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

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Abbreviations

a_w	water activity (dimensionless)
all-*E*, *Z*	carotenoid isomer forms
BC, BC_0	β-carotene, and initial β-carotene content (mg·kg^{-1} NF-DW)
BCX, BCX_0	β-cryptoxanthin, and initial β-cryptoxanthin content (mg·kg^{-1} NF-DW)
BI, BI_0	browning index, and initial browning index (dimensionless)
b_{aw}, b_{BI}, b_{suc}	time to reach the sigmoid's midpoint for a_w, browning index and sucrose (min)
DW	dry weight
E_a	activation energy (J·mol^{-1})
Exp	experimental data
FW	fresh weight
k_{aw}, k_{BI}, k_{suc}	rate constant of a_w, browning index, and sucrose (min^{-1})
k_{BCX}, k_{ref}	β-cryptoxanthin degradation rate constant, and rate constant at reference temperature (kg·mg^{-1}·min^{-1})
k_M	rate of water loss (min^{-1})
k_O	rate of oil uptake (min^{-1})
L*, a*, b*	CIELAB color space parameters (dimensionless)
L_{aw}, L_{BI},	curve's maximum of a_w, and browning index (dimensionless)
L_{suc}	curve's maximum of sucrose (g·100 g^{-1} NF-DW)
LYC, LYC_0	lycopene, and initial lycopene content (mg·kg^{-1} NF-DW)
M, M_0	moisture content, and initial moisture content (g·g^{-1} DW)

NF-DW	non-fat dry weight
O, O_e	oil content, and oil content at infinite time ($g \cdot g^{-1}$ DW)
p	probability
r	correlation coefficient
R	gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$)
R^2	coefficient of determination
RAE	retinol activity equivalent
RDI	reference daily intake
t	time, min
T	temperature (°C or K)
T_{ref}	reference temperature (°C or K)
ΔE	color difference

53 **Abstract**

54 Vacuum frying is an alternative technology to obtain fruit snacks with higher sensory and
55 nutritional quality compared to traditional fried snacks. Vacuum frying of a carotenoid-rich
56 fruit (red-fleshed papaya) was performed at 25 kPa, using soybean oil at 100, 120, and
57 140°C from 0 to 14 min. The study aimed to monitor and model physicochemical changes
58 that chips undergo during vacuum frying, which are related to their sensory and nutritional
59 attributes. Moisture content, a_w, oil uptake, sugar content, browning index (BI) and
60 carotenoid contents were monitored. Water loss and oil uptake followed first-order kinetics
61 while the decrease in a_w followed a logistic trend. Glucose and fructose followed the same
62 degradation pattern while BI and sucrose content increased as a function of frying time and
63 oil temperature. β-cryptoxanthin (BCX) loss followed second-order kinetics and retention
64 was 60 and 40% after 14 min at 120 and 140 °C, respectively. Contents of lycopene and β-
65 carotene were increased suggesting an improvement in availability of these compounds to
66 extraction. Optimal vacuum frying conditions for processing papaya fruit comprise a
67 combination of temperatures (107-120 °C) and frying times (9-14 min) to produce quality
68 papaya chips with a_w ranging from 0.1 to 0.3, low color degradation and BCX loss ≤30 %.

69

70 **Keywords**

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

72

73 **1. Introduction**

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

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

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

Different physicochemical changes occur in foods during frying affecting their sensory and nutritional attributes. During frying, the food product loses water rapidly and gains oil, specially at the food's surface (Fan et al., 2010). Moisture content in dehydrated foods (those with a_w in the range of 0.1 to 0.4) is of upmost importance to obtain a product with adequate mechanical properties, such as crispness. Likewise, during frying, some compounds (e.g., sugars, vitamins, and pigments) undergo reactions in the fried food that 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) (Kopec, & 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

125 product. The information generated from this study will be of great interest for
126 manufacturers of fried products who try to obtain attractive and healthy snacks.
127
128 **2. Materials and methods**
129 *2.1. Materials*
130 Red-fleshed papaya fruits (*Carica papaya* L.) from hermaphrodite plants of the commercial
131 Costa Rican hybrid Pococí were acquired from Orofrut (Orotina, Alajuela, Costa Rica) in
132 October 2019 at ripening stage 4 (41-55% of skin yellowing). Commercial soybean frying
133 oil Clover® (Grupo NUMAR, Costa Rica) was used as frying medium.
134
135 *2.2. Chemicals*
136 The following chemicals were used: SigmaUltra standards for glucose, fructose, and
137 sucrose from Sigma-Aldrich (St. Louis, MO, USA); β-carotene, β-cryptoxanthin and
138 lycopene standards from Sigma-Aldrich (St. Louis, MO, USA). Other analytical grade
139 chemicals and HPLC grade solvents were purchased from JT Baker Inc. (Phillipsburg, NJ,
140 USA).
141
142 *2.3. Sample preparation*
143 Papaya fruits were selected and then washed and peeled manually. Each fruit was vertically
144 cut into 4 pieces and the seeds were removed. The pre-cut pieces were sliced, firstly into 4-
145 mm thick pieces using a food processor (FP-100 Hobart, CA, USA) and then into discs
146 (diameter 30.0 ± 0.2 mm) using a circle-shaped cookie cutter.
147

148 *2.4. Vacuum frying*

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

163

164 *2.5. Study design*

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

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

179

180 *2.6. Physicochemical analyses*

181 *2.6.1 Moisture content, oil content, a_w, protein content and pH*

182 Moisture was determined using AOAC standard method 920.151 (AOAC, 2015). Lipid
183 content was determined by the method described by Carpenter et al. (1993). Water activity
184 of the samples were determined at 25 °C using a water activity meter (Aqualab, model CX-
185 2, Decagon Devices, Inc., Pullman, WA).
186 In addition, protein content and pH value were determined in fresh papaya. Protein content
187 was measured by standard AOAC method 920.152 (AOAC, 2015) using a nitrogen
188 conversion factor of 6.25. To measure pH, a digital pH-meter (Metrohm 827 pH lab meter,
189 Metrohm Ion Analysis, Switzerland) was used.

190

191 *2.6.2. Sugar content*

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

195 tubes. Then 5 mL of distilled H_2O was added and mixed using an IKA® Ultra-Turrax®
196 (Merck KGaA, Darmstadt, Germany) for 5 min. The mixture was incubated for 30 min in a
197 water bath at 70 °C. After incubation, the tubes were cooled in an ice bath and centrifuged
198 at 1400 x g (Allegra 21 Centrifuge, Beckman Coulter, Switzerland) for 10 min at 15 °C.
199 The supernatant was membrane filtered (0.45 μm) prior to sugar analysis.

200 Sugars (sucrose, glucose, and fructose) were determined by the Shimadzu HPLC system
201 (Shimadzu Manufacturing, Inc., Canby, Oregón, USA) equipped with a RID-10A refractive
202 index detector, a DGU-20A5 degasser, a SIL-20AHT autosampler, a CTO-20A column
203 oven and a LC-20AT binary gradient pump. Sugars were separated using a Zorbax
204 carbohydrate column (250 mm x 4.6 mm i.d., 5 μm) (Agilent, CA, USA) with a guard
205 column. The mobile phase was acetonitrile/H_2O (80/20). The operation temperature was set
206 at 30 ºC. The flow rate was set at 1mL/min and the injection volume was 10 μL. Isocratic
207 conditions were programmed with a run time of 15 min. Quantification was performed after
208 obtaining linear calibration curves of glucose, fructose, and sucrose. In order to keep the
209 same basis among samples, the results were expressed as non-fat dry weight.

210

211 *2.6.3. Color analysis in papaya chips*

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

215

216 *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 $CaCl_2$ (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 H_2O 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:

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

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).

240 *2.6.5. Carotenoid content*

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

253 Carotenoid identification was performed by HPLC using an Agilent 1100HPLC-DAD
254 system (Massy, France). Carotenoids were separated using a C30 column (150 mm x 4.6
255 mm i.d., 3 µm) (YMC EUROP GmbH, Germany) with a guard column, and the mobile
256 phase was methanol as eluent A and MTBE as eluent B. Operation temperature was set at
257 30 ºC. The flow rate was set at 0.6 mL/min and the injection volume was 10 µL. The
258 gradient program is described by Soto et al. (2021). All-E-β-cryptoxanthin, all-E-β-carotene
259 and their isomers were detected at 450 nm, and all-E-lycopene and their isomers were
260 detected at 470 nm (Soto et al., 2020). The contents of Z-β-carotene and Z-lycopene were
261 expressed as the sum of all their Z-isomers, respectively. In order to maintain the same
262 basis among samples, the results were expressed on a non-fat dry weight basis.

263

264 *2.6.6. Vitamin A activity*

265 Vitamin A activity was expressed as Retinol Activity Equivalent (RAE). RAE estimate was
266 calculated for a bioconversion ratio (carotenoid:retinol) of 12:1 for all-E-β-carotene, and
267 24:1 for all-E-β-cryptoxanthin and Z-β-carotene (US IOM, 2000).

268

269 *2.7. Kinetic modelling*

270 *2.7.1. Moisture content*

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

276

277 $$M = M_0 * exp^{(-k_M * t)} \quad [2]$$

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

281

282 *2.7.2. Oil content*

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

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

where O is the oil content at time t (g·g^{-1} DW); O_e is the oil content at infinite time (t=∞); (g·g^{-1} DW); k_O represents the specific rate of oil uptake for this model (min^{-1}); t is the frying time (min).

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

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

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

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

2.7.4. β-cryptoxanthin

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

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

where BCX represents the carotenoid concentration at time t and BCX_0 is the initial concentration ($t=0$) (mg·kg^{-1} non-fat dry weight); k_{BCX} is the reaction rate constant (kg·mg^{-1}·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.

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

where k_{ref} is the rate constant (kg·mg^{-1}·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 (J·mol^{-1}), medium temperature (K), and gas constant (8.314 J·mol^{-1}·K^{-1}).

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).

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

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

331 R^2 was calculated from the ratio of the explained variance to the total variance (TSS), with
332 the explained variance being TSS minus RSS:
333
334 $$R^2 = \frac{\sum_{i=1}^{n}(y_i-\bar{y})^2-RSS}{\sum_{i=1}^{n}(y_i-\bar{y})^2} \quad [8]$$
335 where $\bar{y}$ is the mean value of the dependent variable (moisture content, oil content, a_w,
336 sucrose content, browning index, β-cryptoxanthin content), and n is the number of
337 experimental points. Kinetic parameters for different physicochemical properties in papaya
338 chips were identified using SigmaPlot software (Systat Software Inc., CA, USA). The
339 parameter uncertainly was calculated as the standard error of regression.
340
341 *2.9. Statistical analyses*
342 The different frying conditions were performed in three repetitions. Data were presented as
343 mean ± standard deviation of replicates. Kinetic parameters for different physicochemical
344 properties of papaya chips were expressed as mean with its respective standard error. The
345 variation of lycopene and β-carotene isomers in papaya chips during vacuum frying was
346 analyzed by one-way ANOVA and post hoc Tukey-HSD test to detect significant
347 differences ($p<0.05$). ANOVA was performed using Statistica 7.0 (Statsoft Inc., USA).
348 Correlation analyses from experimental data of sugar contents, a_w and BI of papaya chips
349 were done with SigmaPlot software (Systat Software Inc., CA, USA).
350
351 **3. Results and discussion**
352 **3.1 Physicochemical properties of fresh papaya**

353 Some characteristics were determined in fresh Pococí papaya at ripening stage of 4 (RS4:
354 41-55 % of skin yellowing) selected to produce papaya chips. Moisture content (88.99 ±
355 0.67 g·100 g^{-1} fresh weight (FW)) and a_w value (0.989 ± 0.005) were in agreement with
356 previously published data for papaya Pococí (Soto et al., 2021). The protein content was
357 0.58 ± 0.03 g·100 g^{-1} FW. Concerning the lipid content, it was considered negligible as the
358 detection limit is 0.10 g·100 g^{-1} FW. These results were similar to those reported for red-
359 fleshed papaya fruit (USDA, 2020). Total sugar content (sum of glucose and fructose) was
360 6.51 ± 0.44 g·100 g^{-1} FW. Sucrose was not detected in the papaya fruit (detection limit of
361 0.25 g·100 g^{-1} FW) as previously reported in literature (Soto et al., 2020; Soto et al., 2021).
362 The pH value of Pococí papaya was 5.43 ± 0.41, being a fruit with low acidity compared to
363 other tropical fruits. The fruit contained 24.70 ± 5.34 mg·kg^{-1} FW of total carotenoids. This
364 carotenoid content is in agreement with that reported for red-fleshed papaya fruit
365 (Schweiggert et al., 2011; Soto et al., 2020; USDA, 2020).
366
367 **3.2 Moisture content, oil uptake, and a_w**
368 Results of experimental data for the moisture content (dry weight) of papaya chips during
369 frying at different oil temperatures are shown in Fig. 1.a. The treatments at different
370 temperatures were isothermals with minimal variation of oil temperature during the frying
371 process (supplementary material 1). Fig. 1.a shows that the moisture content in papaya
372 chips decreased significantly during frying. Water started evaporating as soon as the raw
373 material was in contact with the oil. Initially, the rate of water loss was high, leading to an
374 initial rapid fall of moisture content (85-98% of water loss, Fig. 1.a) during the first
375 minutes of frying (0-4 min) due mainly to the loss of surface moisture, and then it slowed
376 down as the product reached equilibrium.

As frying temperature increased the moisture content for the same frying time decreased. After 10 min of vacuum frying at 100 and 120 °C the moisture content in papaya chips reached equilibrium values of 0.024 and 0.020 $g \cdot g^{-1}$ DW, respectively. At 140 °C the equilibrium moisture value was of 0.005 $g \cdot g^{-1}$ DW and was reached after 8 min of frying. The moisture content model fitted the experimental data accurately (Fig. 1.a). It was shown that the rate constant of moisture loss (k_M), presented in Table 1, increased with temperature as previously described by several authors during the frying process (Ayustaningwarno et al., 2020b; Krokida et al., 2000; Manjunatha et al., 2014; Troncoso, & Pedreschi, 2009).

Fig. 1.b shows the increase of oil uptake (dry weight) versus frying time applying different oil temperatures. Generally, the longer the product remained in the frying vessel, the more the oil was absorbed. There were no significant differences ($p>0.05$) for the rate constant of oil uptake (k_O) between curves at 120 and 140 °C (Table 1). The general pattern was an initial rapid increase of oil uptake (0-8 min) followed by a gradually decreasing rate, with a final increase for the longest frying time (14 min). At 100 °C the model had a linear behavior with time. In general, at low temperatures and for short times, the proposed model had a linear behavior with time, whereas at higher temperatures (≥120 °C) and for longer times, oil content reached an equilibrium value as is shown in Fig. 1.b.

During frying at low temperatures, oil absorption took place not only during the cooling period but also to some extent during the frying period; this can be explained by the fact that low temperatures and thus weak water flows lead to the formation of a crust with a structure more favorable to oil absorption during the frying period (Pedreschi, & Moyano, 2005; Ziaiifar et al., 2010). This can be observed in Fig 1.b, after 10 min at 100 °C the oil uptake in papaya chips was higher compared to 120 and 140 °C.

401 Moisture loss is directly related to oil absorption because oil enters the voids replacing the
402 water that has evaporated during the frying, which happens especially during cooling
403 (Ziaiifar et al., 2010). Oil uptake increased as the moisture content diminished. In this
404 study, an equilibrium value was observed in moisture content (~2 g·100 g^{-1} FW) when the
405 papaya chips reached oil contents above 25 g oil·100 g^{-1} FW.
406 Fig. 1.c shows the change of a_w values in papaya chips during vacuum frying. It was
407 observed that sigmoidal behavior described a_w values in papaya chips during the frying
408 process. A decreasing logistic function (Eq. 4) fitted the a_w data accurately. The models for
409 a_w at 120 and 140 °C presented a similar behavior. L_{aw} and b_{aw} parameters of curves at 120
410 and 140 °C were significantly different ($p<0.05$) from those obtained at 100°C (Table 1).
411 Fig. 1.c. also shows that a_w values of papaya chips decreased during frying according to
412 three distinct stages: settling period, constant rate period and falling rate period. The
413 settling period occurs during the first minutes of process (0-2 min at 120 and 140 °C, and 0-
414 4 min at 100 °C), with a_w values close to one. Then, there is a constant rate period in which
415 the unbound water is removed. This period represents the condition of equilibrium
416 temperature at the product surface and ends when the surface of the solid is no longer wet
417 and represents the critical moisture content or critical a_w value (Barbosa-Cánovas &
418 Juliano, 2007). Finally, the last stage comprises the period in which the surface of the food
419 product is dried, and the water is removed from the center to the surface as vapor (Barbosa-
420 Cánovas & Juliano, 2007). At this point, the drying rate approaches the equilibrium
421 moisture content as is shown in Fig. 1.a.
422 Water loss and oil uptake phenomena depend not only on the process conditions (oil
423 temperature, frying time, and pressure) but on physical factors related to the food, such as
424 its size, shape, and thickness (Moreira, 2012). The thickness significantly affects the

425 contents of moisture and oil of food products during frying. Water loss and oil uptake are
426 higher at smaller sample thickness (keeping the same oil temperature and frying time)
427 (Krokida et al., 2000). The selection of the thickness of fruit/vegetable slices to obtain the
428 chips depends on the ripening stage and composition of the raw material (moisture,
429 proteins, polysaccharides, sugars) and the physical changes in the fried product (crispness,
430 shrinkage, puffing). For instance, the ripening stage and the chemical composition of fruits
431 are factors that influence the skin/pulp firmness of these food matrices, affecting the
432 process conditions during the peeling, cutting, and slicing steps (Soto et al., 2021). A
433 greater firmness in the fruit allows obtaining a lesser thickness in the product during the
434 slicing operation. In this study was selected a thickness of 4 mm in the papaya discs
435 according to pilot experiments. This value is similar to that applied for other fruits to obtain
436 vacuum-fried chips: 4 mm for mango (Ayustaningwarno et al., 2020a); 3.5-4.5 mm for
437 banana (Yamsaengsung et al., 2011); 5 mm for kiwi (Diamante et al., 2011), and apple
438 (Mariscal, & Bouchon, 2008). For vegetables, with a higher starch content and lower
439 moisture and sugar content than fruits, the thickness is usually less than in fruits. For
440 instance, 1.5 mm for potato (Crosa et al., 2014), blue potato, and sweet potato (Da Silva et
441 al., 2008); 2 mm for carrot (Dueik et al., 2010).
442
443 **3.3 Sugar reactions**
444 Fig. 2 shows the variation of different sugars present in papaya chips during vacuum frying
445 at different oil temperatures. The sugars present in fresh papaya discs (t=0) were glucose
446 and fructose, representing 53 and 47 % of total sugars, respectively. Fig. 2.a and Fig. 2.b
447 show that concentrations of glucose and fructose of papaya chips varied as function of
448 frying time and oil temperature. Curves of glucose and fructose followed the same

449 degradation pattern. At 100 °C, it was observed that concentration of both sugars remained
450 constant until 8 min of frying. Then, after 10 min the concentrations of glucose and fructose
451 decreased significantly ($p<0.05$) as shown in Fig. 2.a and Fig. 2.b. At 120 and 140 °C, these
452 sugars decreased significantly ($p<0.05$) after 4 min of frying (Fig. 2.a and Fig. 2.b). Also, it
453 was observed that the highest retentions of glucose and fructose occurred at 100 °C. For
454 instance, after 14 min of vacuum frying the average retention of glucose and fructose at 100
455 °C was 62%. At 120 and 140 °C after 14 min the average retention of these two sugars was
456 39 and 27%, respectively.
457 On the other hand, during vacuum frying the formation of sucrose occurred. Experimental
458 data for sugar content fitted well with a 3-parameters logistic function (Eq. 4). Sucrose
459 formation in papaya chips also followed sigmoidal behavior during the frying process as
460 shown in Fig 2.c. Experimental data showed that initial formation of sucrose varied
461 according to the oil temperature, increasing at 120 and 140 °C (Fig. 2.c). Moreover, Fig. 2.c
462 shows that the lowest sucrose formation was reached at 100 °C. In fact, the time to reach
463 the sigmoid's midpoint (b_{suc}) was significantly longer ($p<0.05$) at 100 °C than at 120 and
464 140 °C (Table 1). Likewise, the lowest curve's maximum of sucrose formation (L_{suc}) was
465 observed at 100 °C (~17 g·100 g^{-1} NF-DW) while L_{suc} value at 120 and 140 °C was ~2-fold
466 higher than at 100 °C (Table 1, Fig. 2.c).
467 Sucrose content in fresh papaya Pococí is negligible (Soto et al., 2020). Thus, its formation
468 during vacuum frying of papaya could be explained by two simultaneous phenomena: i)
469 condensation reaction between glucose and fructose, or ii) thermal degradation of cell wall
470 and middle lamella polysaccharides (e.g. fructooligosaccharides) that could lead to the
471 release of sucrose during frying of papaya. There is no information in the reviewed
472 literature showing a similar reaction as seen in this study. Nevertheless, sugar condensation

473 reaction is frequently used in chemical industry for producing low-caloric polysaccharides
474 (e.g. polydextrose). The formation of disaccharides by condensation reaction is carried out
475 under temperatures from 100 to 300 °C, preferably at temperatures close or higher to
476 melting point of saccharides serving as the substrate (Shah et al., 2004). In addition,
477 vacuum conditions are required in order to minimize decomposition and discoloration of
478 sugars (Shah et al., 2004).
479 Specific factors related to the frying process such as temperature and rate of water loss as
480 well as intrinsic characteristics of papaya (such as proximal composition, sugar
481 concentration, organic acids, acidity) are involved in sucrose formation. It seemed that high
482 temperatures during processing and low a_w values in food matrix favor this reaction. For
483 instance, a negative linear correlation was observed between sucrose content and a_w.
484 Correlation coefficients (r values) were -0.911, -0.887 and -0.964 for the curves at 100, 120
485 and 140 °C, respectively, as shown in Fig 2.d. As a_w values decreased, sucrose content
486 increased. Furthermore, glucose and fructose could undergo not only condensation reaction
487 to produce sucrose but also Maillard or caramelization reactions to generate colored
488 compounds affecting the browning color of papaya chips.
489
490 **3.4 Color parameters**
491 Color is one of the most important quality parameters in fruit and vegetable food products.
492 The average L*, a* and b* color values of fresh papaya discs were 34.9 ± 2.5, 25.6 ± 2.2
493 and 40.0 ± 2.0, respectively. A low color variation was observed in the papaya chips fried
494 at 100 °C and 120 °C, but at 140 °C the color degradation was higher and more evident
495 with the longest frying times (Fig. 3). For instance, after 14 min at 140 °C, L*, a* and b*
496 parameters significantly decreased ($p<0.05$) to 29.2 ± 1.2, 16.3 ± 0.9 and 22.1 ± 1.8,

497 respectively. On the other hand, at 100 °C and after 14 min of process, color parameters
498 significantly increased ($p<0.05$) and L*, a* and b* values in papaya chips were 47.0 ± 1.3,
499 35.6 ± 0.4 and 52.2 ± 1.6, respectively. At 120 °C there was only a significant difference
500 ($p<0.05$) for b* parameter; after 14 min of frying, papaya chips had a b* value of 28.1 ±
501 0.5.
502 There was not a clear trend for color change in papaya chips during vacuum frying and the
503 L*, a*, b* parameters could not be modeled during the process (data not shown). Papaya
504 fruit is a complex matrix and the color variations in vacuum-fried papaya chips could be the
505 result of carotenoid degradation (loss of red-orange color) and formation of molecules from
506 Maillard or caramelization reactions (development of browning), and to a lesser extent the
507 adsorbed oil in the chips during the frying process.
508 Nevertheless, the measurement of browning index (BI) in aqueous extracts obtained from
509 papaya chips allowed the browning reaction that alters the color in the chips to be evaluated
510 more accurately. Fig. 3 clearly shows that the browning color in aqueous extracts increased
511 with increasing frying time and oil temperature. The variation of dimensionless value of
512 browning index (BI/BI_0) in aqueous extracts of papaya chips at different temperatures is
513 shown in Fig. 4.a. Experimental data for BI/BI_0 were fitted well with a 3-parameters
514 logistic function (Eq. 4). Fig. 4.a shows that BI of aqueous extracts was sensitive to
515 temperature change. For instance, the constant rate of browning formation (k_{BI}) increased
516 by ~2-fold when the frying temperature was increased from 100 to 120 °C but increased by
517 ~5.4-fold when temperature was increased from 120 to 140 °C (Table 1). Contrary to
518 L*a*b* parameters of papaya chips, BI obtained by L*a*b* measurements on aqueous
519 extracts was much more sensitive to the processing conditions and therefore more relevant
520 for monitoring color variation.

521 Browning in papaya chips could be more related to caramelization than Maillard reaction
522 due to intrinsic characteristics of papaya fruit. Papaya is a low acidity fruit (pH= 5.43) with
523 a reducing sugar content of 6.51g/100 FW (59.19 g/100 g DW), specifically glucose and
524 fructose, and a low protein content (~0.6 g·100 g^{-1} FW). The Maillard reaction takes place
525 where reducing sugars react with amino acids and proteins during heating (Purlis, 2010;
526 Martins et al., 2000). Caramelization requires temperatures >120 °C and starts with an
527 enolization reaction of sugars, in particular reducing sugars and sucrose (Kroh, 1994).
528 Thus, BI is related to sugar degradation, specifically to reducing sugars (glucose and
529 fructose). Fig. 4.b showed the linear correlation between BI and concentration of reducing
530 sugars at different oil temperatures: r values were -0.760, -0.949 and -0.979 for the curves
531 at 100, 120 and 140 °C, as reducing sugars decreased, browning index increased.
532 Moreover, browning reactions mainly depend on temperature and a_w since this variable
533 represents the availability of water for chemical reactions in food. Low a_w and high
534 temperatures favor the formation of color during thermal treatment (Purlis, 2010). For
535 instance, the production of colored compounds such as HMF always needs at least one
536 dehydration step during the Maillard and caramelization reactions (Kroh, 1994).
537 In vacuum-fried papaya chips a negative linear correlation was observed between a_w and
538 BI/BI_0 as shown in Fig. 4.c with a higher slope at 140 °C: r values were -0.972, -0.929 and
539 -0.996 for the curves at 100, 120 and 140 °C, respectively. As oil temperature increased and
540 a_w decreased in papaya chips during frying, browning development increased being faster
541 at temperatures >120 °C.
542
543 **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.

568 There are few reports about carotenoid reactivity in foods during atmospheric frying and
569 even less during vacuum frying. Degradation of β-carotene during deep-fat frying (under
570 atmospheric conditions) varied according to the fruit or vegetable matrix. For instance,
571 retentions of 80-98% was found in plantain cylinders (Rojas-Gonzalez et al., 2006); 72-
572 86% in orange-fleshed sweet potato chips (Vimala et al., 2006); 28-32% in carrot crisps
573 (Dueik et al., 2010); 32% in mango chips (Nunes, & Moreira, 2009). In the case of the
574 impact of frying on lycopene degradation the information is scarce. The phenomenon of the
575 extractability of β-carotene and especially of lycopene increasing during vacuum frying of
576 papaya could be explained by two factors: i) a greater release of these carotenoids from
577 papaya cell tissues (e.g. chromoplasts) due to the matrix structure disruption during frying
578 (100-140 °C), and ii) an increase of their solubility enhanced by frying oil absorption in the
579 chips. These findings are in agreement with those reported for several studies that described
580 an increase of β-carotene and lycopene extractability during thermal processing of certain
581 vegetables such as tomato, sweet potato and bell pepper (Colle et al., 2010; Dewanto et al.,
582 2002; Re et al., 2002; Kidmose et al., 2006).
583 On the other hand, BCX presented a different behavior and was the least stable carotenoid
584 compared to the others. There was an effect of frying time on dimensionless concentrations
585 of BCX, expressed as non-fat dry weight at 120 and 140 °C (Fig. 5). For instance at 120
586 and 140°C, after 14 min of process there were losses of 40 and 60%, respectively. At 100
587 °C there was no BCX degradation. Notably, BCX decreased more rapidly at higher
588 temperatures (120–140 °C). The mathematical model that best described the trend of BCX
589 degradation in papaya chips was the second-order model as described previously during
590 storage (Soto et al., 2020). The resulting rate constants are presented in Table 1. The rate

591 constant of degradation (k_{BCX}) increased with temperature (Table 1). BCX followed the
592 Arrhenius temperature-dependency pattern (R^2 = 0.85). The rate constant of reference (k_{ref})
593 at the reference temperature of 120 °C was 4.0×10^{-4} kg·mg^{-1}·min^{-1} and the activation
594 energy (E_a) was 52 kJ·mol^{-1}.The E_a value of BCX in the papaya chips was in accordance
595 with that previously reported by Hadjal et al. (2013) in thermally treated blood orange juice
596 (62 kJ·mol^{-1}). Aparicio-Ruiz et al. (2011) also found similar activation energies in virgin
597 olive oil enriched with BCX during a heat treatment, 63-69 kJ·mol^{-1}.
598 These results show that orange color degradation in papaya chips, measuring by L*a*b*
599 parameters, is related to BCX degradation and not to BC or LYC loss. Chemical differences
600 between xanthophyll and carotenes could affect their reactivity during vacuum frying. In
601 the case of BCX, there was no effect of vacuum frying on its extractability as with
602 carotenes. BC and LYC have poor solubility compared to BCX. For instance, lycopene has
603 the lowest solubility and accumulates in the papaya matrix as crystals associated with the
604 plastid membranes (Schweiggert et al., 2011). Thus, the oil uptake in the chips allows the
605 crystalline structures of lycopene to dissolve increasing its extractability during analyses.
606 For total BC, the maximum extractability was reached when the oil content was ~0.13 g
607 oil·g^{-1} chip DW. The maximum extractability of total LYC occurred when the chips had
608 ~0.26 g oil·g^{-1} chip DW (at 120 and 140 °C) and ~0.33 g oil·g^{-1} chip DW (at 100 °C).
609 Conformation, concentration, and lipid solubility of carotenoids in the papaya chips seemed
610 to have a key effect on reactivity of these compounds during vacuum frying.
611
612 **3.6 Optimization of vacuum frying process of papaya**
613 In our study we focused on the influence of oil temperature and frying time on the main
614 physicochemical properties that are related to sensory attributes and nutritional value of

615 vacuum-fried papaya chips as summarized in Fig. 6. Desirability of a_w, color and nutritional
616 value in papaya chips was determined according to literature considering the most relevant
617 physicochemical characteristics for this kind of products.
618
619 **3.6.1 Desirability of a_w, color and nutritional value**
620 *a_w*
621 Control of a_w in dried fruit products with high hygroscopicity such as papaya chips (due to
622 low moisture content and high sugar content), is critical to ensure microbiological quality
623 and to maintain texture quality during storage. Physical changes such as loss of crispness
624 occur when the dried products gain water above the critical a_w, when they become soft or
625 rubbery (Welti-Chanes et al., 2007). It was observed that adequate crispness is obtained
626 when a_w values in papaya chips ranged from 0.1 to 0.3 (moisture content $\leq$2 g·100 g^{-1} chip
627 FW) (Soto et al., 2021). Konopacka et al. (2002) found a critical a_w value of 0.2 for fat-free
628 apple chips (moisture content 3.5 g·100 g^{-1} chips); they described that increasing a_w in
629 these chips above 0.3 resulted in complete loss of crispness. Critical a_w values for fruit
630 chips are usually lower than those for chips based primarily on starch-protein mixtures (a_w
631 0.35-0.50) (Konopacka et al., 2002).
632
633 *Color*
634 The reaction impacting the color in papaya chips was browning (Maillard or
635 caramelization) which affects quality. Therefore, it is desired that the browning index (BI)
636 be as low as possible. There is no information in the reviewed literature about decoupling
637 the pigment degradation from browning during fruit or vegetable processing and even less
638 about BI determination in aqueous extracts from a solid food matrix as control parameter.

639 Food color acceptance by consumers depends on the food product. Some authors suggested
640 that a color difference between raw and vacuum-fried fruits (ΔE) of 20 or less is acceptable;
641 for instance, this was found for gold kiwifruit (Diamante et al., 2011) and apple (Mariscal,
642 & Bouchon, 2008). In our case when aqueous extracts from papaya chips obtained BI/BI_0
643 greater than 5, the papaya chips presented ΔE >20 (data not shown). For this reason, it was
644 determined that a BI/BI_0 of 5 (or $5*BI_0$, Fig. 3) should be considered as a criterion for a
645 maximum limit in the chips.
646
647 *Nutritional value*
648 Our results showed that papaya chips are a good source of carotenoids, especially lycopene
649 (70-77% of total carotenoids), and could be an alternative for vitamin A consumption as
650 they provide retinol activity thanks to β-carotene and β-cryptoxanthin. For instance, after
651 10 min of vacuum frying the papaya chips presented a nutritional value of 91-128 μg
652 Retinol Activity Equivalent (RAE) (portion of 40 g chips), which corresponds to 10-14% of
653 the reference daily intake (RDI) (900 μg for adults and children ≥4 years) (FDA, 2020). It
654 could be claimed that food products with 10% or more of the RDI for vitamin A (RAE) as
655 "good source of vitamin A" (FDA, 2020). In papaya chips, the BCX represented ~70 % of
656 total provitamin A activity expressed as RAE (see section 2.6.6). Therefore, the retention of
657 BCX during vacuum frying is of importance for having provitamin A activity in papaya
658 chips. In our study it was calculated that BCX losses lower than 30% ensured 10% or more
659 of the RDI for vitamin A (RAE) in the papaya chips.
660
661 **3.6.2 Optimization of vacuum frying conditions**

662 Prediction of a_w, BI and BCX loss in papaya chips using the developed kinetic models is
663 shown in Fig. 7. This figure shows that values of a_w between 0.1 and 0.3 (grey zone) are
664 reached with frying times that range from 7 to 14 min. When the chips have a_w values ≤ 0.3
665 an equilibrium is reached, thus a_w is slightly affected by temperature. Contrary to final a_w,
666 BCX and BI were more affected by oil temperature. BCX degradation and color variation
667 increased with increasing oil temperature and frying time (Fig. 7). Low BCX loss and BI
668 (under 20 % and $3*BI_0$, respectively) are not of interest because a_w values in papaya chips
669 are close or above to 0.3 and would generate a product that is neither stable nor crispy. On
670 the contrary, obtaining papaya chips with a_w values lower than 0.1 implies not only longer
671 frying times but also higher BCX degradation and browning.
672 Fig. 7 shows a triangular zone with stripes embedded in the a_w stable zone in which the loss
673 of BCX is lower than 30%, thus ensuring ≥10% RDI of vitamin A (RAE) in the final
674 product. This region comprises a combination of temperatures from 107 to 120 °C and
675 frying times from 9 to14 min that produce quality papaya chips with a_w values from 0.1 to
676 0.3 and low color degradation (BI $<4*BI_0$). These frying conditions could be useful for
677 processing papaya or other carotenoid-rich fruits keeping the same vacuum pressure and
678 isothermal conditions. However, these conditions could change depending on the type of
679 vacuum frying machine, type of oil, size, thickness, and shape of fruit slices, ratio
680 product/oil, and ripening stage of fruit, among other factors.
681
682 **3.7 Other sensory and nutritional attributes**
683 Other factors, such as oil type, oil content, and sugar content, may be analyzed for
684 producing vacuum-fried fruit chips. The sugars and oil not only provide calories in fruit
685 chips but also contribute to their final taste. Therefore, it is important to control the quality

686 and content of these compounds. The type of oil affects the nutritional value of the final
687 fried product. For instance, unsaturated vegetable oils are a source of essential fatty acids
688 such as linoleic and alpha-linolenic acids, which are susceptible to oxidation during
689 atmospheric frying (Márquez-Ruíz et al., 2010). However, one of the benefits of vacuum
690 frying is preserving the oil quality because of the low temperatures employed and the
691 minimal exposure to oxygen (Andrés-Bello et al., 2011; Belkova et al., 2018). For instance,
692 the fatty acid profile of the soybean oil used as frying medium remained similar during
693 vacuum frying of papaya fruit, after 12 trials at 120 °C (supplementary material 3).
694 Nevertheless, it is necessary to verify the quality of frying medium by analyzing other
695 parameters such as total polar compounds, oxidised fatty acids, and polymer triglycerides,
696 which are the most reliable methods for monitoring oils during frying process (Gertz,
697 2000).
698 In the current study, the soybean oil used was mainly composed of polyunsaturated fatty
699 acids such as linoleic acid (ω-6, 49.3% of total lipids), oleic acid (25.8% of total lipids),
700 and alpha-linolenic acid (ω-3, 6.3% of total lipids). Therefore, it is relevant to find the right
701 balance between the caloric intake provided by the oil and the contribution of essential fatty
702 acids in the final product. In order to reduce the oil content in the chips, it is necessary to
703 allow adequate oil drainage (using a centrifuge) when the product is removed from the fryer
704 under vacuum (before pressurization of the vessel). For instance, by applying a higher
705 centrifugation speed to the fried product, higher oil content is removed from the product
706 surface (Moreira et al., 2009).
707 In the case of sugars, they provide the sweetness of the fried product. In addition, Maillard
708 and caramelization reactions, which are involved in browning, depend on sugars. During
709 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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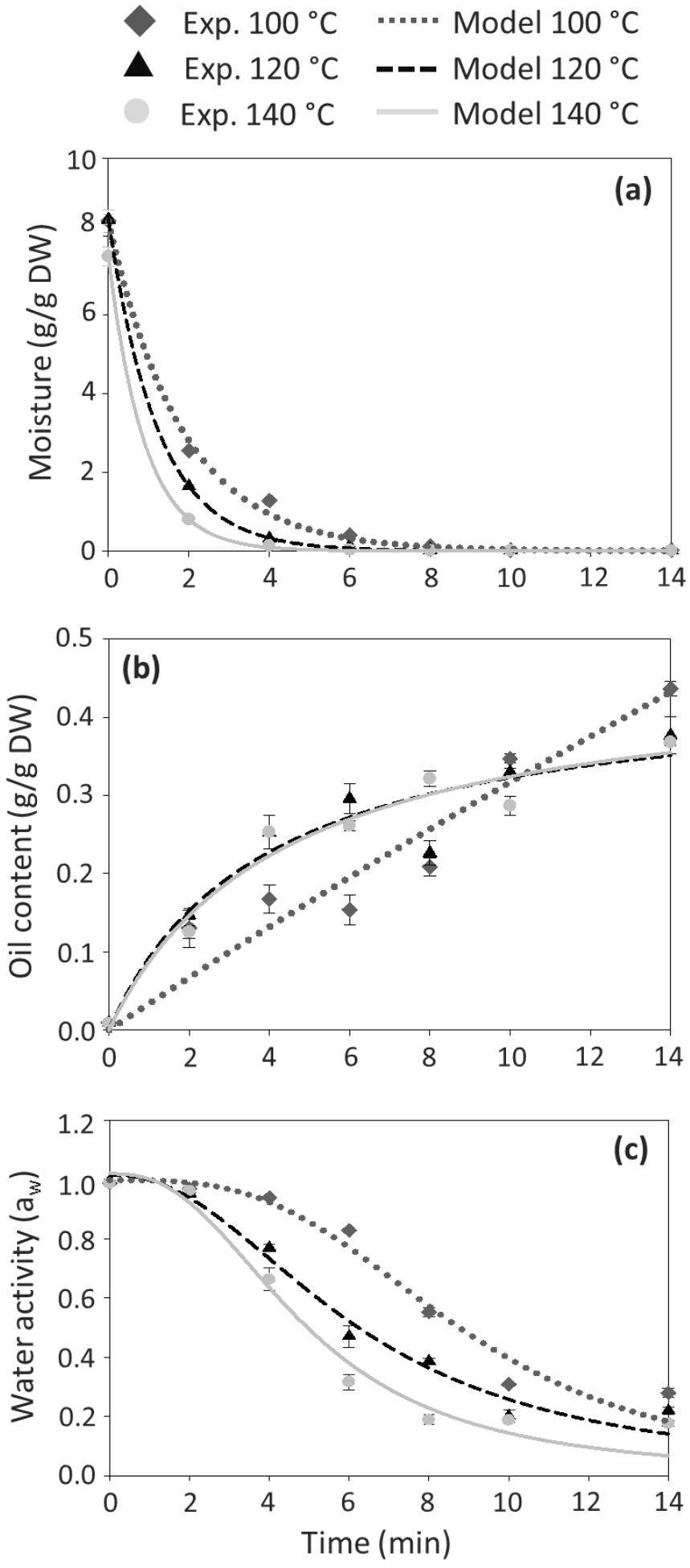
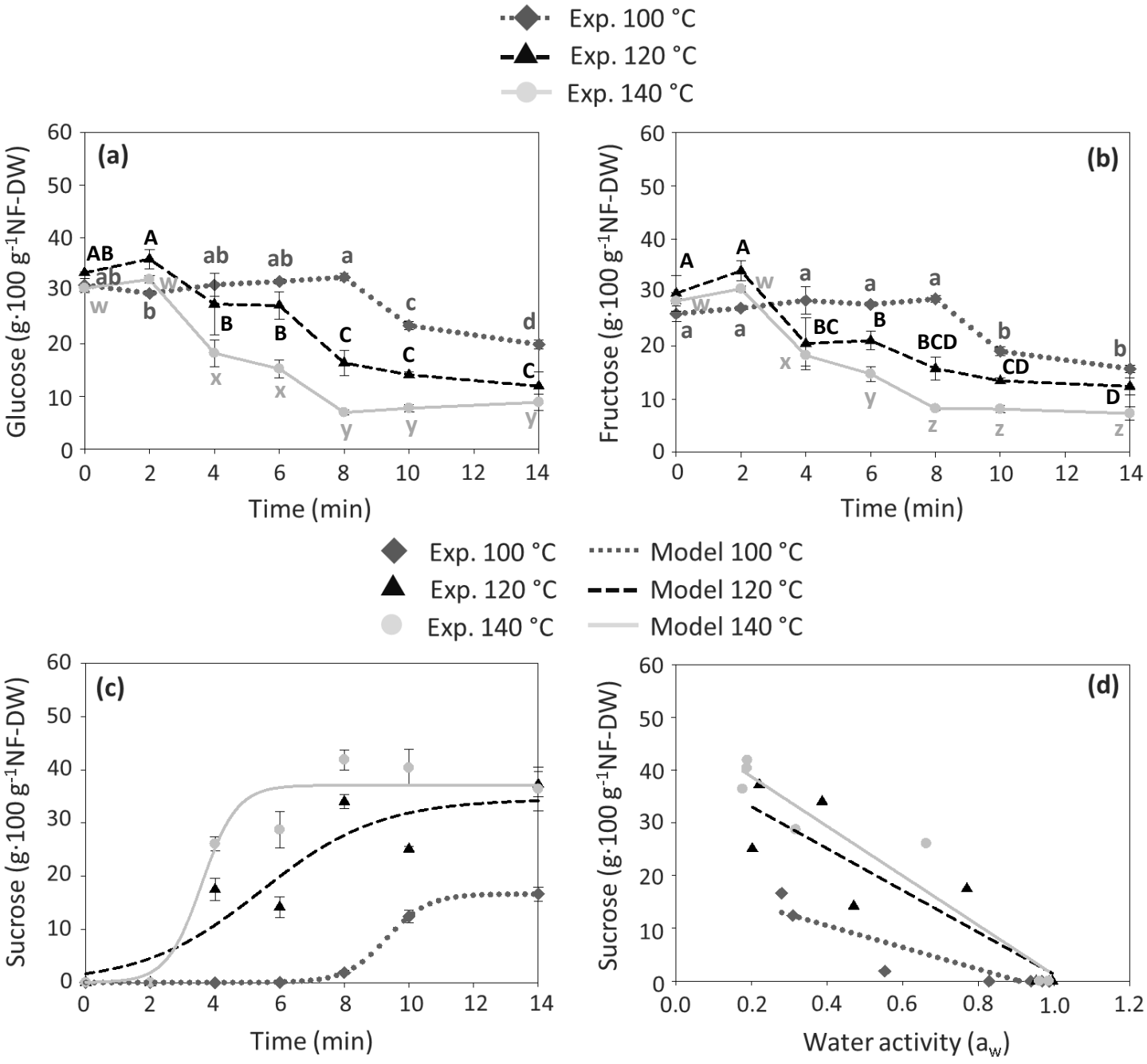
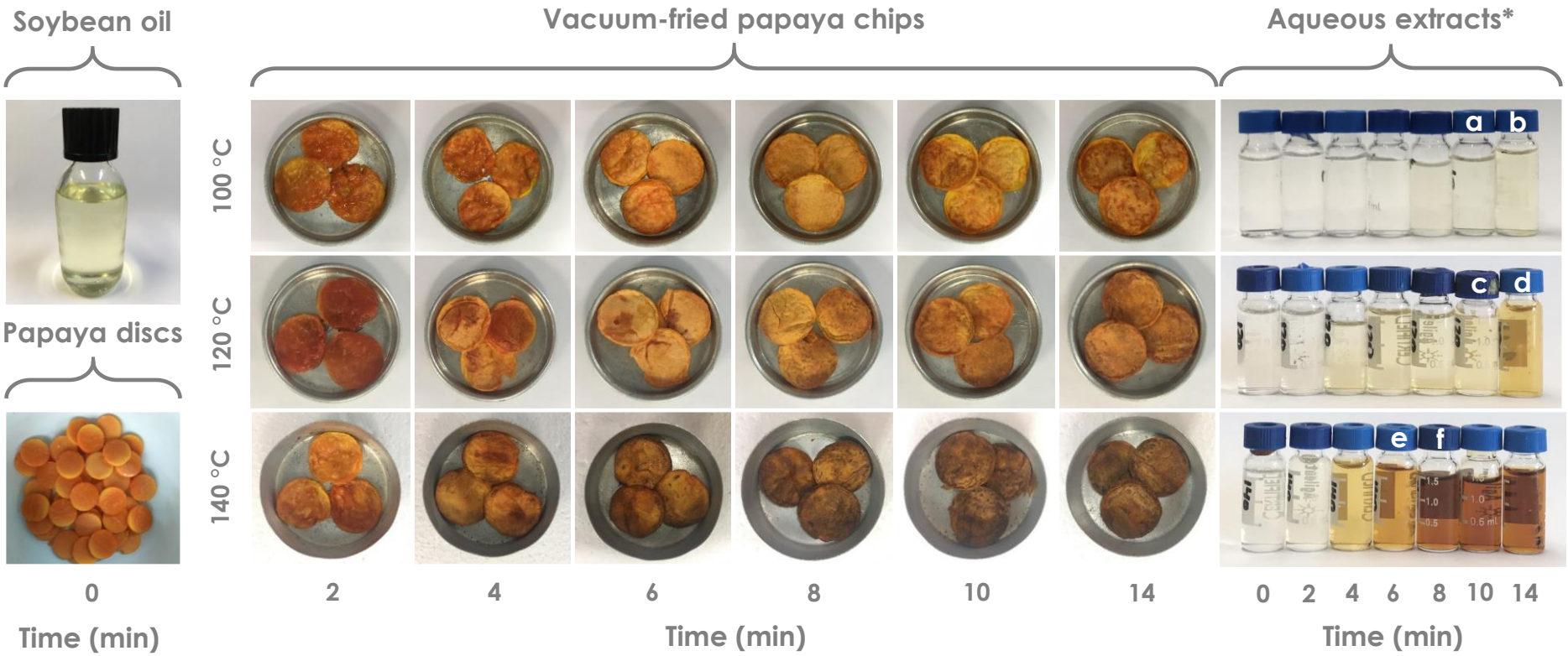
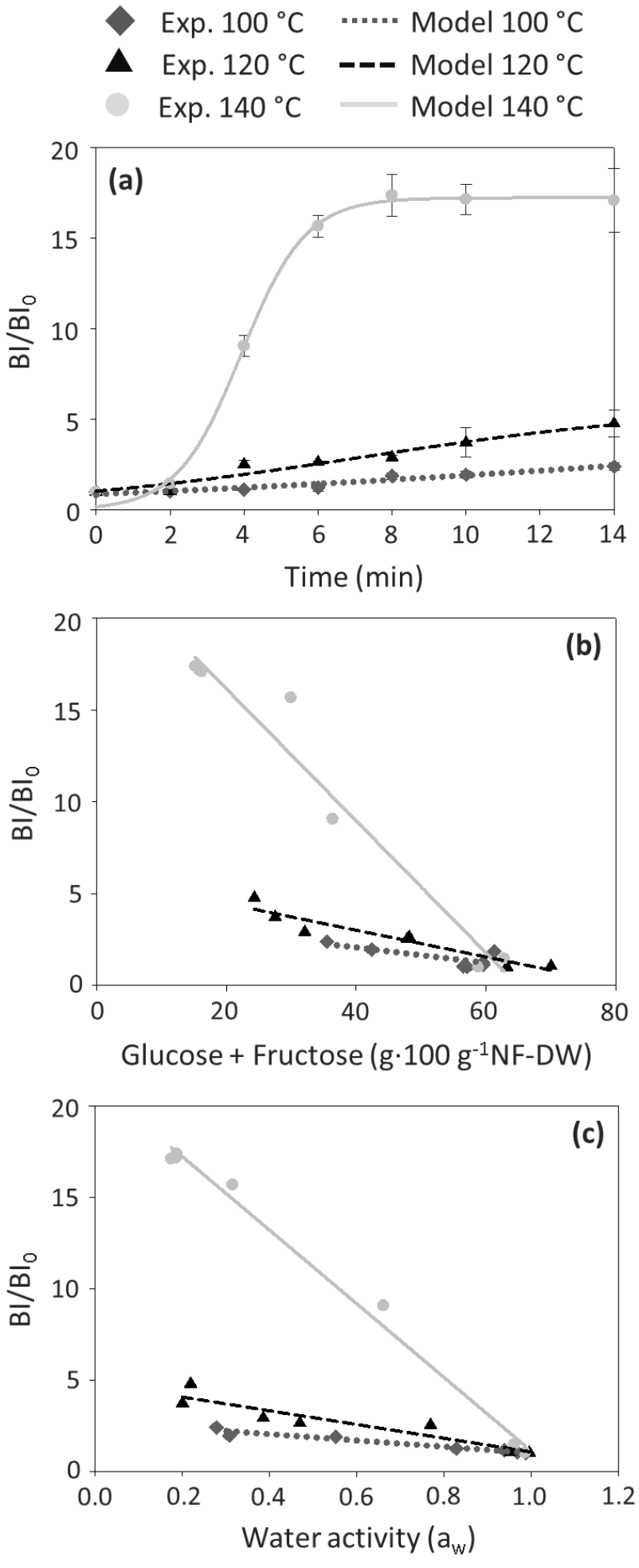
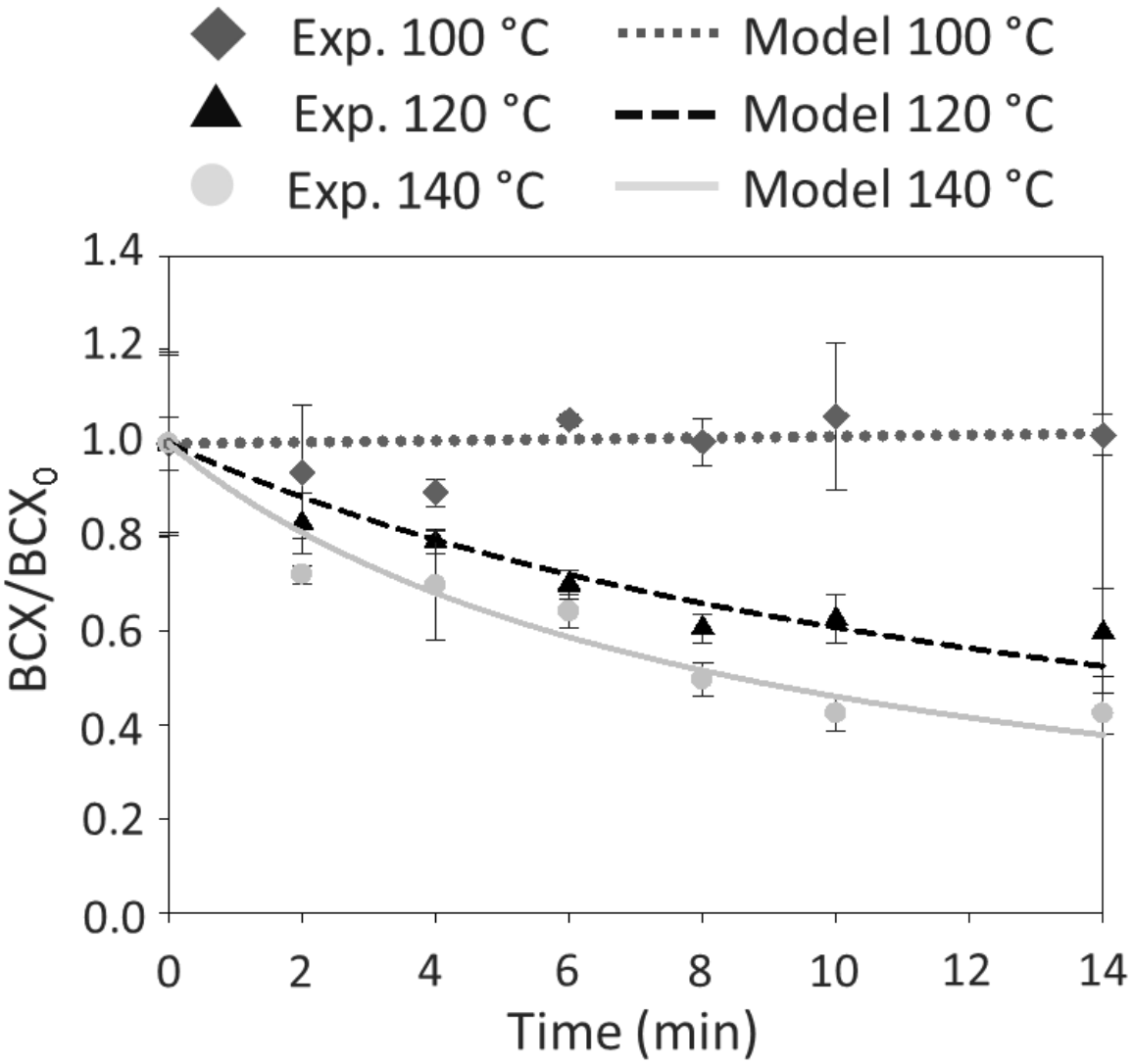
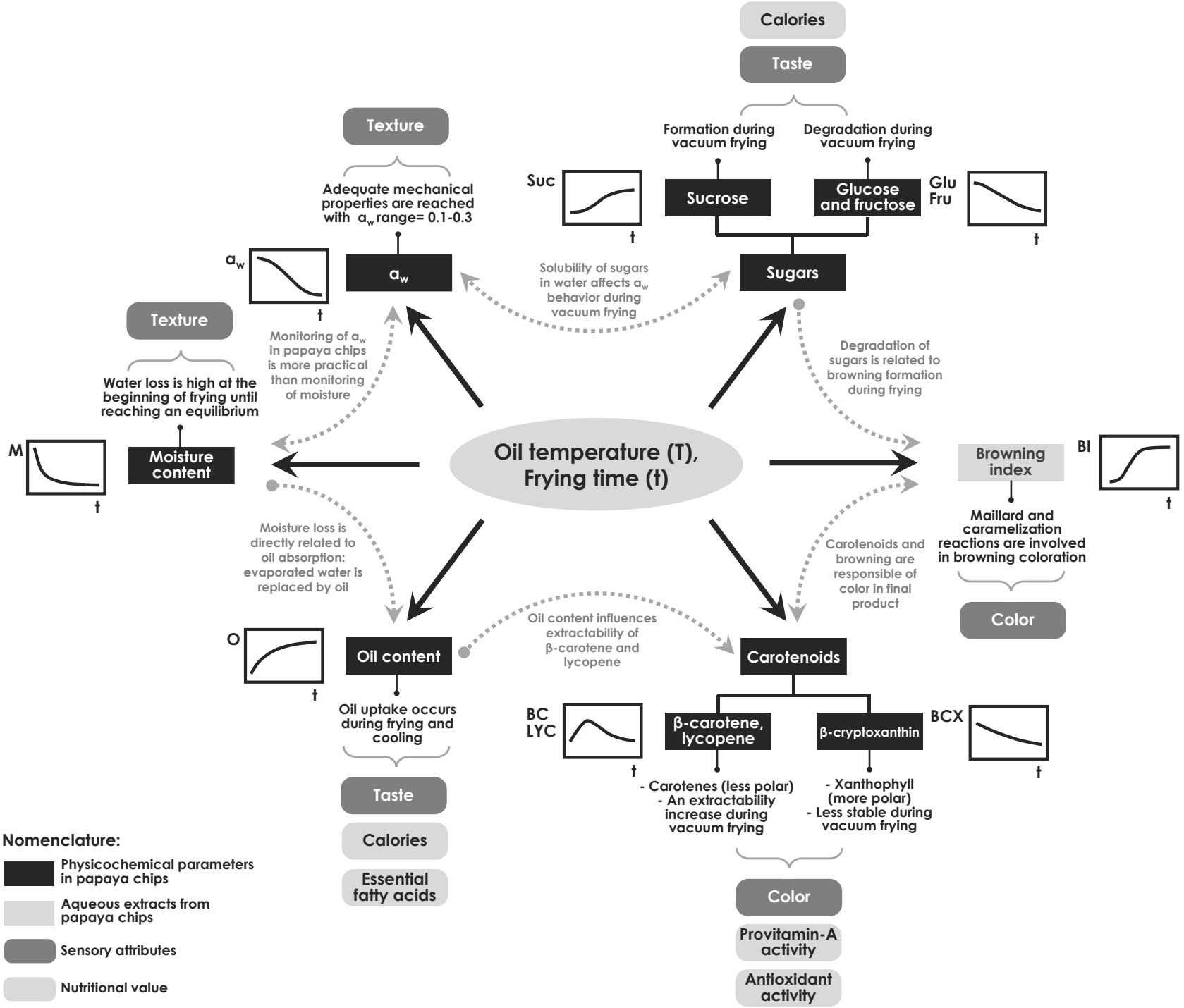

Exp. 100 °C
Exp. 120 °C
Exp. 140 °C
Model 100 °C
Model 120 °C
Model 140 °C
(a)
Moisture (g/g DW)
(b)
Oil content (g/g DW)
(c)
Water activity (a_w)
Time (min)

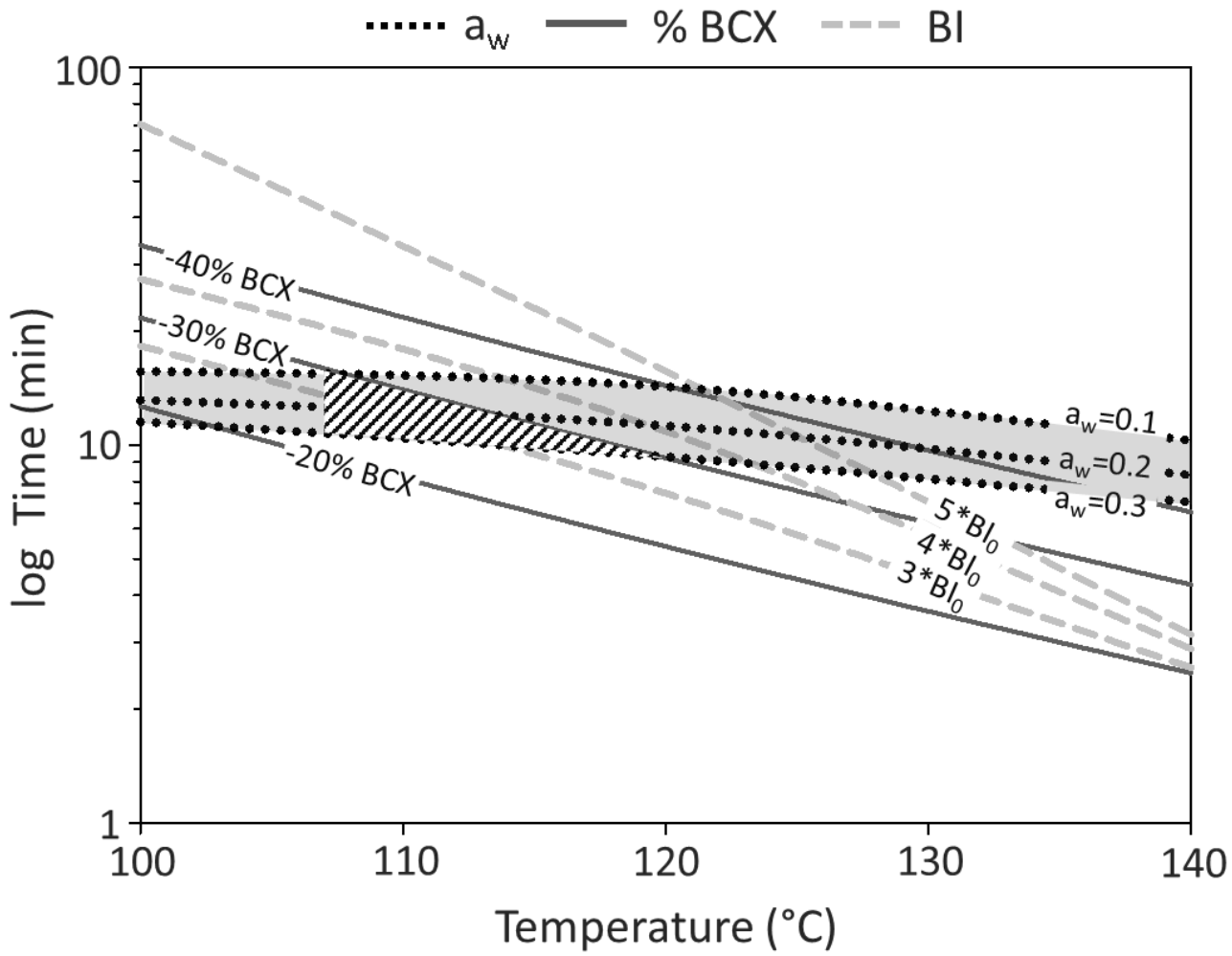

Exp. 100 °C
Exp. 120 °C
Exp. 140 °C
(a)
Glucose (g·100 g-1NF-DW)
Time (min)
(b)
Fructose (g·100 g-1NF-DW)
Time (min)
Exp. 100 °C
Exp. 120 °C
Exp. 140 °C
Model 100 °C
Model 120 °C
Model 140 °C
(c)
Sucrose (g·100 g-1NF-DW)
Time (min)
(d)
Sucrose (g·100 g-1NF-DW)
Water activity (aw)


Soybean oil
Papaya discs
0
Time (min)
Vacuum-fried papaya chips
100 °C
120 °C
140 °C
2
4
6
8
10
14
Time (min)
Aqueous extracts*
a
b
c
d
e
f
0
2
4
6
8
10
14
Time (min)


Exp. 100 °C
Exp. 120 °C
Exp. 140 °C
Model 100 °C
Model 120 °C
Model 140 °C
(a)
BI/BI0
Time (min)
(b)
Glucose + Fructose (g·100 g-1NF-DW)
(c)
Water activity (aw)


Exp. 100 °C
Model 100 °C
Exp. 120 °C
Model 120 °C
Exp. 140 °C
Model 140 °C
BCX/BCX0
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
12
14
Time (min)


Oil temperature (T), Frying time (t)
Texture
Adequate mechanical properties are reached with a_w range= 0.1-0.3
a_w
a_w
t
Monitoring of a_w in papaya chips is more practical than monitoring of moisture
Texture
Water loss is high at the beginning of frying until reaching an equilibrium
M
t
Moisture content
Moisture loss is directly related to oil absorption: evaporated water is replaced by oil
O
t
Oil content
Oil uptake occurs during frying and cooling
Taste
Calories
Essential fatty acids
Oil content influences extractability of β-carotene and lycopene
Calories
Taste
Formation during vacuum frying
Degradation during vacuum frying
Suc
t
Sucrose
Glucose and fructose
Glu Fru
t
Sugars
Solubility of sugars in water affects a_w behavior during vacuum frying
Degradation of sugars is related to browning formation during frying
Browning index
BI
t
Maillard and caramelization reactions are involved in browning coloration
Color
Carotenoids and browning are responsible of color in final product
Carotenoids
BC LYC
t
β-carotene, lycopene
β-cryptoxanthin
BCX
t
- Carotenes (less polar)
- An extractability increase during vacuum frying
- Xanthophyll (more polar)
- Less stable during vacuum frying
Color
Provitamin-A activity
Antioxidant activity
Nomenclature:
Physicochemical parameters in papaya chips
Aqueous extracts from papaya chips
Sensory attributes
Nutritional value


a_w
% BCX
BI
100
10
1
log Time (min)
100
110
120
130
140
Temperature (°C)
-40% BCX
-30% BCX
-20% BCX
a_w=0.1
a_w=0.2
a_w=0.3
5*BI_0
4*BI_0
3*BI_0

Tables

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

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 x10^{-4} (4.27 x10^{-5})
	140	<0.0001	0.940	k_{BCX}= 9.00 x10^{-4} (8.04 x10^{-5})

Standard error is expressed in brackets (n=3). Units of kinetic parameters: k_M, k_O, k_{aw}, k_{suc}, and k_{BI}, are expressed in min^{-1}, and k_{BCX} is expressed in $kg \cdot mg^{-1} \cdot min^{-1}$; O_e is expressed in $g \cdot g^{-1}$ DW; L_{aw}, and L_{BI} are expressed in dimensionless form, and L_{suc} is expressed in $g \cdot 100\ g^{-1}$ 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**
				all-E-BC/Total BC$_0$			
100	$0.91 \pm 0.19^{c,A}$	$2.93 \pm 0.56^{a,A}$	$2.76 \pm 0.13^{a,A}$	$2.05 \pm 0.07^{b,A}$	$1.75 \pm 0.02^{b,A}$	$1.93 \pm 0.15^{b,A}$	$1.68 \pm 0.10^{b,A}$
120	$0.95 \pm 0.16^{bc,A}$	$1.98 \pm 0.21^{a,B}$	$1.22 \pm 0.05^{b,B}$	$1.22 \pm 0.04^{b,B}$	$0.93 \pm 0.08^{bc,B}$	$0.78 \pm 0.10^{c,B}$	$0.74 \pm 0.13^{c,B}$
140	$0.92 \pm 0.28^{bc,A}$	$1.41 \pm 0.03^{a,B}$	$1.00 \pm 0.15^{b,B}$	$0.94 \pm 0.09^{bc,C}$	$0.65 \pm 0.09^{bc,C}$	$0.57 \pm 0.03^{c,B}$	$0.62 \pm 0.10^{bc,B}$
				Z-BC/Total BC$_0$			
100	$0.093 \pm 0.003^{d,A}$	$0.62 \pm 0.09^{bc,A}$	$0.59 \pm 0.07^{c,A}$	$0.82 \pm 0.07^{b,A}$	$0.81 \pm 0.04^{b,A}$	$0.81 \pm 0.12^{bc,A}$	$1.05 \pm 0.09^{a,A}$
120	$0.053 \pm 0.001^{d,C}$	$0.45 \pm 0.01^{c,A}$	$0.68 \pm 0.15^{ab,A}$	$0.68 \pm 0.09^{ab,AB}$	$0.74 \pm 0.05^{a,A}$	$0.49 \pm 0.01^{bc,B}$	$0.57 \pm 0.12^{abc,B}$
140	$0.085 \pm 0.003^{d,B}$	$0.44 \pm 0.13^{c,A}$	$0.51 \pm 0.11^{bc,A}$	$0.53 \pm 0.07^{bc,B}$	$0.51 \pm 0.08^{bc,B}$	$0.83 \pm 0.09^{a,A}$	$0.70 \pm 0.09^{ab,B}$
				Total BC/Total BC$_0$			
100	$1.00 \pm 0.18^{c,A}$	$3.55 \pm 0.64^{a,A}$	$3.35 \pm 0.20^{ab,A}$	$2.86 \pm 0.04^{ab,A}$	$2.56 \pm 0.04^{b,A}$	$2.74 \pm 0.27^{b,A}$	$2.74 \pm 0.19^{b,A}$
120	$1.00 \pm 0.16^{d,A}$	$2.42 \pm 0.20^{a,B}$	$1.91 \pm 0.19^{b,B}$	$1.90 \pm 0.13^{b,B}$	$1.67 \pm 0.13^{bc,B}$	$1.26 \pm 0.11^{cd,B}$	$1.31 \pm 0.25^{cd,B}$
140	$1.00 \pm 0.28^{b,A}$	$1.85 \pm 0.15^{a,B}$	$1.50 \pm 0.25^{ab,B}$	$1.46 \pm 0.16^{ab,C}$	$1.15 \pm 0.15^{b,C}$	$1.40 \pm 0.11^{ab,B}$	$1.32 \pm 0.15^{b,B}$
				all-E-LYC/Total LYC$_0$			
100	$0.83 \pm 0.12^{d,A}$	$1.72 \pm 0.25^{c,A}$	$2.14 \pm 0.12^{b,A}$	$2.12 \pm 0.09^{b,A}$	$2.38 \pm 0.07^{ab,A}$	$2.54 \pm 0.04^{a,A}$	$2.20 \pm 0.15^{ab,A}$
120	$0.84 \pm 0.10^{d,A}$	$1.98 \pm 0.06^{b,A}$	$2.49 \pm 0.21^{a,A}$	$2.07 \pm 0.13^{ab,A}$	$1.88 \pm 0.26^{bc,B}$	$1.83 \pm 0.18^{bc,B}$	$1.53 \pm 0.07^{c,B}$
140	$0.83 \pm 0.07^{c,A}$	$1.66 \pm 0.08^{b,A}$	$2.07 \pm 0.27^{a,A}$	$1.51 \pm 0.02^{b,B}$	$1.06 \pm 0.04^{c,C}$	$0.99 \pm 0.05^{c,C}$	$0.87 \pm 0.10^{c,C}$
				Z-LYC/Total LYC$_0$			
100	$0.17 \pm 0.01^{e,A}$	$0.32 \pm 0.00^{d,A}$	$0.41 \pm 0.03^{bc,B}$	$0.34 \pm 0.01^{cd,C}$	$0.39 \pm 0.02^{bcd,C}$	$0.46 \pm 0.04^{b,B}$	$0.56 \pm 0.00^{a,C}$
120	$0.16 \pm 0.02^{d,A}$	$0.30 \pm 0.02^{c,A}$	$0.53 \pm 0.02^{b,B}$	$0.59 \pm 0.03^{b,B}$	$0.58 \pm 0.05^{b,B}$	$0.57 \pm 0.01^{b,B}$	$0.70 \pm 0.03^{a,B}$
140	$0.17 \pm 0.01^{c,A}$	$0.38 \pm 0.07^{c,A}$	$0.89 \pm 0.12^{b,A}$	$1.17 \pm 0.03^{a,A}$	$1.12 \pm 0.05^{a,A}$	$1.01 \pm 0.12^{ab,A}$	$1.03 \pm 0.06^{ab,A}$
				Total LYC/Total LYC$_0$			
100	$1.00 \pm 0.13^{d,A}$	$2.04 \pm 0.26^{c,A}$	$2.56 \pm 0.08^{b,A}$	$2.47 \pm 0.10^{b,A}$	$2.78 \pm 0.08^{ab,A}$	$3.00 \pm 0.05^{a,A}$	$2.76 \pm 0.16^{ab,A}$
120	$1.00 \pm 0.12^{c,A}$	$2.27 \pm 0.08^{b,A}$	$3.02 \pm 0.23^{a,A}$	$2.66 \pm 0.15^{ab,A}$	$2.45 \pm 0.31^{b,AB}$	$2.41 \pm 0.17^{b,B}$	$2.23 \pm 0.08^{b,B}$
140	$1.00 \pm 0.07^{d,A}$	$2.04 \pm 0.15^{c,A}$	$2.95 \pm 0.39^{a,A}$	$2.68 \pm 0.03^{ab,A}$	$2.19 \pm 0.09^{cb,B}$	$2.00 \pm 0.16^{c,C}$	$1.90 \pm 0.10^{c,C}$

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). BC_0 and LYC_0, initial content (t=0) of β-carotene and lycopene, respectively.