is the reaction rate constant ($\text{kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); t is the frying time (min). The rate constants were assumed to vary with the temperature according to the Arrhenius equation described by Eq. 6.

315

$$k = k_{ref} \exp \left(\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \quad [6]$$

where k_{ref} is the rate constant ($\text{kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) at the reference temperature T_{ref} chosen in the middle of the studied temperature range (393 K), with E_a , T , and R respectively denoting the activation energy ($\text{J} \cdot \text{mol}^{-1}$), medium temperature (K), and gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$).

321

2.8. Parameter identification

The estimation of kinetic parameters was performed using a non-linear regression analysis method which is based on the minimization of the residual sum of squares (RSS) between the prediction and experimental data set for each model (Eq. 7).

326

$$RSS = \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad [7]$$

where y_i is the experimental value of the dependent variable (moisture content, oil content, a_w , sucrose content, browning index, β -cryptoxanthin content); \hat{y}_i is the calculated value from the model; n_i is the number of experimental points. The coefficient of determination

R^2 was calculated from the ratio of the explained variance to the total variance (TSS), with the explained variance being TSS minus RSS:

$$R^2 = \frac{\sum_{i=1}^n (y_i - \bar{y})^2 - RSS}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad [8]$$

where \bar{y} is the mean value of the dependent variable (moisture content, oil content, a_w , sucrose content, browning index, β -cryptoxanthin content), and n is the number of experimental points. Kinetic parameters for different physicochemical properties in papaya chips were identified using SigmaPlot software (Systat Software Inc., CA, USA). The parameter uncertainty was calculated as the standard error of regression.

2.9. Statistical analyses

The different frying conditions were performed in three repetitions. Data were presented as mean \pm standard deviation of replicates. Kinetic parameters for different physicochemical properties of papaya chips were expressed as mean with its respective standard error. The variation of lycopene and β -carotene isomers in papaya chips during vacuum frying was analyzed by one-way ANOVA and post hoc Tukey-HSD test to detect significant differences ($p < 0.05$). ANOVA was performed using Statistica 7.0 (Statsoft Inc., USA). Correlation analyses from experimental data of sugar contents, a_w and BI of papaya chips were done with SigmaPlot software (Systat Software Inc., CA, USA).

3. Results and discussion

3.1 Physicochemical properties of fresh papaya

Some characteristics were determined in fresh Pococí papaya at ripening stage of 4 (RS4: 41-55 % of skin yellowing) selected to produce papaya chips. Moisture content (88.99 ± 0.67 g·100 g⁻¹ fresh weight (FW)) and a_w value (0.989 ± 0.005) were in agreement with previously published data for papaya Pococí (Soto et al., 2021). The protein content was 0.58 ± 0.03 g·100 g⁻¹ FW. Concerning the lipid content, it was considered negligible as the detection limit is 0.10 g·100 g⁻¹ FW. These results were similar to those reported for red-fleshed papaya fruit (USDA, 2020). Total sugar content (sum of glucose and fructose) was 6.51 ± 0.44 g·100 g⁻¹ FW. Sucrose was not detected in the papaya fruit (detection limit of 0.25 g·100 g⁻¹ FW) as previously reported in literature (Soto et al., 2020; Soto et al., 2021). The pH value of Pococí papaya was 5.43 ± 0.41 , being a fruit with low acidity compared to other tropical fruits. The fruit contained 24.70 ± 5.34 mg·kg⁻¹ FW of total carotenoids. This carotenoid content is in agreement with that reported for red-fleshed papaya fruit (Schweigert et al., 2011; Soto et al., 2020; USDA, 2020).

3.2 Moisture content, oil uptake, and a_w

Results of experimental data for the moisture content (dry weight) of papaya chips during frying at different oil temperatures are shown in Fig. 1.a. The treatments at different temperatures were isothermals with minimal variation of oil temperature during the frying process (supplementary material 1). Fig. 1.a shows that the moisture content in papaya chips decreased significantly during frying. Water started evaporating as soon as the raw material was in contact with the oil. Initially, the rate of water loss was high, leading to an initial rapid fall of moisture content (85-98% of water loss, Fig. 1.a) during the first minutes of frying (0-4 min) due mainly to the loss of surface moisture, and then it slowed down as the product reached equilibrium.

377 As frying temperature increased the moisture content for the same frying time decreased.
 378 After 10 min of vacuum frying at 100 and 120 °C the moisture content in papaya chips
 379 reached equilibrium values of 0.024 and 0.020 g·g⁻¹ DW, respectively. At 140 °C the
 380 equilibrium moisture value was of 0.005 g·g⁻¹ DW and was reached after 8 min of frying.
 381 The moisture content model fitted the experimental data accurately (Fig. 1.a). It was shown
 382 that the rate constant of moisture loss (k_M), presented in Table 1, increased with
 383 temperature as previously described by several authors during the frying process
 384 (Ayustaningwarno et al., 2020b; Krokida et al., 2000; Manjunatha et al., 2014; Troncoso, &
 385 Pedreschi, 2009).
 386 Fig. 1.b shows the increase of oil uptake (dry weight) versus frying time applying different
 387 oil temperatures. Generally, the longer the product remained in the frying vessel, the more
 388 the oil was absorbed. There were no significant differences ($p>0.05$) for the rate constant of
 389 oil uptake (k_O) between curves at 120 and 140 °C (Table 1). The general pattern was an
 390 initial rapid increase of oil uptake (0-8 min) followed by a gradually decreasing rate, with a
 391 final increase for the longest frying time (14 min). At 100 °C the model had a linear
 392 behavior with time. In general, at low temperatures and for short times, the proposed model
 393 had a linear behavior with time, whereas at higher temperatures (≥ 120 °C) and for longer
 394 times, oil content reached an equilibrium value as is shown in Fig. 1.b.
 395 During frying at low temperatures, oil absorption took place not only during the cooling
 396 period but also to some extent during the frying period; this can be explained by the fact
 397 that low temperatures and thus weak water flows lead to the formation of a crust with a
 398 structure more favorable to oil absorption during the frying period (Pedreschi, & Moyano,
 399 2005; Ziaifar et al., 2010). This can be observed in Fig 1.b, after 10 min at 100 °C the oil
 400 uptake in papaya chips was higher compared to 120 and 140 °C.

Moisture loss is directly related to oil absorption because oil enters the voids replacing the water that has evaporated during the frying, which happens especially during cooling (Ziaifar et al., 2010). Oil uptake increased as the moisture content diminished. In this study, an equilibrium value was observed in moisture content ($\sim 2 \text{ g} \cdot 100 \text{ g}^{-1} \text{ FW}$) when the papaya chips reached oil contents above $25 \text{ g oil} \cdot 100 \text{ g}^{-1} \text{ FW}$.

Fig. 1.c shows the change of a_w values in papaya chips during vacuum frying. It was observed that sigmoidal behavior described a_w values in papaya chips during the frying process. A decreasing logistic function (Eq. 4) fitted the a_w data accurately. The models for a_w at 120 and 140 °C presented a similar behavior. L_{aw} and b_{aw} parameters of curves at 120 and 140 °C were significantly different ($p < 0.05$) from those obtained at 100°C (Table 1).

Fig. 1.c. also shows that a_w values of papaya chips decreased during frying according to three distinct stages: settling period, constant rate period and falling rate period. The settling period occurs during the first minutes of process (0-2 min at 120 and 140 °C, and 0-4 min at 100 °C), with a_w values close to one. Then, there is a constant rate period in which the unbound water is removed. This period represents the condition of equilibrium temperature at the product surface and ends when the surface of the solid is no longer wet and represents the critical moisture content or critical a_w value (Barbosa-Cánovas & Juliano, 2007). Finally, the last stage comprises the period in which the surface of the food product is dried, and the water is removed from the center to the surface as vapor (Barbosa-Cánovas & Juliano, 2007). At this point, the drying rate approaches the equilibrium moisture content as is shown in Fig. 1.a.

Water loss and oil uptake phenomena depend not only on the process conditions (oil temperature, frying time, and pressure) but on physical factors related to the food, such as its size, shape, and thickness (Moreira, 2012). The thickness significantly affects the

contents of moisture and oil of food products during frying. Water loss and oil uptake are higher at smaller sample thickness (keeping the same oil temperature and frying time) (Krokida et al., 2000). The selection of the thickness of fruit/vegetable slices to obtain the chips depends on the ripening stage and composition of the raw material (moisture, proteins, polysaccharides, sugars) and the physical changes in the fried product (crispness, shrinkage, puffing). For instance, the ripening stage and the chemical composition of fruits are factors that influence the skin/pulp firmness of these food matrices, affecting the process conditions during the peeling, cutting, and slicing steps (Soto et al., 2021). A greater firmness in the fruit allows obtaining a lesser thickness in the product during the slicing operation. In this study was selected a thickness of 4 mm in the papaya discs according to pilot experiments. This value is similar to that applied for other fruits to obtain vacuum-fried chips: 4 mm for mango (Ayustaningwarno et al., 2020a); 3.5-4.5 mm for banana (Yamsaengsung et al., 2011); 5 mm for kiwi (Diamante et al., 2011), and apple (Mariscal, & Bouchon, 2008). For vegetables, with a higher starch content and lower moisture and sugar content than fruits, the thickness is usually less than in fruits. For instance, 1.5 mm for potato (Crosa et al., 2014), blue potato, and sweet potato (Da Silva et al., 2008); 2 mm for carrot (Dueik et al., 2010).

3.3 Sugar reactions

Fig. 2 shows the variation of different sugars present in papaya chips during vacuum frying at different oil temperatures. The sugars present in fresh papaya discs ($t=0$) were glucose and fructose, representing 53 and 47 % of total sugars, respectively. Fig. 2.a and Fig. 2.b show that concentrations of glucose and fructose of papaya chips varied as function of frying time and oil temperature. Curves of glucose and fructose followed the same

degradation pattern. At 100 °C, it was observed that concentration of both sugars remained constant until 8 min of frying. Then, after 10 min the concentrations of glucose and fructose decreased significantly ($p < 0.05$) as shown in Fig. 2.a and Fig. 2.b. At 120 and 140 °C, these sugars decreased significantly ($p < 0.05$) after 4 min of frying (Fig. 2.a and Fig. 2.b). Also, it was observed that the highest retentions of glucose and fructose occurred at 100 °C. For instance, after 14 min of vacuum frying the average retention of glucose and fructose at 100 °C was 62%. At 120 and 140 °C after 14 min the average retention of these two sugars was 39 and 27%, respectively.

On the other hand, during vacuum frying the formation of sucrose occurred. Experimental data for sugar content fitted well with a 3-parameters logistic function (Eq. 4). Sucrose formation in papaya chips also followed sigmoidal behavior during the frying process as shown in Fig 2.c. Experimental data showed that initial formation of sucrose varied according to the oil temperature, increasing at 120 and 140 °C (Fig. 2.c). Moreover, Fig. 2.c shows that the lowest sucrose formation was reached at 100 °C. In fact, the time to reach the sigmoid's midpoint (b_{suc}) was significantly longer ($p < 0.05$) at 100 °C than at 120 and 140 °C (Table 1). Likewise, the lowest curve's maximum of sucrose formation (L_{suc}) was observed at 100 °C ($\sim 17 \text{ g} \cdot 100 \text{ g}^{-1} \text{ NF-DW}$) while L_{suc} value at 120 and 140 °C was ~ 2 -fold higher than at 100 °C (Table 1, Fig. 2.c).

Sucrose content in fresh papaya Pococí is negligible (Soto et al., 2020). Thus, its formation during vacuum frying of papaya could be explained by two simultaneous phenomena: i) condensation reaction between glucose and fructose, or ii) thermal degradation of cell wall and middle lamella polysaccharides (e.g. fructooligosaccharides) that could lead to the release of sucrose during frying of papaya. There is no information in the reviewed literature showing a similar reaction as seen in this study. Nevertheless, sugar condensation

reaction is frequently used in chemical industry for producing low-caloric polysaccharides (e.g. polydextrose). The formation of disaccharides by condensation reaction is carried out under temperatures from 100 to 300 °C, preferably at temperatures close or higher to melting point of saccharides serving as the substrate (Shah et al., 2004). In addition, vacuum conditions are required in order to minimize decomposition and discoloration of sugars (Shah et al., 2004).

Specific factors related to the frying process such as temperature and rate of water loss as well as intrinsic characteristics of papaya (such as proximal composition, sugar concentration, organic acids, acidity) are involved in sucrose formation. It seemed that high temperatures during processing and low a_w values in food matrix favor this reaction. For instance, a negative linear correlation was observed between sucrose content and a_w . Correlation coefficients (r values) were -0.911, -0.887 and -0.964 for the curves at 100, 120 and 140 °C, respectively, as shown in Fig 2.d. As a_w values decreased, sucrose content increased. Furthermore, glucose and fructose could undergo not only condensation reaction to produce sucrose but also Maillard or caramelization reactions to generate colored compounds affecting the browning color of papaya chips.

3.4 Color parameters

Color is one of the most important quality parameters in fruit and vegetable food products. The average L^* , a^* and b^* color values of fresh papaya discs were 34.9 ± 2.5 , 25.6 ± 2.2 and 40.0 ± 2.0 , respectively. A low color variation was observed in the papaya chips fried at 100 °C and 120 °C, but at 140 °C the color degradation was higher and more evident with the longest frying times (Fig. 3). For instance, after 14 min at 140 °C, L^* , a^* and b^* parameters significantly decreased ($p < 0.05$) to 29.2 ± 1.2 , 16.3 ± 0.9 and 22.1 ± 1.8 ,

respectively. On the other hand, at 100 °C and after 14 min of process, color parameters significantly increased ($p < 0.05$) and L^* , a^* and b^* values in papaya chips were 47.0 ± 1.3 , 35.6 ± 0.4 and 52.2 ± 1.6 , respectively. At 120 °C there was only a significant difference ($p < 0.05$) for b^* parameter; after 14 min of frying, papaya chips had a b^* value of 28.1 ± 0.5 .

There was not a clear trend for color change in papaya chips during vacuum frying and the L^* , a^* , b^* parameters could not be modeled during the process (data not shown). Papaya fruit is a complex matrix and the color variations in vacuum-fried papaya chips could be the result of carotenoid degradation (loss of red-orange color) and formation of molecules from Maillard or caramelization reactions (development of browning), and to a lesser extent the adsorbed oil in the chips during the frying process.

Nevertheless, the measurement of browning index (BI) in aqueous extracts obtained from papaya chips allowed the browning reaction that alters the color in the chips to be evaluated more accurately. Fig. 3 clearly shows that the browning color in aqueous extracts increased with increasing frying time and oil temperature. The variation of dimensionless value of browning index (BI/BI_0) in aqueous extracts of papaya chips at different temperatures is shown in Fig. 4.a. Experimental data for BI/BI_0 were fitted well with a 3-parameters logistic function (Eq. 4). Fig. 4.a shows that BI of aqueous extracts was sensitive to temperature change. For instance, the constant rate of browning formation (k_{BI}) increased by ~2-fold when the frying temperature was increased from 100 to 120 °C but increased by ~5.4-fold when temperature was increased from 120 to 140 °C (Table 1). Contrary to $L^*a^*b^*$ parameters of papaya chips, BI obtained by $L^*a^*b^*$ measurements on aqueous extracts was much more sensitive to the processing conditions and therefore more relevant for monitoring color variation.

Browning in papaya chips could be more related to caramelization than Maillard reaction due to intrinsic characteristics of papaya fruit. Papaya is a low acidity fruit (pH= 5.43) with a reducing sugar content of 6.51g/100 FW (59.19 g/100 g DW), specifically glucose and fructose, and a low protein content ($\sim 0.6 \text{ g} \cdot 100 \text{ g}^{-1}$ FW). The Maillard reaction takes place where reducing sugars react with amino acids and proteins during heating (Purlis, 2010; Martins et al., 2000). Caramelization requires temperatures $>120^\circ\text{C}$ and starts with an enolization reaction of sugars, in particular reducing sugars and sucrose (Kroh, 1994). Thus, BI is related to sugar degradation, specifically to reducing sugars (glucose and fructose). Fig. 4.b showed the linear correlation between BI and concentration of reducing sugars at different oil temperatures: r values were -0.760, -0.949 and -0.979 for the curves at 100, 120 and 140°C , as reducing sugars decreased, browning index increased.

Moreover, browning reactions mainly depend on temperature and a_w since this variable represents the availability of water for chemical reactions in food. Low a_w and high temperatures favor the formation of color during thermal treatment (Purlis, 2010). For instance, the production of colored compounds such as HMF always needs at least one dehydration step during the Maillard and caramelization reactions (Kroh, 1994).

In vacuum-fried papaya chips a negative linear correlation was observed between a_w and BI/BI_0 as shown in Fig. 4.c with a higher slope at 140°C : r values were -0.972, -0.929 and -0.996 for the curves at 100, 120 and 140°C , respectively. As oil temperature increased and a_w decreased in papaya chips during frying, browning development increased being faster at temperatures $>120^\circ\text{C}$.

3.5 Carotenoid reactivity

544 In terms of carotenoid reactivity, a clear difference was observed between carotenes and
545 xanthophyll during vacuum frying of papaya fruit. Carotenes such as β -carotene (BC) and
546 lycopene (LYC), contain only a parent hydrocarbon chain while xanthophylls such as β -
547 cryptoxanthin (BCX), contain an oxygen functional group (Ribeiro et al., 2018).

548 The variation of dimensionless concentrations of total BC and total LYC and their
549 respective isomers (expressed in non-fat dry weight) are represented in Table 2. In general,
550 at first there was an increase in BC and LYC attributed to an extractability phenomenon in
551 the first minutes of frying followed by a decrease phase because of degradation during the
552 rest of the process including isomerization (all-E- to Z-forms).

553 For all-E-BC (the main β -carotene isomer) the highest content ($p < 0.05$) was reached at 2
554 min of vacuum frying for all tested temperatures. In the case of Z-BC, there was an increase
555 in the formation of these isomers throughout the frying process, reaching the highest
556 concentrations after 8-14 min (Table 2). The Z-BC isomers found in papaya chips were 9Z-
557 and 13Z- β -carotene (Soto et al., 2020; Soto et al., 2021). It was observed that above 100 °C
558 the total BC degradation generally increased with oil temperature during the period studied.

559 The highest retentions ($p < 0.05$) of total BC and all-E-BC in papaya chips were obtained at
560 100 °C. In the case of all-E-LYC, there was a constant increase of extractability during
561 frying at 100 °C. For longest frying times all-E-LYC was better preserved at 100 °C than at
562 120 and 140 °C (Table 2). The Z-LYC content increased during vacuum frying, with the
563 highest concentration after 14 min at 100 and 120 °C and after 6 min at 140 °C. In general,
564 isomerization of lycopene increased at 140°C compared to 100 or 120 °C. The main Z-LYC
565 isomers found in papaya chips were 5Z-, 9Z- and 13Z-lycopene. In addition, at 120 and 140
566 °C there was a formation of two di-Z-lycopene forms but in a lower concentration
567 compared to the mono-Z-lycopene isomers.

There are few reports about carotenoid reactivity in foods during atmospheric frying and even less during vacuum frying. Degradation of β -carotene during deep-fat frying (under atmospheric conditions) varied according to the fruit or vegetable matrix. For instance, retentions of 80-98% was found in plantain cylinders (Rojas-Gonzalez et al., 2006); 72-86% in orange-fleshed sweet potato chips (Vimala et al., 2006); 28-32% in carrot crisps (Dueik et al., 2010); 32% in mango chips (Nunes, & Moreira, 2009). In the case of the impact of frying on lycopene degradation the information is scarce. The phenomenon of the extractability of β -carotene and especially of lycopene increasing during vacuum frying of papaya could be explained by two factors: i) a greater release of these carotenoids from papaya cell tissues (e.g. chromoplasts) due to the matrix structure disruption during frying (100-140 °C), and ii) an increase of their solubility enhanced by frying oil absorption in the chips. These findings are in agreement with those reported for several studies that described an increase of β -carotene and lycopene extractability during thermal processing of certain vegetables such as tomato, sweet potato and bell pepper (Colle et al., 2010; Dewanto et al., 2002; Re et al., 2002; Kidmose et al., 2006).

On the other hand, BCX presented a different behavior and was the least stable carotenoid compared to the others. There was an effect of frying time on dimensionless concentrations of BCX, expressed as non-fat dry weight at 120 and 140 °C (Fig. 5). For instance at 120 and 140°C, after 14 min of process there were losses of 40 and 60%, respectively. At 100 °C there was no BCX degradation. Notably, BCX decreased more rapidly at higher temperatures (120–140 °C). The mathematical model that best described the trend of BCX degradation in papaya chips was the second-order model as described previously during storage (Soto et al., 2020). The resulting rate constants are presented in Table 1. The rate

constant of degradation (k_{BCX}) increased with temperature (Table 1). BCX followed the Arrhenius temperature-dependency pattern ($R^2 = 0.85$). The rate constant of reference (k_{ref}) at the reference temperature of 120 °C was $4.0 \times 10^{-4} \text{ kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ and the activation energy (E_a) was $52 \text{ kJ} \cdot \text{mol}^{-1}$. The E_a value of BCX in the papaya chips was in accordance with that previously reported by Hadjal et al. (2013) in thermally treated blood orange juice ($62 \text{ kJ} \cdot \text{mol}^{-1}$). Aparicio-Ruiz et al. (2011) also found similar activation energies in virgin olive oil enriched with BCX during a heat treatment, $63\text{-}69 \text{ kJ} \cdot \text{mol}^{-1}$.

These results show that orange color degradation in papaya chips, measuring by $L^*a^*b^*$ parameters, is related to BCX degradation and not to BC or LYC loss. Chemical differences between xanthophyll and carotenes could affect their reactivity during vacuum frying. In the case of BCX, there was no effect of vacuum frying on its extractability as with carotenes. BC and LYC have poor solubility compared to BCX. For instance, lycopene has the lowest solubility and accumulates in the papaya matrix as crystals associated with the plastid membranes (Schweiggert et al., 2011). Thus, the oil uptake in the chips allows the crystalline structures of lycopene to dissolve increasing its extractability during analyses. For total BC, the maximum extractability was reached when the oil content was $\sim 0.13 \text{ g oil} \cdot \text{g}^{-1} \text{ chip DW}$. The maximum extractability of total LYC occurred when the chips had $\sim 0.26 \text{ g oil} \cdot \text{g}^{-1} \text{ chip DW}$ (at 120 and 140 °C) and $\sim 0.33 \text{ g oil} \cdot \text{g}^{-1} \text{ chip DW}$ (at 100 °C). Conformation, concentration, and lipid solubility of carotenoids in the papaya chips seemed to have a key effect on reactivity of these compounds during vacuum frying.

3.6 Optimization of vacuum frying process of papaya

In our study we focused on the influence of oil temperature and frying time on the main physicochemical properties that are related to sensory attributes and nutritional value of

vacuum-fried papaya chips as summarized in Fig. 6. Desirability of a_w , color and nutritional value in papaya chips was determined according to literature considering the most relevant physicochemical characteristics for this kind of products.

3.6.1 Desirability of a_w , color and nutritional value

a_w

Control of a_w in dried fruit products with high hygroscopicity such as papaya chips (due to low moisture content and high sugar content), is critical to ensure microbiological quality and to maintain texture quality during storage. Physical changes such as loss of crispness occur when the dried products gain water above the critical a_w , when they become soft or rubbery (Wolti-Chanes et al., 2007). It was observed that adequate crispness is obtained when a_w values in papaya chips ranged from 0.1 to 0.3 (moisture content ≤ 2 g·100 g⁻¹ chip FW) (Soto et al., 2021). Konopacka et al. (2002) found a critical a_w value of 0.2 for fat-free apple chips (moisture content 3.5 g·100 g⁻¹ chips); they described that increasing a_w in these chips above 0.3 resulted in complete loss of crispness. Critical a_w values for fruit chips are usually lower than those for chips based primarily on starch-protein mixtures (a_w 0.35-0.50) (Konopacka et al., 2002).

Color

The reaction impacting the color in papaya chips was browning (Maillard or caramelization) which affects quality. Therefore, it is desired that the browning index (BI) be as low as possible. There is no information in the reviewed literature about decoupling the pigment degradation from browning during fruit or vegetable processing and even less about BI determination in aqueous extracts from a solid food matrix as control parameter.

Food color acceptance by consumers depends on the food product. Some authors suggested that a color difference between raw and vacuum-fried fruits (ΔE) of 20 or less is acceptable; for instance, this was found for gold kiwifruit (Diamante et al., 2011) and apple (Mariscal, & Bouchon, 2008). In our case when aqueous extracts from papaya chips obtained BI/BI_0 greater than 5, the papaya chips presented $\Delta E > 20$ (data not shown). For this reason, it was determined that a BI/BI_0 of 5 (or $5 \cdot BI_0$, Fig. 3) should be considered as a criterion for a maximum limit in the chips.

Nutritional value

Our results showed that papaya chips are a good source of carotenoids, especially lycopene (70-77% of total carotenoids), and could be an alternative for vitamin A consumption as they provide retinol activity thanks to β -carotene and β -cryptoxanthin. For instance, after 10 min of vacuum frying the papaya chips presented a nutritional value of 91-128 μg Retinol Activity Equivalent (RAE) (portion of 40 g chips), which corresponds to 10-14% of the reference daily intake (RDI) (900 μg for adults and children ≥ 4 years) (FDA, 2020). It could be claimed that food products with 10% or more of the RDI for vitamin A (RAE) as “good source of vitamin A” (FDA, 2020). In papaya chips, the BCX represented ~70 % of total provitamin A activity expressed as RAE (see section 2.6.6). Therefore, the retention of BCX during vacuum frying is of importance for having provitamin A activity in papaya chips. In our study it was calculated that BCX losses lower than 30% ensured 10% or more of the RDI for vitamin A (RAE) in the papaya chips.

3.6.2 Optimization of vacuum frying conditions

Prediction of a_w , BI and BCX loss in papaya chips using the developed kinetic models is shown in Fig. 7. This figure shows that values of a_w between 0.1 and 0.3 (grey zone) are reached with frying times that range from 7 to 14 min. When the chips have a_w values ≤ 0.3 an equilibrium is reached, thus a_w is slightly affected by temperature. Contrary to final a_w , BCX and BI were more affected by oil temperature. BCX degradation and color variation increased with increasing oil temperature and frying time (Fig. 7). Low BCX loss and BI (under 20 % and $3 \cdot BI_0$, respectively) are not of interest because a_w values in papaya chips are close or above to 0.3 and would generate a product that is neither stable nor crispy. On the contrary, obtaining papaya chips with a_w values lower than 0.1 implies not only longer frying times but also higher BCX degradation and browning.

Fig. 7 shows a triangular zone with stripes embedded in the a_w stable zone in which the loss of BCX is lower than 30%, thus ensuring $\geq 10\%$ RDI of vitamin A (RAE) in the final product. This region comprises a combination of temperatures from 107 to 120 °C and frying times from 9 to 14 min that produce quality papaya chips with a_w values from 0.1 to 0.3 and low color degradation ($BI < 4 \cdot BI_0$). These frying conditions could be useful for processing papaya or other carotenoid-rich fruits keeping the same vacuum pressure and isothermal conditions. However, these conditions could change depending on the type of vacuum frying machine, type of oil, size, thickness, and shape of fruit slices, ratio product/oil, and ripening stage of fruit, among other factors.

3.7 Other sensory and nutritional attributes

Other factors, such as oil type, oil content, and sugar content, may be analyzed for producing vacuum-fried fruit chips. The sugars and oil not only provide calories in fruit chips but also contribute to their final taste. Therefore, it is important to control the quality

and content of these compounds. The type of oil affects the nutritional value of the final fried product. For instance, unsaturated vegetable oils are a source of essential fatty acids such as linoleic and alpha-linolenic acids, which are susceptible to oxidation during atmospheric frying (Márquez-Ruíz et al., 2010). However, one of the benefits of vacuum frying is preserving the oil quality because of the low temperatures employed and the minimal exposure to oxygen (Andrés-Bello et al., 2011; Belkova et al., 2018). For instance, the fatty acid profile of the soybean oil used as frying medium remained similar during vacuum frying of papaya fruit, after 12 trials at 120 °C (supplementary material 3). Nevertheless, it is necessary to verify the quality of frying medium by analyzing other parameters such as total polar compounds, oxidised fatty acids, and polymer triglycerides, which are the most reliable methods for monitoring oils during frying process (Gertz, 2000).

In the current study, the soybean oil used was mainly composed of polyunsaturated fatty acids such as linoleic acid (ω -6, 49.3% of total lipids), oleic acid (25.8% of total lipids), and alpha-linolenic acid (ω -3, 6.3% of total lipids). Therefore, it is relevant to find the right balance between the caloric intake provided by the oil and the contribution of essential fatty acids in the final product. In order to reduce the oil content in the chips, it is necessary to allow adequate oil drainage (using a centrifuge) when the product is removed from the fryer under vacuum (before pressurization of the vessel). For instance, by applying a higher centrifugation speed to the fried product, higher oil content is removed from the product surface (Moreira et al., 2009).

In the case of sugars, they provide the sweetness of the fried product. In addition, Maillard and caramelization reactions, which are involved in browning, depend on sugars. During vacuum frying, the sugars are concentrated, which is intrinsic to the process and inevitable.

But it is relevant to determine the process conditions that generate the least degradation of sugars, thus preserving the color and flavor of the final product. Because our study aimed to study the changes of the main physicochemical properties in chips, further sensory evaluation with consumers should be conducted to validate our results.

4. Conclusions

Physicochemical parameters measured in a carotenoid-rich fruit such as moisture, a_w , oil uptake, sucrose content, and browning index (BI) could be modeled as function of frying time at different oil temperatures. During vacuum frying of papaya fruit, the degradation of reducing sugars (glucose and fructose) was observed whereas the formation of sucrose occurred. Reducing sugars could be related to a condensation reaction producing sucrose and to Maillard or caramelization reactions producing colored compounds. BI in aqueous extracts obtained from papaya chips facilitated the characterization of the kinetics of Maillard or caramelization reactions that alter color in the chips. However, further studies in papaya and other carotenoid-rich fruits are needed to identify the specific compounds involved in browning and elucidate the mechanisms involved in sugar reactions during frying. There was a clear difference in reactivity between xanthophylls (BCX) and carotenes (BC and LYC). BCX was the less stable carotenoid while BC and LYC contents were influenced by the extraction efficiency from the matrix. Moisture content (measured by a_w) plays a key role for most of the important quality parameters, either directly, e.g. oil uptake and texture, or indirectly for chemical reactions, e.g. browning. Prediction of a_w , BI (in aqueous extracts), and BCX loss can be used to optimize process conditions to produce quality fried chips from papaya fruit. The results obtained allowed the monitoring and modelling of physicochemical parameters related to sensory and nutritional attributes of

great relevance for this type of product. This research brings new information about the reactivity of carotenoids and sugars during the frying of fruits. From a practical point of view, this information will be useful for snack producers who want to make fried products based on fruits rich in carotenoids with high moisture and sugar content.

Declaration of competing interest

No conflict of interest involving any of the authors.

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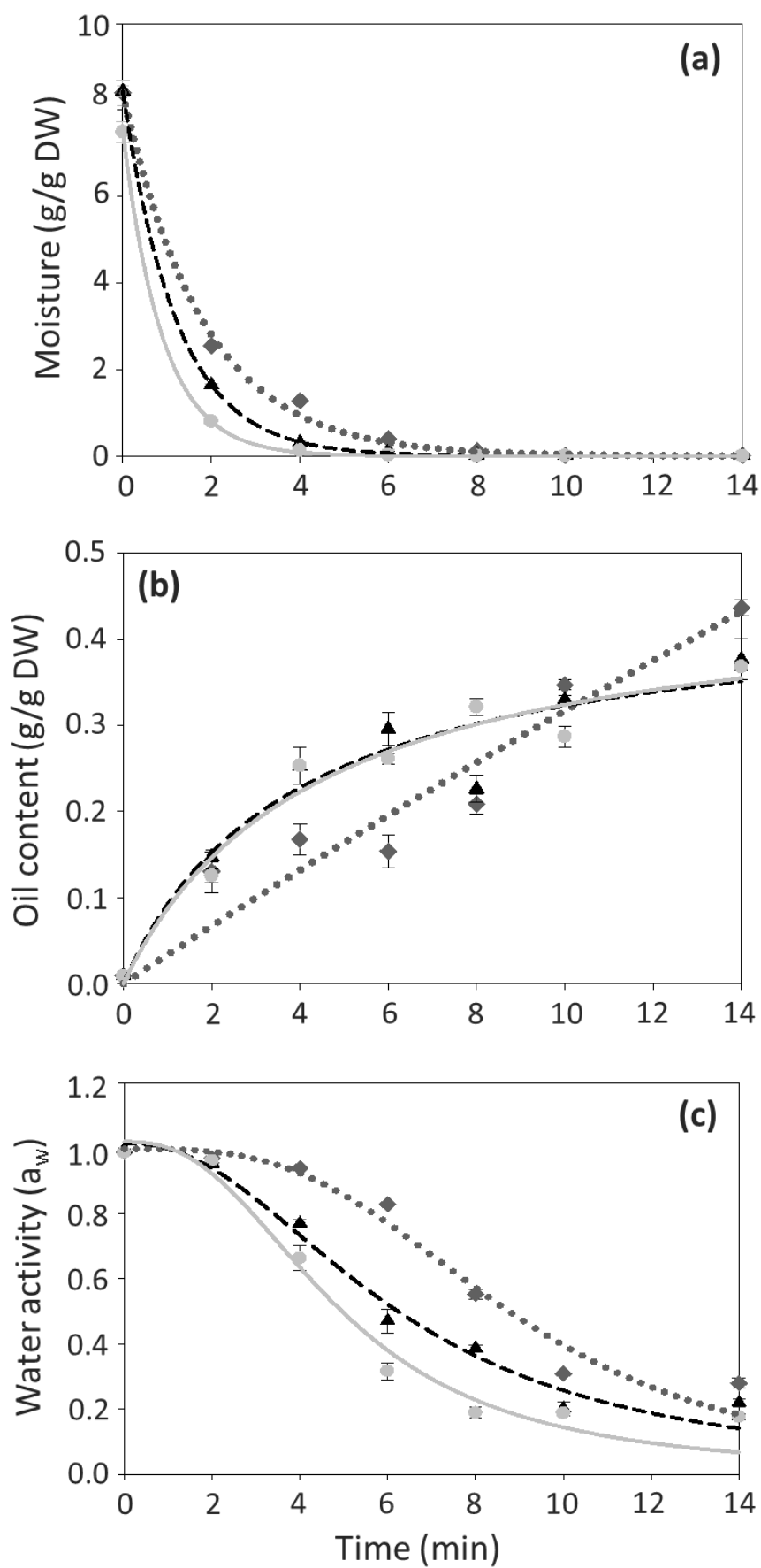
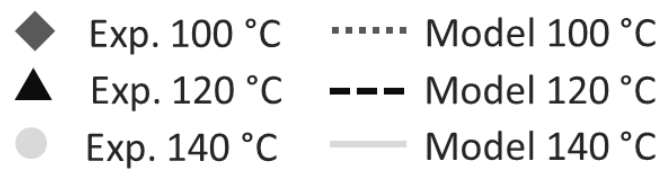
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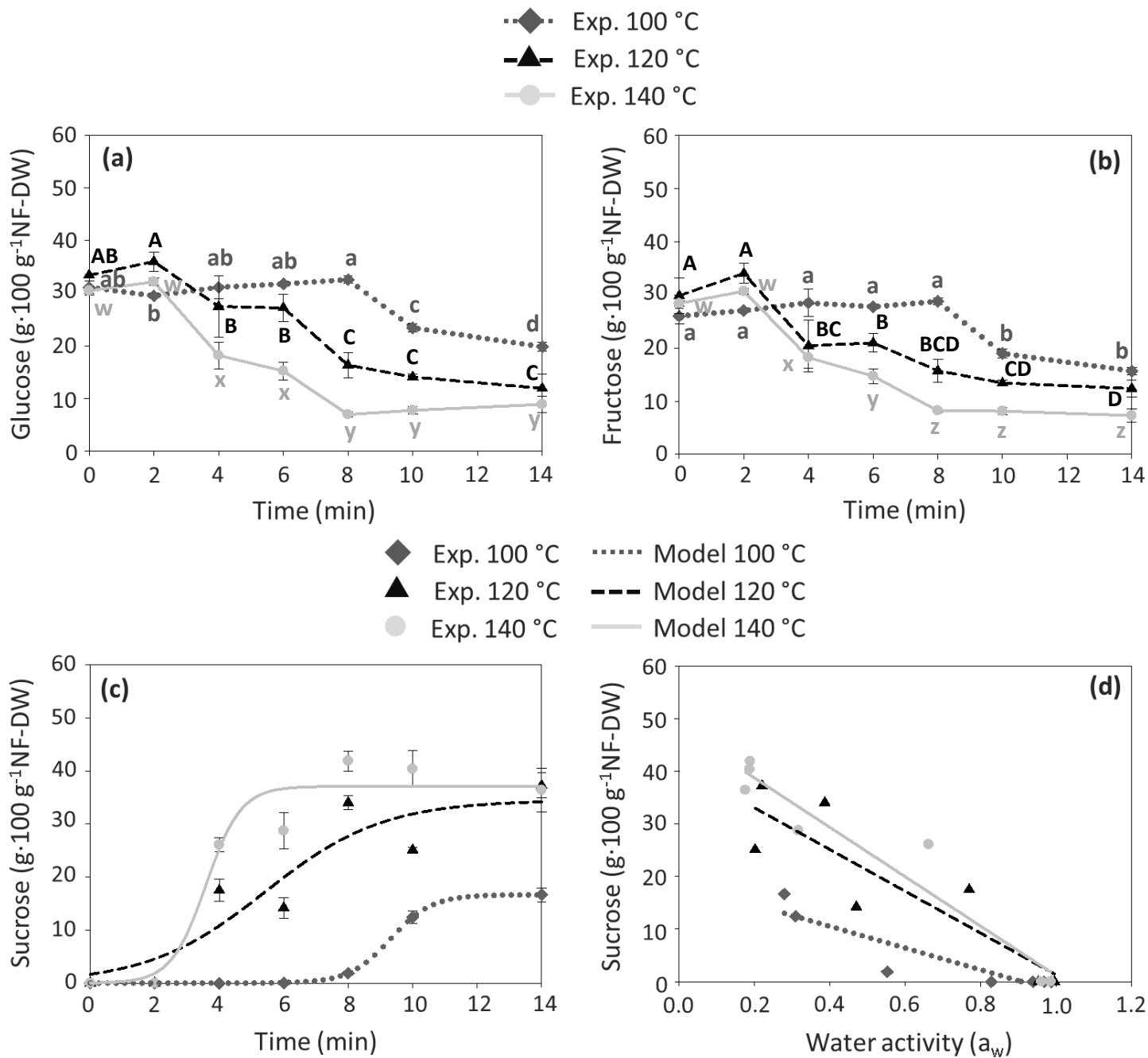
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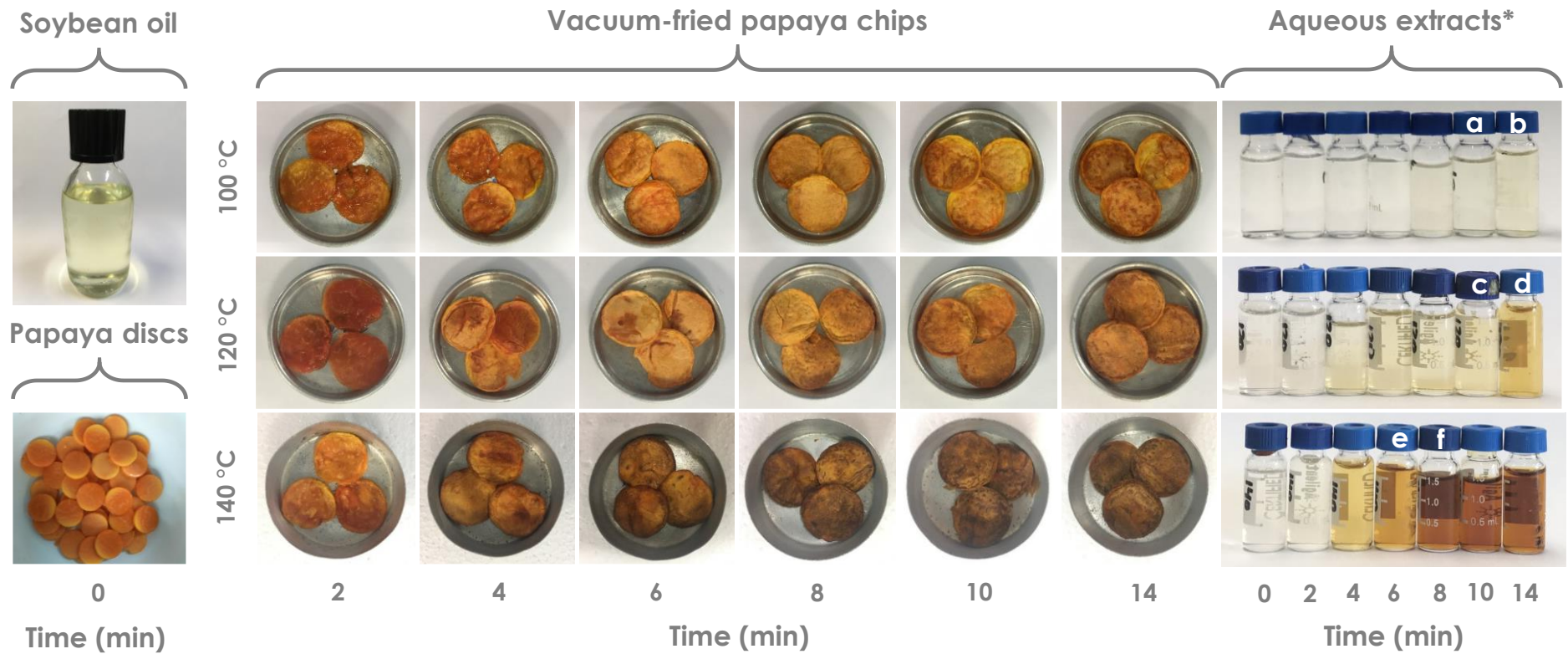
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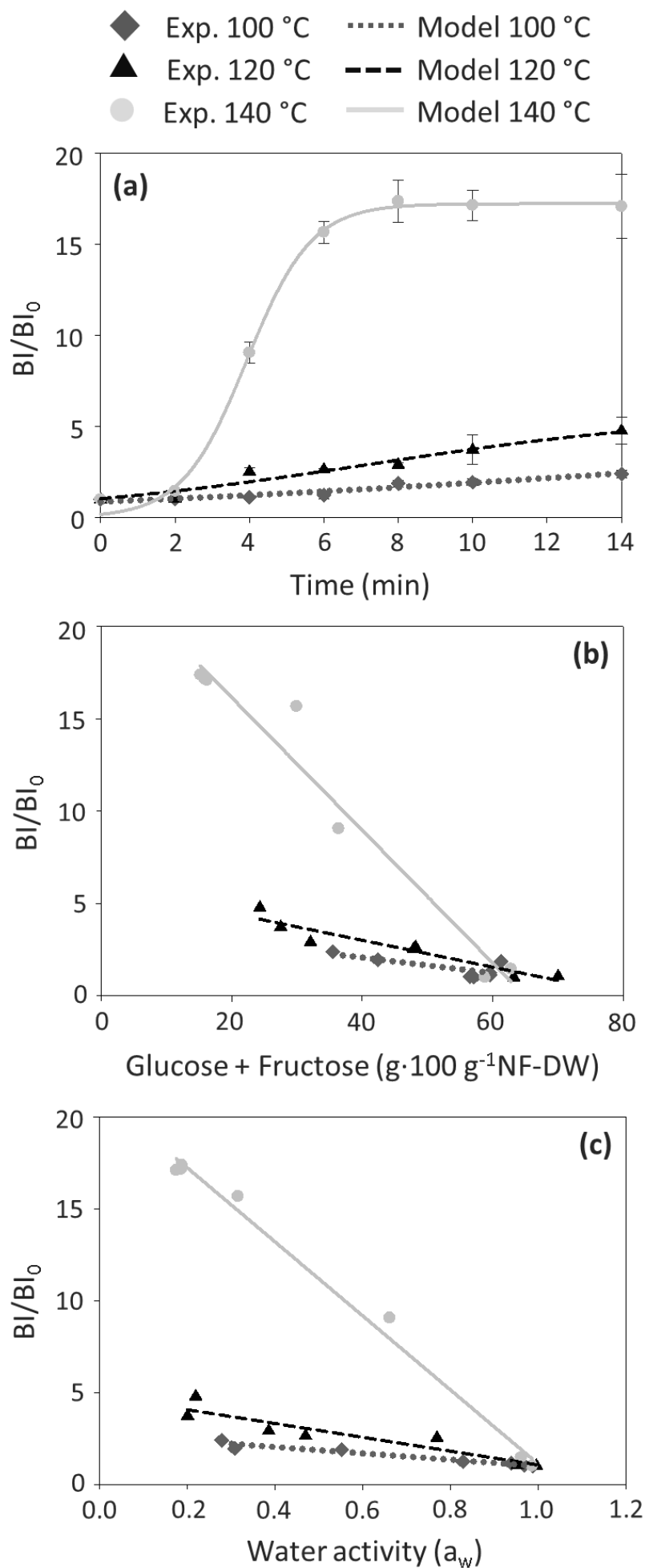
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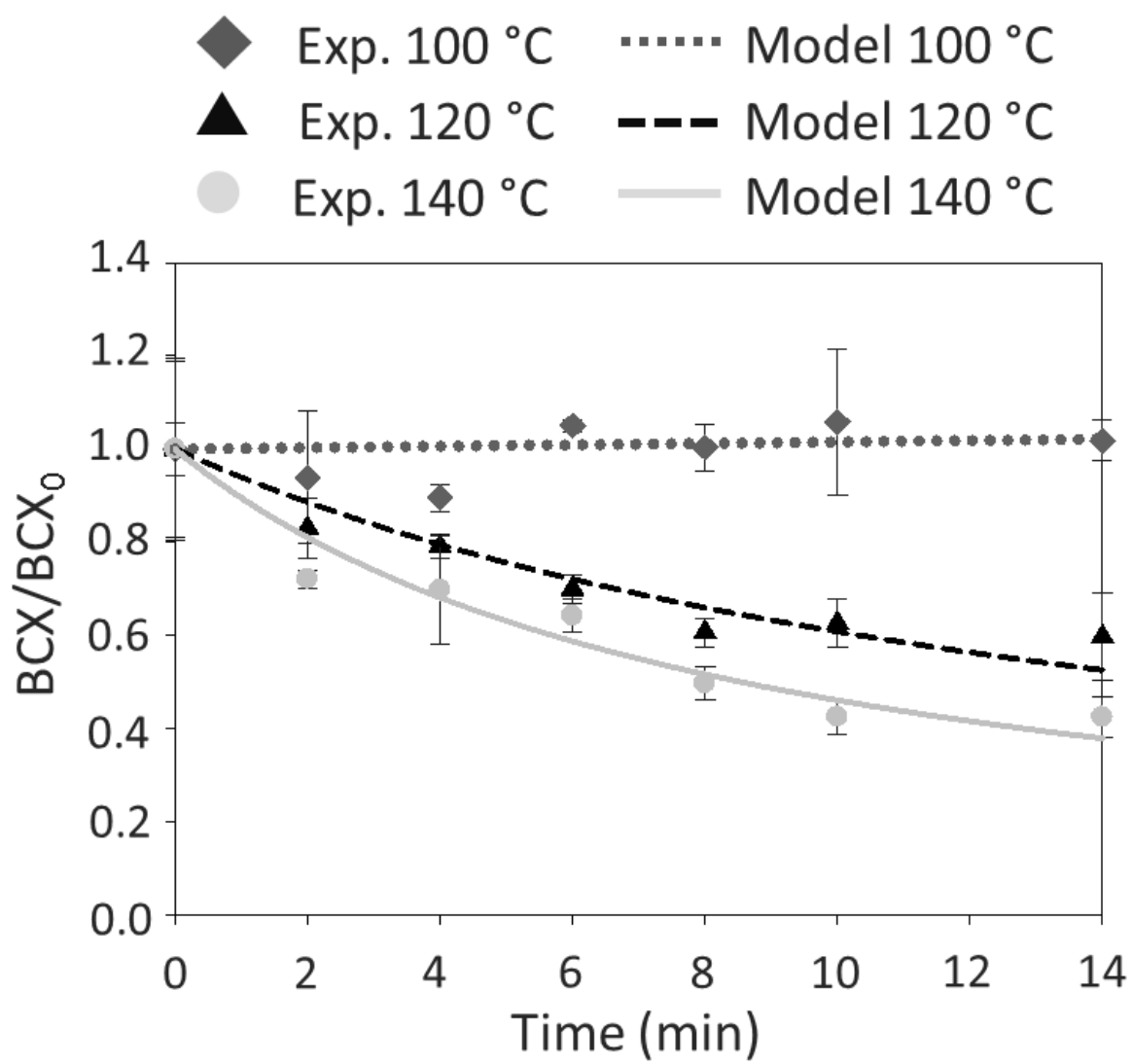
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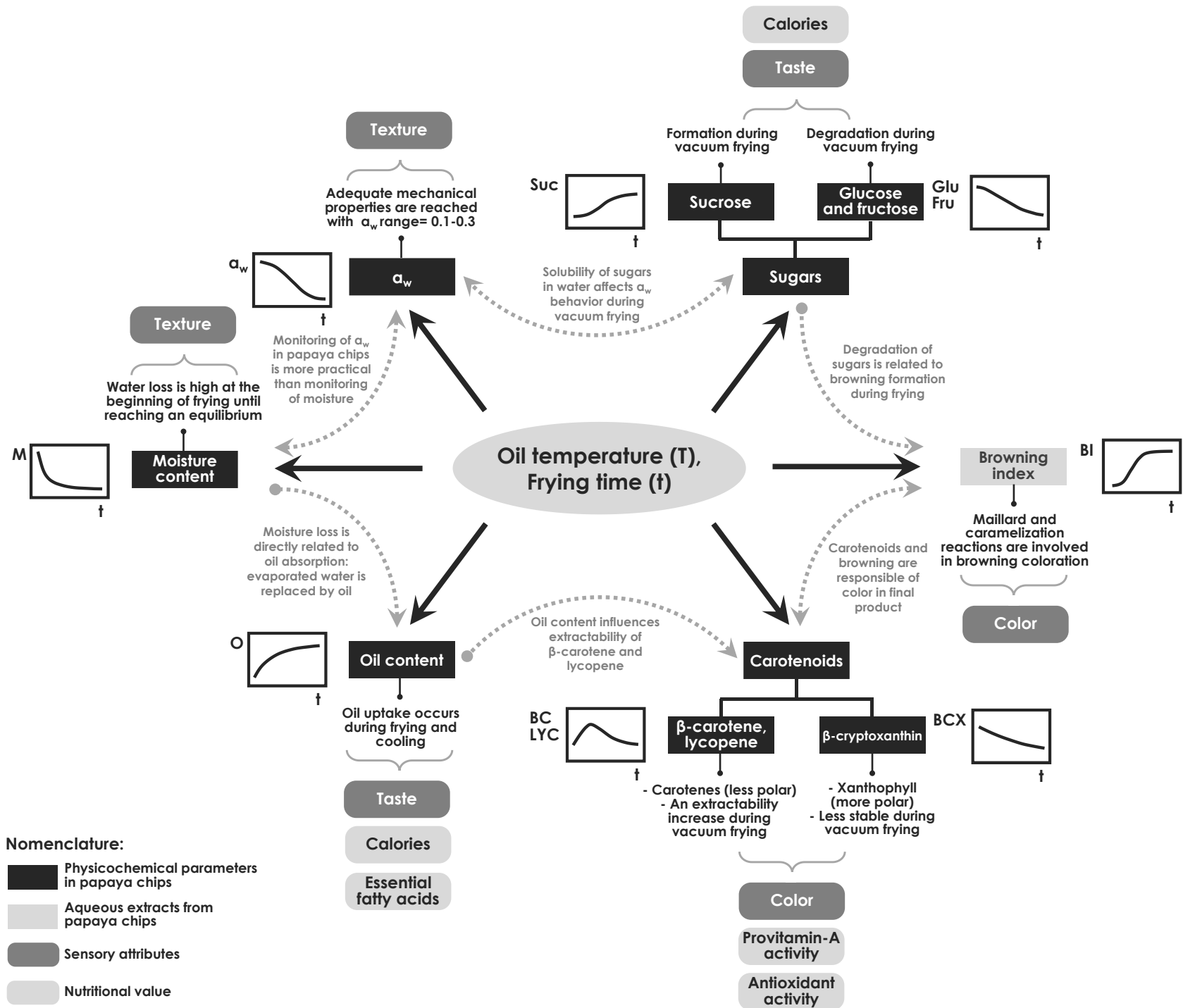


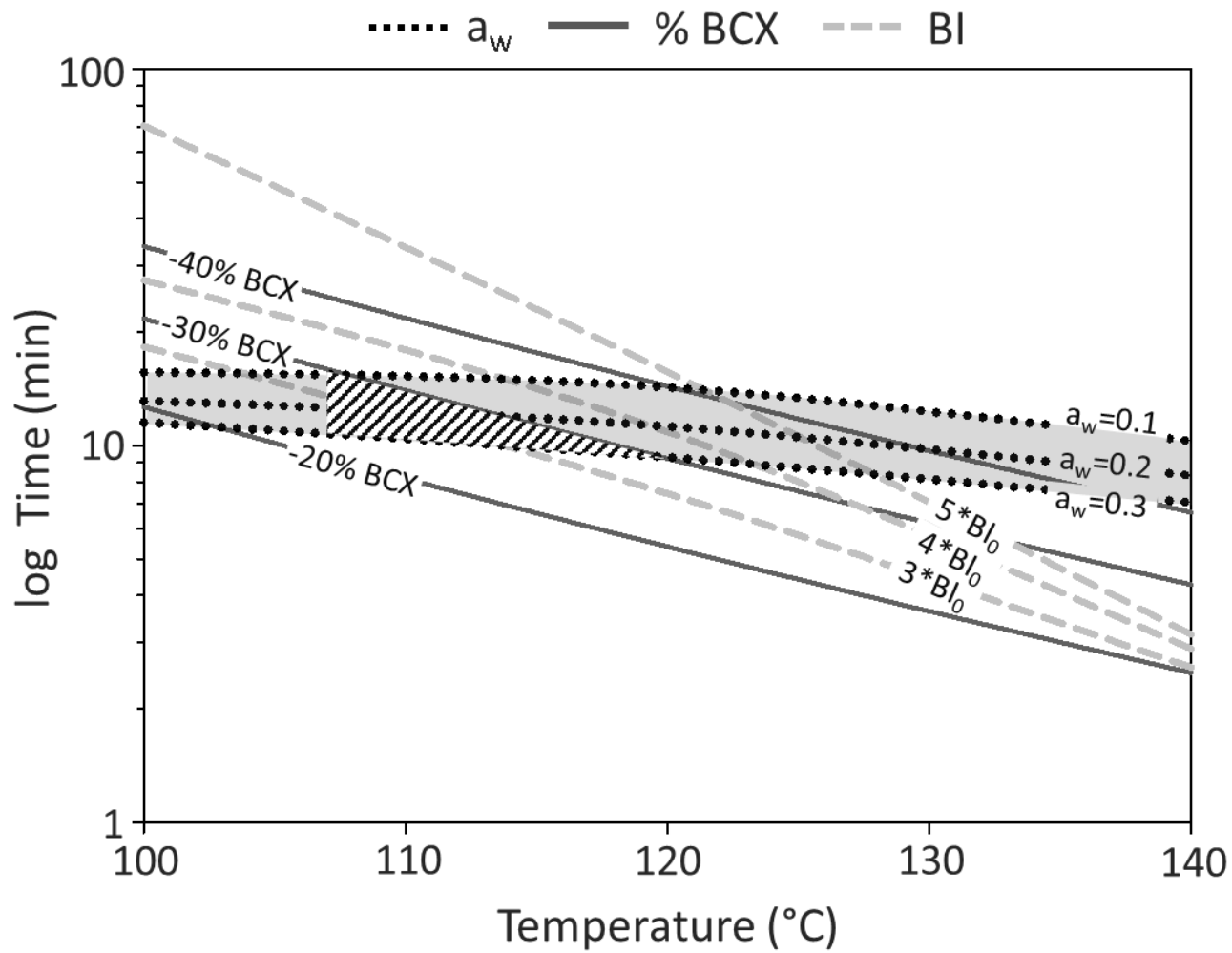












1 Tables

2 **Table 1.** Kinetic parameters from models generated for moisture content, oil content, a_w ,
3 sucrose, browning index and β -cryptoxanthin.

4

Parameter	T (°C)	p-value of model	R ²	Kinetic parameters
Moisture content (M)	100	<0.0001	0.997	$k_M = 0.5474$ (0.0253)
	120	<0.0001	0.999	$k_M = 0.8145$ (0.0086)
	140	<0.0001	0.999	$k_M = 1.1132$ (0.0115)
Oil content (O)	100	0.0007	0.915	$O_e = 2.6259$ (8.5157); $k_O = 0.0129$ (0.0447)
	120	0.0010	0.903	$O_e = 0.3518$ (0.0424); $k_O = 0.2594$ (0.0901)
	140	0.0001	0.961	$O_e = 0.3567$ (0.0285); $k_O = 0.2470$ (0.0551)
Water activity (a_w)	100	0.0042	0.9355	$L_{aw} = 1.0968$ (0.1491); $b_{aw} = 8.4770$ (1.2244); $k_{aw} = -0.3214$ (0.1111)
	120	0.0020	0.9551	$L_{aw} = 1.3988$ (0.4917); $b_{aw} = 4.2074$ (3.2026); $k_{aw} = -0.2549$ (0.0930)
	140	0.0037	0.9394	$L_{aw} = 1.2307$ (0.3446); $b_{aw} = 4.2260$ (1.8508); $k_{aw} = -0.4012$ (0.1621)
Sucrose (suc)	100	<0.0001	1.0000	$L_{suc} = 16.6508$ (0.0463); $b_{suc} = 9.31601$ (0.0100); $k_{suc} = 1.5685$ (0.0160)
	120	0.0214	0.8536	$L_{suc} = 34.4856$ (6.7104); $b_{suc} = 5.4333$ (1.3868); $k_{suc} = 0.5479$ (0.3291)
	140	0.0028	0.9470	$L_{suc} = 37.0830$ (2.5857); $b_{suc} = 3.5910$ (0.4192); $k_{suc} = 1.8472$ (1.4312)
Browning index (BI)	100	0.0038	0.939	$L_{BI} = 5.0128$ (5.8417); $b_{BI} = 14.5270$ (20.9550); $k_{BI} = 0.1064$ (0.0655)
	120	0.0025	0.950	$L_{BI} = 5.8191$ (1.4827); $b_{BI} = 7.1559$ (2.8715); $k_{BI} = 0.2124$ (0.0721)
	140	<0.0001	0.997	$L_{BI} = 17.2378$ (0.2696); $b_{BI} = 3.9264$ (0.0925); $k_{BI} = 1.1519$ (0.1210)
β -crypto-xanthin (BCX)	100	0.6043	0.037	$k_{BCX} = 0$
	120	<0.0001	0.910	$k_{BCX} = 5.00 \times 10^{-4}$ (4.27×10^{-5})
	140	<0.0001	0.940	$k_{BCX} = 9.00 \times 10^{-4}$ (8.04×10^{-5})

5 Standard error is expressed in brackets (n=3). Units of kinetic parameters: k_M , k_O , k_{aw} , k_{suc} ,

6 and k_{BI} , are expressed in min^{-1} , and k_{BCX} is expressed in $\text{kg} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$; O_e is expressed in $\text{g} \cdot \text{g}^{-1}$

7 $^1 \text{DW}$; L_{aw} , and L_{BI} are expressed in dimensionless form, and L_{suc} is expressed in $\text{g} \cdot 100 \text{ g}^{-1}$

8 NF-DW; b_{aw} , b_{suc} , and b_{BI} are expressed in min.

Table 2. Variation of dimensionless concentration of total lycopene and total β -carotene and their isomers in papaya chips during vacuum frying at different temperatures.

T (°C)	Time (min)						
	0	2	4	6	8	10	14
<i>all-E-BC/Total BC₀</i>							
100	0.91 ± 0.19 ^{c,A}	2.93 ± 0.56 ^{a,A}	2.76 ± 0.13 ^{a,A}	2.05 ± 0.07 ^{b,A}	1.75 ± 0.02 ^{b,A}	1.93 ± 0.15 ^{b,A}	1.68 ± 0.10 ^{b,A}
120	0.95 ± 0.16 ^{bc,A}	1.98 ± 0.21 ^{a,B}	1.22 ± 0.05 ^{b,B}	1.22 ± 0.04 ^{b,B}	0.93 ± 0.08 ^{bc,B}	0.78 ± 0.10 ^{c,B}	0.74 ± 0.13 ^{c,B}
140	0.92 ± 0.28 ^{bc,A}	1.41 ± 0.03 ^{a,B}	1.00 ± 0.15 ^{b,B}	0.94 ± 0.09 ^{bc,C}	0.65 ± 0.09 ^{bc,C}	0.57 ± 0.03 ^{c,B}	0.62 ± 0.10 ^{bc,B}
<i>Z-BC/Total BC₀</i>							
100	0.093 ± 0.003 ^{d,A}	0.62 ± 0.09 ^{bc,A}	0.59 ± 0.07 ^{c,A}	0.82 ± 0.07 ^{b,A}	0.81 ± 0.04 ^{b,A}	0.81 ± 0.12 ^{bc,A}	1.05 ± 0.09 ^{a,A}
120	0.053 ± 0.001 ^{d,C}	0.45 ± 0.01 ^{c,A}	0.68 ± 0.15 ^{ab,A}	0.68 ± 0.09 ^{ab,AB}	0.74 ± 0.05 ^{a,A}	0.49 ± 0.01 ^{bc,B}	0.57 ± 0.12 ^{abc,B}
140	0.085 ± 0.003 ^{d,B}	0.44 ± 0.13 ^{c,A}	0.51 ± 0.11 ^{bc,A}	0.53 ± 0.07 ^{bc,B}	0.51 ± 0.08 ^{bc,B}	0.83 ± 0.09 ^{a,A}	0.70 ± 0.09 ^{ab,B}
<i>Total BC/Total BC₀</i>							
100	1.00 ± 0.18 ^{c,A}	3.55 ± 0.64 ^{a,A}	3.35 ± 0.20 ^{ab,A}	2.86 ± 0.04 ^{ab,A}	2.56 ± 0.04 ^{b,A}	2.74 ± 0.27 ^{b,A}	2.74 ± 0.19 ^{b,A}
120	1.00 ± 0.16 ^{d,A}	2.42 ± 0.20 ^{a,B}	1.91 ± 0.19 ^{b,B}	1.90 ± 0.13 ^{b,B}	1.67 ± 0.13 ^{bc,B}	1.26 ± 0.11 ^{cd,B}	1.31 ± 0.25 ^{cd,B}
140	1.00 ± 0.28 ^{b,A}	1.85 ± 0.15 ^{a,B}	1.50 ± 0.25 ^{ab,B}	1.46 ± 0.16 ^{ab,C}	1.15 ± 0.15 ^{b,C}	1.40 ± 0.11 ^{ab,B}	1.32 ± 0.15 ^{b,B}
<i>all-E-LYC/Total LYC₀</i>							
100	0.83 ± 0.12 ^{d,A}	1.72 ± 0.25 ^{c,A}	2.14 ± 0.12 ^{b,A}	2.12 ± 0.09 ^{b,A}	2.38 ± 0.07 ^{ab,A}	2.54 ± 0.04 ^{a,A}	2.20 ± 0.15 ^{ab,A}
120	0.84 ± 0.10 ^{d,A}	1.98 ± 0.06 ^{b,A}	2.49 ± 0.21 ^{a,A}	2.07 ± 0.13 ^{ab,A}	1.88 ± 0.26 ^{bc,B}	1.83 ± 0.18 ^{bc,B}	1.53 ± 0.07 ^{c,B}
140	0.83 ± 0.07 ^{c,A}	1.66 ± 0.08 ^{b,A}	2.07 ± 0.27 ^{a,A}	1.51 ± 0.02 ^{b,B}	1.06 ± 0.04 ^{c,C}	0.99 ± 0.05 ^{c,C}	0.87 ± 0.10 ^{c,C}
<i>Z-LYC/Total LYC₀</i>							
100	0.17 ± 0.01 ^{e,A}	0.32 ± 0.00 ^{d,A}	0.41 ± 0.03 ^{bc,B}	0.34 ± 0.01 ^{cd,C}	0.39 ± 0.02 ^{bcd,C}	0.46 ± 0.04 ^{b,B}	0.56 ± 0.00 ^{a,C}
120	0.16 ± 0.02 ^{d,A}	0.30 ± 0.02 ^{c,A}	0.53 ± 0.02 ^{b,B}	0.59 ± 0.03 ^{b,B}	0.58 ± 0.05 ^{b,B}	0.57 ± 0.01 ^{b,B}	0.70 ± 0.03 ^{a,B}
140	0.17 ± 0.01 ^{c,A}	0.38 ± 0.07 ^{c,A}	0.89 ± 0.12 ^{b,A}	1.17 ± 0.03 ^{a,A}	1.12 ± 0.05 ^{a,A}	1.01 ± 0.12 ^{ab,A}	1.03 ± 0.06 ^{ab,A}
<i>Total LYC/Total LYC₀</i>							
100	1.00 ± 0.13 ^{d,A}	2.04 ± 0.26 ^{c,A}	2.56 ± 0.08 ^{b,A}	2.47 ± 0.10 ^{b,A}	2.78 ± 0.08 ^{ab,A}	3.00 ± 0.05 ^{a,A}	2.76 ± 0.16 ^{ab,A}
120	1.00 ± 0.12 ^{c,A}	2.27 ± 0.08 ^{b,A}	3.02 ± 0.23 ^{a,A}	2.66 ± 0.15 ^{ab,A}	2.45 ± 0.31 ^{b,AB}	2.41 ± 0.17 ^{b,B}	2.23 ± 0.08 ^{b,B}
140	1.00 ± 0.07 ^{d,A}	2.04 ± 0.15 ^{c,A}	2.95 ± 0.39 ^{a,A}	2.68 ± 0.03 ^{ab,A}	2.19 ± 0.09 ^{cb,B}	2.00 ± 0.16 ^{c,C}	1.90 ± 0.10 ^{c,C}

Values are expressed as the mean ± standard deviation (n=3). For each carotenoid, mean values in the same row with the same lower case letters are not significantly different from each other; and mean values in the same column with the same upper case letters are not significantly different from each other (Tukey's test, $p < 0.05$). Carotenoids: all-E-BC, all-E- β -carotene; Z-BC, Z- β -carotene; Total BC, total β -carotene (sum of all-E-BC + Z-BC); all-E-LYC, all-E-lycopene; Z-LYC, Z-lycopene; Total LYC, total lycopene (sum of all-E-LYC + Z-LYC). BC₀ and LYC₀, initial content (t=0) of β -carotene and lycopene, respectively.