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# A kinetic study of carotenoid degradation during storage of papaya chips obtained by vacuum frying with saturated and unsaturated oils

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## ABSTRACT

The aim of the study was to evaluate the degradation kinetics of carotenoids (CTs) in vacuum-fried papaya (*Carica papaya* L.) chips (PCs) during storage at four temperatures (15, 25, 35 and 45 °C) for 52 and 94 days for the two highest and lowest temperatures, respectively. Three treatments were applied to obtain the chips: chips with soy oil (24% lipids) and chips with palm oil (24% and 29% lipids). All the chips were packaged under air or nitrogen conditions. The CTs analyzed by HPLC-DAD were per order of content all-E-lycopene (LYC), Z-lycopene (Z-LYC), all-E-β-carotene (BC), all-E-β-cryptoxanthin (BCX) and Z-β-carotene (Z-BC). The all-E-forms represented 80% of carotenoids in PCs. No significant carotenoid degradation was observed in the PCs packaged under nitrogen conditions during storage. For chips stored under air conditions, a second-order kinetic model best fitted the experimental data. Rate constants for LYC degradation were the lowest, while BCX and BC presented similar rate constants 4–23-fold higher depending on lipid composition. All Z-isomers degraded faster than all-E-forms, but Z-BC degraded only 2–4-fold faster than Z-LYC. All CTs followed Arrhenius temperature-dependency pattern and LYC showed the lowest activation energies (5–21 kJ/mol). A higher lipid content in the chips with palm oil enhanced the carotenoid retention in PCs. Moreover, a greater retention ( $p < 0.05$ ) of CTs was observed in PCs with soy oil. The use of soy oil instead of palm oil increased the theoretical half-life (at 25 °C) by 2.2, 1.3 and 5.9-fold for BCX, BC and LYC, respectively. Packaging under nitrogen conditions and lipid composition may be considered to optimize the shelf life and carotenoid retention in PCs during storage.

## 1. Introduction

Fruits and vegetables are a source of bioactive compounds such as vitamins, polyphenols and carotenoids (CTs). The beneficial effects of CTs on human health have been reviewed and evaluated in several studies. For instance, CTs such as β-carotene (BC) and β-cryptoxanthin (BCX) represent an important nutritional source of vitamin A in the human diet which is necessary for vision, growth, cell differentiation, and other physiological processes (Fernández-García et al., 2012). Other CTs without provitamin A activity such as lycopene (LYC) have health-promoting properties. For example, the consumption of lycopene-rich foods has been reported to be inversely associated with the incidence of cardiovascular disease and cancer (Müller, Caris-Veyrat, Lowe, & Böhm, 2016; Rao & Agarwal, 2000).

The papaya fruit (*Carica papaya* L.) is a valuable source of

micronutrients, in particular pro-vitamin A carotenoids, BC and BCX, and red-fleshed papaya genotypes contain higher amounts of LYC compared with other fruits and vegetables such as mango, pumpkin, carrot and grapefruit (USDA, 2019). Besides its nutritional value, the papaya fruit represents a commercial importance in the developing countries where this crop is grown. During the past two decades, high growth rates for papaya production were reported worldwide. On average, total papaya world production increased from 5.49 million tons in 1994 to 13.02 million tons in 2017 (FAO, 2019).

Papaya is traded as both a fresh and processed product. During processing and storage, the concentration of nutrients and their biological activity may be changed. It is well known that food processing can cause many effects, not all of which result in a loss of quality and health properties. Because of this it is important to understand how food processing and storage influence the nutritional properties of food

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products.

Frying is a process widely used in the food industry that involves a process of simultaneous heat and mass transfers. During this operation, the food is cooked, dried, and formulated because of the oil uptake in the product. Nowadays, consumers are more interested in healthy products with good sensory and nutritional properties. Following this trend, vacuum frying is an alternative technology to atmospheric frying as it improves the sensory and nutritional quality of fried foods because of better control of oil quality and content in the fried products. In addition, during vacuum frying, the product is heated at a lower temperature and lower oxygen pressure thus inhibiting lipid and pigment oxidation and therefore, preserving the natural color and nutrients of fried fruits (Andrés-Bello, García-Segovia, & Martínez-Monzó, 2011; Da Silva & Moreira, 2008; Dueik & Bouchon, 2011). Da Silva and Moreira (2008) showed that vacuum frying retained 1.2 and 2-fold more CTs than atmospheric frying in mango and sweet potato chips, respectively.

However, after frying, the chips are usually stored at ambient temperature for several weeks or months. The loss of CTs during storage may reach 90% as a function of storage conditions (Bechoff et al., 2010). Therefore, there is an issue when choosing a process that preserves CTs to match it with optimal storage conditions that enable their maximum retention during the shelf-life of chips.

During processing and storage of dried products, CTs are prone to isomerization and oxidation as a result of exposure to high temperature, oxygen, light or pro-oxidant molecules (Achir et al., 2016; Achir, Randrianatoandro, Bohuon, Laffargue, & Avallone, 2010; Caris-Veyrat, Schmid, Carail, & Böhm, 2003; Colle, Lemmens, Van Buggenhout, Van Loey, & Hendrickx, 2010b; Xiao et al., 2018). Isomerization of all-E-carotenoids to Z-forms and cleavage occur due to heating during thermal treatments, while oxidation is a slower reaction that may occur at ambient temperature during storage in the presence of oxygen, metals, enzymes, unsaturated lipids, and other pro-oxidant compounds (Pénicaud, Achir, Dhuique-Mayer, Dornier, & Bohuon, 2011). Kinetic studies of carotenoid degradation during storage have been conducted in carotenoid degradation of non-fat dehydrated products (low  $a_w$ ) (Bechoff et al., 2010; Song et al., 2018). It has been shown that storage of dehydrated products under nitrogen conditions enhanced the retention of carotenoids. For instance, Bechoff et al. (2010) found a  $\beta$ -carotene loss of 16 and 83% in sweet potato chips stored under  $N_2$  and air, respectively, at 40 °C after 21 days. Also, storage of dehydrated pumpkins under  $N_2$  packaging retained more  $\beta$ -carotene and induced a low rate of carotenoid isomerization (especially at 4 °C) in comparison with storage under air conditions (Song et al., 2018). Moreover, the presence or addition of lipids has demonstrated an increase in extractability and bioaccessibility of carotenoids in different food matrices. Oil can then play a role as carrier of carotenoids during processing, storage as well as during digestion (Colle, Van Buggenhout, Lemmens, Van Loey, & Hendrickx, 2012; Dhuique-Mayer et al., 2016, 2018; Lemmens et al., 2014; Maity, Bawa, & Raju, 2014).

There is no information about behavior of vacuum-fried papaya chips. What is more, there is no literature about kinetic parameters of carotenoids in this kind of product during storage. In the present study,  $\beta$ -carotene,  $\beta$ -cryptoxanthin and lycopene degradation kinetics were investigated in vacuum-fried papaya chips during storage influenced by temperature (range of 15–45 °C), taking into account the lipid composition of the chips and the presence of oxygen inside the packages. This study gives insight into carotenoid degradation trends as a function of their chemical structure and gives an indication of how to optimize frying oil choice and storage conditions especially under different scenarios to maximize carotenoid retention.

## 2. Materials and methods

### 2.1. Materials

Red-fleshed papaya fruits (*Carica papaya* L. var. Formosa from

**Table 1**

Physicochemical properties of the oils (palm and soy oils) and the papaya products (fresh papaya and papaya chips obtained by vacuum frying at  $t = 0$ ).

Frying oils		
Compound	Palm oil	Soy oil
Lipids (g/100 g FW)*	99.97 $\pm$ 0.02	99.99 $\pm$ 0.01
Vitamin A (mg/100 g FW)*	ND	ND
Vitamin E (mg/100 g FW)*	228.10 $\pm$ 23.77	265.24 $\pm$ 0.83
Fatty acid profile (% relative):		
Saturated	54.47	15.45
Monounsaturated	36.18	19.08
Polyunsaturated (ALA, n-3)	0.22	9.13
Polyunsaturated (LA, n-6)	9.15	56.34
Papaya products		
Compound	Fresh papaya	Papaya chips
Moisture (g/100 g FW)**	86.96 $\pm$ 0.40	1.90 $\pm$ 0.12
Water activity, $a_w$ **	0.988 $\pm$ 0.003	0.226 $\pm$ 0.013
Lipids (g/100 g FW)**	ND	23.90 $\pm$ 1.38 <sup>a</sup> 29.25 $\pm$ 1.43 <sup>b</sup> 24.10 $\pm$ 0.96 <sup>c</sup>
Total sugars (g/100 g FW)**	8.51 $\pm$ 0.24	44.33 $\pm$ 0.75
Carotenoids (mg/kg FW)***:		
all-E- $\beta$ -cryptoxanthin	4.20 $\pm$ 0.46	9.56 $\pm$ 1.57
all-E- $\beta$ -carotene	3.30 $\pm$ 0.70	11.11 $\pm$ 2.29
all-E-lycopene	13.07 $\pm$ 1.73	105.06 $\pm$ 14.86
Z- $\beta$ -carotene	0.40 $\pm$ 0.06	7.46 $\pm$ 1.43
Z-lycopene	0.56 $\pm$ 0.09	23.26 $\pm$ 3.49
Total carotenoids	21.53 $\pm$ 2.16	156.45 $\pm$ 20.98
Carotenoids (mg/kg NF-DM)***:		
all-E- $\beta$ -cryptoxanthin	32.42 $\pm$ 2.84	13.42 $\pm$ 2.29
all-E- $\beta$ -carotene	25.37 $\pm$ 4.84	15.38 $\pm$ 3.22
all-E-lycopene	101.01 $\pm$ 13.15	145.97 $\pm$ 25.66
Z- $\beta$ -carotene	3.09 $\pm$ 0.41	10.32 $\pm$ 2.00
Z-lycopene	4.34 $\pm$ 0.62	32.22 $\pm$ 5.10
Total carotenoids	166.25 $\pm$ 14.24	217.14 $\pm$ 35.0

\* Values are expressed as the mean  $\pm$  standard deviation ( $n = 2$ ).

\*\* Values are expressed as the mean  $\pm$  standard deviation ( $n = 3$ ).

\*\*\* Values are expressed as the mean  $\pm$  standard deviation ( $n = 9$ ). FW, fresh weight; NF-DM, non-fat dry matter; ND, not detectable (vitamin A < 0.18 mg/100 g; lipids < 0.10 g/100 g). ALA, alpha linolenic acid; LA, linoleic acid. Lipid content in papaya chips:

<sup>a</sup> For S-Min treatment

<sup>b</sup> For S-Max treatment

<sup>c</sup> For UnS-Min treatment.

Brazil) from a single batch were acquired from TerreAzur (Montpellier, France) at ripening stage 4 (41–55% of skin yellowing). Papaya skin color was assessed as a percentage of skin yellowing on the whole fruit (0–100%).

Commercial frying oils, soy oil (Huileries Cauvin, Nimes, France) and hydrogenated palm oil Risso® (Vandemoortele, Gent, Belgium) were used. These oils were chosen because they are widely used for frying purposes and they present a very different fatty acid profile, a saturated oil (palm) and an unsaturated oil (soy) as is shown in Table 1. In addition, these oils present a lower vitamin E content in contrast to other vegetable oils (Table 1) to avoid any interaction with CTs.

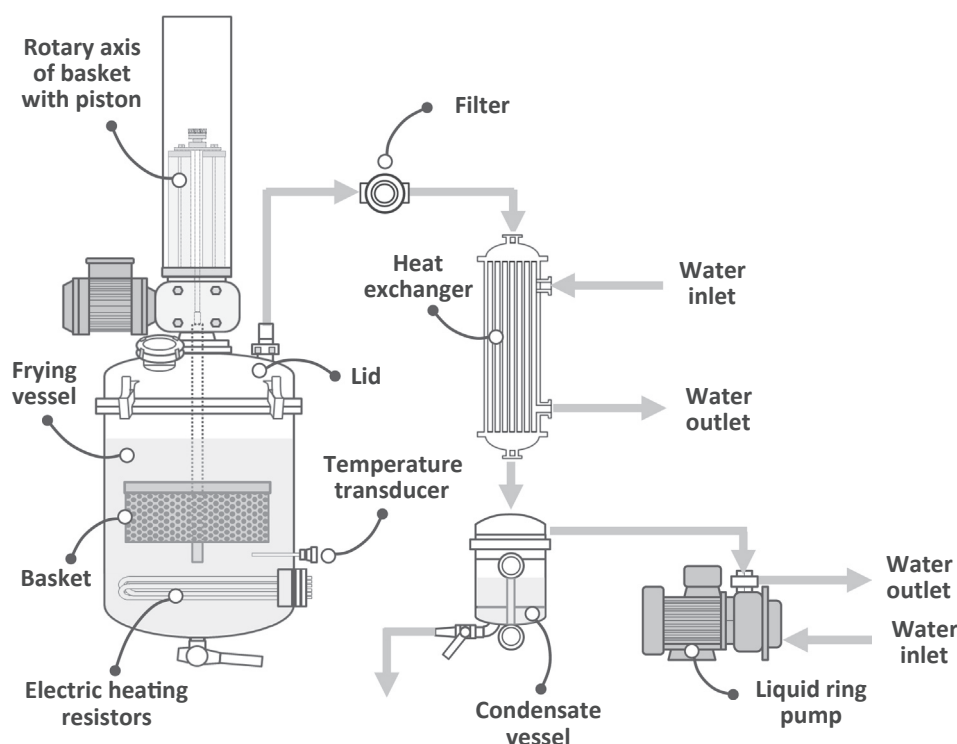


Fig. 1. Sketch of the vacuum frying system used for obtaining the papaya chips.

## 2.2. Sample preparation

Papaya fruits were selected and then washed and peeled manually. Each fruit was vertically cut into 4 pieces and then the seeds were removed. The pre-cut pieces were cut into 4-mm thick slices (dimensions of approximately 3 cm × 3 cm × 6 cm) using a slicing machine prior to vacuum frying.

## 2.3. Vacuum frying

The papaya chips (PCs) were obtained using a vacuum frying system (Auriol, Marmande, France) as is shown in Fig. 1. This system consists of a stainless-steel vessel (capacity of 80 L), electric heat resistors for heating the oil, a lid with a rotary axis coupled to a piston where is placed a stainless-steel basket (radius of 16.5 cm), 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 process consists of heating the oil (55 L) to the target temperature (120 °C). Then loading the papaya slices (about 1 kg) into the basket, closing the lid, and depressurizing the vessel. Once the pressure reached 25 kPa, the basket was immersed into the oil (palm or soy) for 13 min to achieve a final moisture content of 2%. When the chips were fried, the basket was raised, and the centrifuging system was applied for 3 min in order to control the oil content absorbed by the samples. Two speed values were applied during centrifugation of papaya chips with palm oil, 530 rpm or 51.8 × g (maximal speed) and 100 rpm or 2.1 × g (minimal speed), to reach 24% and 29% lipid content, respectively. For papaya chips with soy oil a centrifugation speed of 100 rpm was applied to obtain 24% lipids in the chips. Finally, the vessel was pressurized, and the papaya chips were removed from the fryer and cooled down at ambient temperature prior to packaging and storage.

Three treatments were evaluated: (1) S-Min, chips with saturated oil and a minimum lipid content; (2) S-Max, chips with saturated oil and a maximum lipid content; (3) UnS-Min, chips with unsaturated oil and a minimum lipid content. Five frying trials or repetitions were carried out

for each frying treatment. After each trial extra oil was added to the vessel to keep the volume of 55 L. Then, the chips from each trial (repetition) were combined manually to obtain a better homogenization of samples prior to packaging and storage. New oil was used for each treatment (2 batches of palm oil was used for S-Min and S-Max treatments, and 1 batch of soy oil was used for UnS-Min treatment).

## 2.4. Packaging and storage conditions

Papaya chips obtained by the different treatments were packaged in polyethylene terephthalate metallized/polyethylene (PETm/PE, 12/70 μm) bags (Multivac, France) under compressed air or N<sub>2</sub> conditions using a sealing machine (C200, Multivac, Germany). These bags have a water vapor transmission rate of 1 g/m<sup>2</sup>·day and an oxygen transmission rate of 1 cm<sup>3</sup>/m<sup>2</sup>, representing a good barrier against moisture and oxygen, avoiding oxidation reactions in the product. Approximately 5 g of papaya chips were weighed and placed in each package and a gas injection pressure of 0.5 bar was applied into the bags (air or N<sub>2</sub>) and then sealed. Samples were stored at 15 °C and 25 °C for 94 days (with sampling times at 15, 25, 45, 60, 75 and 94 days) and at 35 °C and 45 °C for 52 days (with sampling times at 3, 8, 15, 25, 35 and 52 days). For each frying treatment, packaging atmosphere and storage temperature, 3 packages of chips (repetitions) were analyzed at each sampling time. A total of 432 packages were stored for the study.

## 2.5. Kinetic modelling

Kinetic experimental data were presented in the dimensionless form  $C/C_0$  at different storage time intervals  $t$ , where  $C$  is the carotenoid concentration and  $C_0$  is the initial amount of the different carotenoids in the chips ( $t = 0$ ). Carotenoid degradation can be described by Eq. (1).

$$\frac{dC}{dt} = -kC^n \quad (1)$$

where  $C$  represents the carotenoid concentration (mg/kg fresh weight),

$t$  the storage time (day),  $k$  the reaction rate constant (kg/mg-day), and  $n$  the apparent reaction order.

The apparent order 0, 1 and 2 were tested. To discriminate the appropriate kinetic model, goodness of fit for each kinetic mathematical model (order 0, 1 and 2) was evaluated by  $R^2$  as follow:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \quad (2)$$

with  $SS_{res}$  being the residual sum of square ( $SS_{res} = \sum_i^n (y_i - \hat{y}_i^2)$ ) measuring the discrepancy between the experimental data  $y_i$  and the simulated ones  $\hat{y}_i$ . A small  $SS_{res}$  indicates a suitable goodness of fit of the model to the data.  $SS_{tot} = \sum_i^n (y_i - \bar{y}^2)$  is the total variance between the experimental data  $y_i$  and the mean of the data set  $\bar{y}^2$ .

The rate constants were assumed to vary with the temperature according to the Arrhenius equation described by Eq. (3).

$$k = k_{ref} \exp \left( \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \quad (3)$$

where  $k_{ref}$  is the rate constant (kg/mg-day) at the reference temperature  $T_{ref}$  chosen in the middle of the studied temperature range (303 K), with  $E_a$ ,  $T$ , and  $R$  respectively denoting the activation energy (J/mol), medium temperature (K), and gas constant (8.314 J/mol·K). Kinetic constants and activation energies were identified by nonlinear least-squares regression with SigmaPlot software (Systat Software Inc., CA, USA). The model's parameters were identified from experimental data measured in triplicate. The uncertainty of the parameters was calculated by non-linear error propagation using SigmaPlot software (Systat Software Inc., CA, USA).

## 2.6. Physicochemical analyses

Moisture was determined using AOAC standard method 920.151 (AOAC, 2012). Lipid content was determined by the method described by Carpenter, Ngeh-Ngwainbi, and Lee (1993). Sugars (sucrose, glucose, and fructose) were determined by HPLC using a Shimadzu LC-6A (Kyoto, Japan) equipped with an Econosphere™ NH2 column (Alltech Associates, Deerfield, IL, USA) and a Shimadzu RID-6A refractive index detector (Kyoto, Japan), using conditions described previously (Gancel, Feneuil, Acosta, Pérez, & Vaillant, 2011). The fatty acid profile was determined using AOAC standard method 996.06 (AOAC, 2012) and AOCS method Ce 1e-91 (AOCS, 2012). Water activities of the samples at 25 °C were determined in triplicate using a water activity meter (Aqualab, model CX-2, Decagon Devices, Inc., Pullman, WA). Vitamins A and E were determined by the method described previously (Lee, Kwak, Ahn, Jeong, & Shim, 2011) with certain modifications. Identification of both vitamins was performed on a reverse-phase HPLC-DAD Shimadzu Prominence (Kyoto, Japan) equipped with a Zorbax Eclipse XDB-C8 column (150 × 4.6 mm i.d., 5 μm) (Agilent, CA, USA) with a guard column, and the mobile phase was a mixture of methanol and water (95:5, v/v). Operation temperature was set at 50 °C. The flow rate was set at 1 mL/min and the injection volume was 10 μL. For vitamin A, retinol-acetate and retinol-palmitate were detected and quantified at 325 nm using their standard curves. For vitamin E, α-tocopherol, δ-tocopherol and γ-tocopherol were detected and quantified at 295 nm using their standard curves.

## 2.7. Carotenoid analyses

Extraction procedures and conditions for analysis were described previously by Dhuique-Mayer et al. (2016). Briefly, samples were ground and then weighed (500 mg for papaya fruit and 200 mg for papaya chips) in 20 mL tubes. The papaya chip samples were rehydrated with 2 mL of distilled water and homogenized. 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 the samples saponification 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 combined and evaporated to dryness using a vacuum evaporation system (GeneVac EZ-2, SP Scientific, UK). 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 on a reverse-phase HPLC-DAD Agilent 1100 system (Massy, France) with a diode array detector according to Dhuique-Mayer et al. (2007). Carotenoids were separated using a C30 column (250 × 4.6 mm i.d., 5 μm) (YMC EUROPE GmbH, Germany) with a guard column, and the mobile phase was H<sub>2</sub>O as eluent A, methanol as eluent B, MTBE as eluent C. Operation temperature was set at 25 °C. The flow rate was set at 1 mL/min and the injection volume was 20 μL. A solvent gradient was programmed as follows: 0–2 min, isocratic 40% A–60% B (initial conditions); 2–5 min, 20% A–80% B; 5–10 min, 4% A–81% B–15% C; 10–60 min, 4% A–11% B–85% C; 60–70 min, isocratic 4% A–11% B–85% C; 70–71 min, 100% B; 71–72 min, with a return to the initial conditions for rebalancing. All-E-β-cryptoxanthin, all-E-β-carotene and its isomer were detected at 450 nm, and all-E-lycopene and their isomers were detected at 470 nm (Dhuique-Mayer et al., 2007). Z-lycopene content was expressed as the sum of all Z-lycopene isomers. Isomers were identified according to their relative retention times, i.e. elution order and the combined use of their spectral data. The identifications were based on previously published data obtained with the same mobile phase (water/methanol/MTBE) and the same detection wavelength range (Achir et al., 2010; Achir, Hadjal, Madani, Dornier, & Dhuique-Mayer, 2015; Chanforan, Loonis, Mora, Caris-Veyrat, & Dufour, 2012; Martins, Fabi, Mercadante, & de Rosso, 2016; Schweiggert, Steingass, Esquivel, & Carle, 2012).

## 2.8. Statistical analyses

The influence of vacuum frying was evaluated using the Student's *t*-test to detect significant differences ( $p < 0.05$ ) between treatment values. In order to evaluate the effect of lipid content and type of oil on carotenoid degradation in papaya chips packaged under air conditions during storage a comparison of Arrhenius parameters was carried out using the Student's *t*-test ( $p < 0.05$ ). Two-way ANOVA was used to analyze the effects of storage temperature and packaging atmosphere (effects were considered significant when  $p < 0.05$ ). If significantly different, means were further compared using Tukey's test. Statistical analyses were performed with JMP 14 software (SAS Institute Inc., USA).

## 3. Results and discussion

### 3.1. Physicochemical properties of fresh papaya and papaya chips

Table 1 shows moisture, lipids, sugar contents,  $a_w$  and carotenoid contents in fresh papaya and papaya chips obtained after vacuum frying. The means of the different physicochemical properties of the chips obtained from the 3 frying treatments were reported, except for the lipid content. The papaya chips presented a low moisture content (~2 g/100 g) and  $a_w$  (~0.2), which are typical values for this kind of food product. The lipid content was ~24 g/100 g fresh weight (FW) for S-Min and UnS-Min treatments, and ~29 g/100 g FW from S-Max treatment as expected (Section 3.4). Sugar content in fresh papaya was less than 10% of its composition (fresh weight). Whereas, in papaya chips almost 44% of the product (fresh weight) was made up of sugars.

Eight carotenoids were identified in papaya chips using HPLC-DAD (Fig. 2, Table 2). Three E-carotenoids, all-E-β-cryptoxanthin (BCX), all-



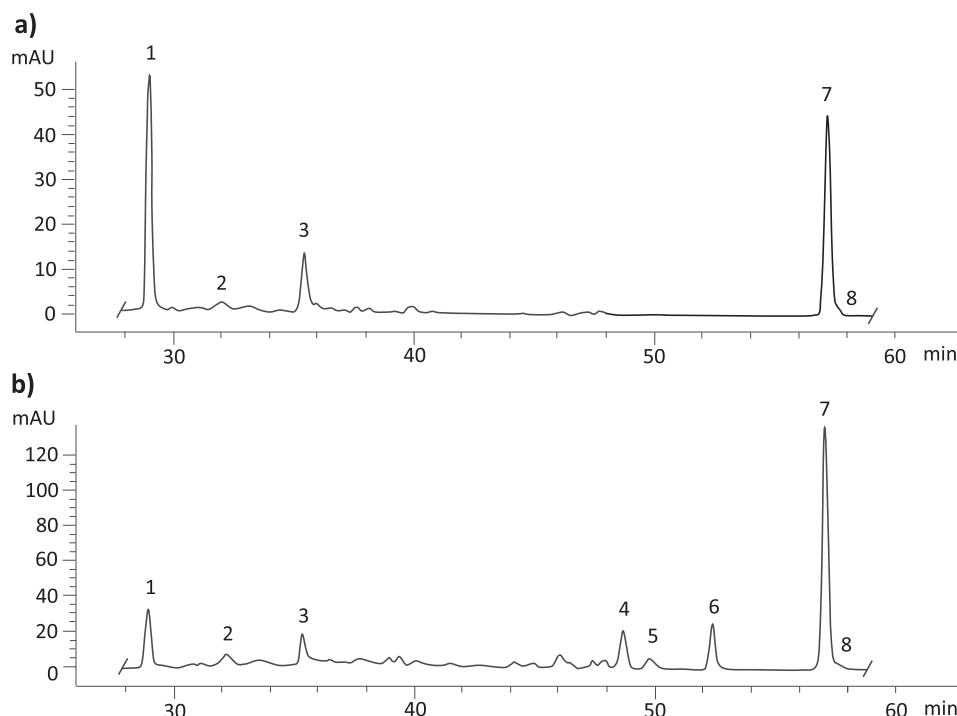


Fig. 2. HPLC separation of analyzed carotenoids monitored at  $\lambda = 450$  nm from: (a) fresh papaya, (b) papaya chips. For peak assignment see Table 2.

E- $\beta$ -carotene (BC), and all-E-lycopene (LYC) were identified according to their standard retention times and the combined use of their spectral data (Chanforan et al., 2012; Martins et al., 2016; Schweiggert et al., 2012). One Z-isomer for  $\beta$ -carotene (Z-BC) was tentatively identified, namely 13Z- $\beta$ -carotene (Achir et al., 2010, 2015) (Table 2). Finally, four Z-lycopene isomers (Z-LYC) were detected, these were tentatively identified, namely 13Z-, 5Z-13'Z-, 9Z- and 5Z-lycopene according to their III/II ratio, their *cis* peak intensity, and maximal absorption wavelength (Chanforan et al., 2012; Schweiggert et al., 2012) (Table 2). Fresh papaya fruit presented only one LYC isomer (5Z) as is shown in Fig. 2.a. Otherwise, three more Z-LYC isomers were detected in papaya chip samples (Fig. 2.b) as a consequence of heating during vacuum frying.

Table 1 also shows the carotenoid contents in fresh papaya and papaya chips. Fresh papaya samples contained  $21.53 \pm 2.16$  mg/kg fresh weight (FW) of total carotenoids. These results are similar to those reported for red-fleshed papaya fruit (Gayosso-García Sancho, Yahia, & González-Aguilar, 2011; Schweiggert, Steingass, Heller, Esquivel, & Carle, 2011a; Schweiggert, Steingass, Mora, Esquivel, & Carle, 2011b; USDA, 2019). Total carotenoid content in papaya chips was  $156.45 \pm 20.98$  mg/kg FW. There is no previous information about carotenoid content in papaya chips, but this content is comparable to

other similar products such as non-fat orange sweet potato chips (Bechoff et al., 2010) and fried orange sweet potato chips (Da Silva & Moreira, 2008), but it is 11 and 17-fold higher in comparison to fried carrot chips (Dueik & Bouchon, 2011), and fried mango chips (Da Silva & Moreira, 2008), respectively. These results showed that papaya chips are a good source of carotenoids, especially LYC, and could be an alternative for vitamin A consumption as they provide retinol activity thanks to BC and BCX.

LYC in both fresh papaya and chip samples was the main carotenoid, representing 61 and 67% of total carotenoids, respectively. Moreover, BC and BCX decreased their relative proportion after vacuum frying, from 15% (BC) and 20% (BCX) in fresh papaya to 7% (BC) and 6% (BCX) in the chips. The relative proportion of Z-BC increased from 2% (fresh papaya) to 5% (chips), and from 3% (fresh papaya) to 15% (chips) for Z-LYC.

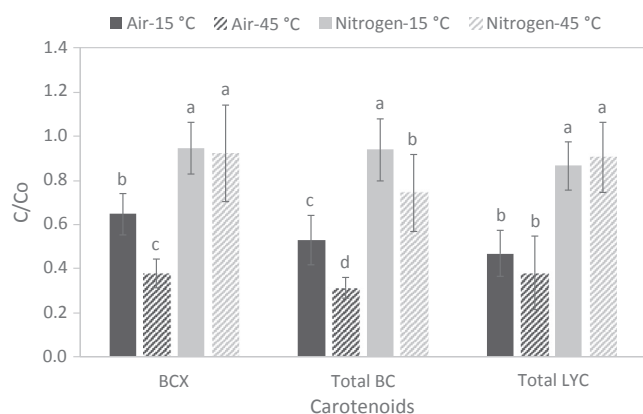
Indeed, by comparing the amount of CTs expressed as non-fat dry matter between fresh papaya and papaya chips (Table 1), there was a significant effect of vacuum frying on all carotenoid contents according to Student's *t*-test ( $p < 0.05$ ). Under the applied conditions ( $T = 120$  °C,  $P = 0.25$  bar,  $t = 13$  min), 60% and 40% of BCX and BC degradation occurred, respectively, whereas LYC showed an increase of 45% after vacuum frying. LYC has poor solubility and accumulates in

Table 2

UV-Vis spectra of analyzed carotenoids in fresh papaya and papaya chips.

No.	Retention time (min)	Carotenoid	HPLC-DAD UV-Vis spectrum (nm)	III/II (%)	$A_B/A_{II}$ (%)
1	28.9	<i>all-E</i> - $\beta$ -cryptoxanthin	(424), 450, 478	19	–
2	31.9	13Z- $\beta$ -carotene	342, (418), <b>438</b> , 464	6	35
3	35.4	<i>all-E</i> - $\beta$ -carotene	(422), <b>452</b> , 476	10	–
4	47.5	13Z-lycopene	362, 440, <b>466</b> , 496	49	62
5	48.8	5Z-13'Z-lycopene	360, 432, <b>458</b> , 488	46	30
6	51.9	9Z-lycopene	362, 440, <b>466</b> , 496	63	18
7	57.3	<i>all-E</i> -lycopene	446, <b>472</b> , 502	68	–
8	57.8	5Z-lycopene	446, <b>472</b> , 502	69	–

Values in bold represent the main maximum. Values in brackets mark point of inflection. III/II, ratio of the height of the longest-wavelength absorption peak (III) and that of the middle absorption peak (II), taking the minimum between the two peaks as baseline, multiplied by 100.  $A_B/A_{II}$ , ratio of the height of *cis*-peak ( $A_B$ ) and that of the middle main absorption peak ( $A_{II}$ ), multiplied by 100.



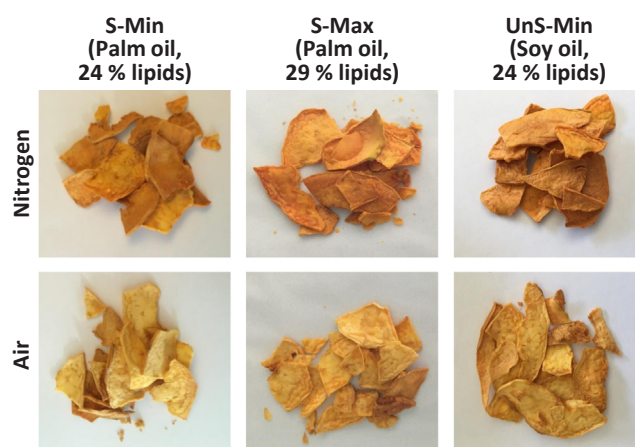
**Fig. 3.** Variation of dimensionless concentrations ( $C/C_o$ ) of different carotenoids in papaya chips packaged under air or nitrogen conditions after 1 month of storage at 15 and 45 °C. Bars are expressed as the means  $\pm$  standard deviation ( $n = 9$ ). For each carotenoid means with the same letter are not significantly different (Student's  $t$ -test,  $p < 0.05$ ). BCX, all-E- $\beta$ -cryptoxanthin; Total BC, all-E- $\beta$ -carotene + Z- $\beta$ -carotene; Total LYC, all-E-lycopene + Z-lycopene.

the papaya matrix as crystals associated with the plastid membranes (Schweiggert et al., 2011a). Thus, oil uptake in the chips allows the crystalline structures of lycopene to dissolve which increases its extractability. For the Z-forms, there was an increase in Z-BC and Z-LYC of 2.3 and 6.4-fold, respectively. This is in agreement with previously reported literature, which indicates that food processing favors the conversion of CTs from all-E to Z-isomers at temperatures higher than 100 °C especially when these compounds are dissolved in lipids (Achir et al., 2015; Achir, Pénicaud, Avallone, & Bohuon, 2011; Ahmed, Shivhare, & Sandhu, 2002; Ayari, Achir, Servent, Ricci, & Brat, 2015; Kourouma, Mu, Zhang, & Sun, 2019).

### 3.2. Effect of packaging atmosphere (air versus nitrogen) and storage temperature on carotenoid degradation in papaya chips

The oxygen present in packaging had a drastic effect on total carotenoid content. Indeed, for all chips stored under nitrogen, a slight or no significant degradation was observed whatever the temperature, the type of oil or the lipid content. Fig. 3 compares the means of carotenoid retention of chips packaged under both air and  $N_2$  conditions after 1 month of storage at 15 and 45 °C (chips obtained from the 3 treatments). Results from the two-way ANOVA showed that the interactions between the two factors (storage temperature and packaging atmosphere) were significant ( $p < 0.05$ ) only for BCX retention. Total BC was affected by both packaging atmosphere and storage temperature ( $p < 0.05$ ). In the case of LYC, only the packaging atmosphere was significant ( $p < 0.05$ ). Stored samples packaged under compressed air (21% oxygen) exhibited a higher degradation of BCX (35–62%), total BC (47–69%) and total LYC (53–63%). With no oxygen present during the storage conditions (bags flushed with  $N_2$ ), only a small decrease was observed in most CTs. This phenomenon was observed throughout the storage study for all the test temperatures. Minimal or no degradation of CTs was achieved regardless of lipid composition (type of oil and lipid content) in papaya chips (data not shown). Papaya chips packaged under  $N_2$  and stored at 15 and 45 °C did not present significantly different BCX and total LYC concentrations ( $p > 0.05$ ). In the case of the chips packaged under air conditions, the storage temperature altered only BCX and total BC retention ( $p < 0.05$ ); after 1 month of storage, an increase of 30 °C caused a degradation of 42% and 41% of BCX and total BC, respectively.

Fig. 4 shows the clear positive effect of packaging papaya chips under  $N_2$  conditions at 45 °C (maximum temperature evaluated in this study). These results showed how oxygen in package head space has a



**Fig. 4.** Papaya chips packaged under air or nitrogen conditions after 1 month of storage at 45 °C.

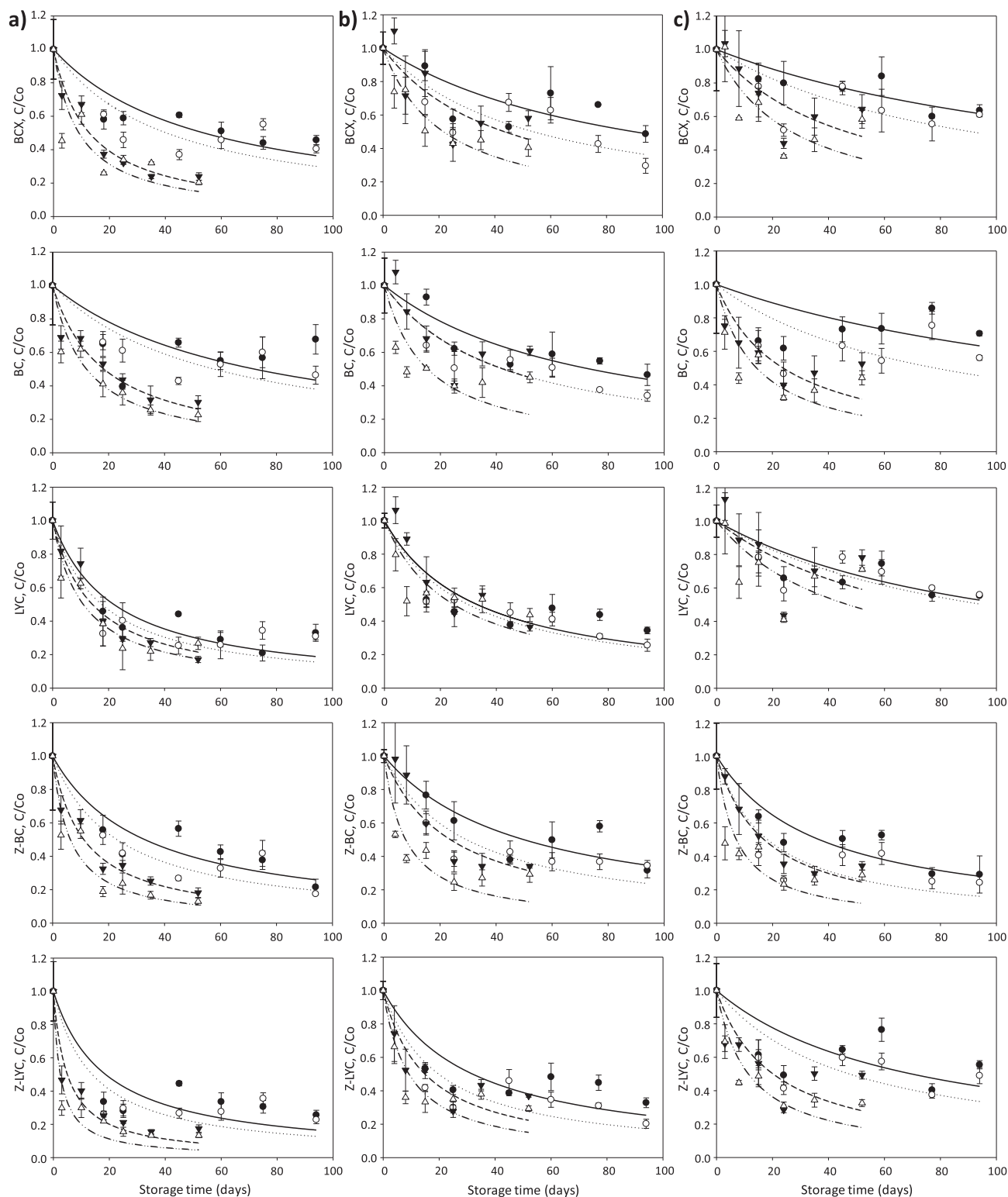
severe impact on carotenoid degradation. Oxygen diffuses in the fried product and generates carotenoid oxidation during storage, having an even greater effect than during the vacuum-frying process. This reveals that packaging under low oxygen conditions may be applied to preserve the maximal carotenoid content in this kind of food product during storage.

### 3.3. Carotenoid degradation kinetics in papaya chips packaged with air during storage

In the case of papaya chips packaged with air, a degradation of different CTs was observed during the storage time, regardless of the treatment as is shown in Fig. 5. The dimensionless concentrations of all CTs decreased with storage time at all the test temperatures. Notably, CTs decreased more rapidly at higher temperatures (35–45 °C). Kinetic models were set up on the basis of the analysis of experimental dimensionless concentrations over the storage time for each carotenoid. Second-order kinetics appeared to best fit the experimental data compare to first or zero-order reactions. Indeed, calculations made for BCX, BC and LYC revealed that second order showed the highest  $R^2$  (Eq. (2)) for 32 data set over 36. Therefore, the mathematical model that describe best the trend of carotenoid degradation in papaya chips is the second-order model. This is in accordance with the results of different studies that deal with carotenoid degradation during thermal degradation (Achir et al., 2011; Hadjal, Dhuique-Mayer, Madani, Dornier, & Achir, 2013). When considering an elementary reaction, the second order model is associated to a bimolecular reaction. In our case, this is probable since degradation was proven to be linked with oxidation and the co-reactant may be a reactive species derived from oxygen. However, it is not possible to go further into the reaction mechanism since this order is only an apparent one and do not represent precisely the complex reaction mechanism that involve isomerization reaction and various oxidation pathways as depicted in a paper about  $\beta$ -carotene degradation in dried orange-fleshed sweet potato during storage (Achir et al., 2014).

Carotenoid degradation is a complex reaction in food that is supposed to change as a function of the matrix and its storage conditions (Pénicaud et al., 2011). In this case, carotenoid degradation in the chips occurs due to oxidative reactions because of the presence of oxygen inside the bags.

The resulting rate constants are presented in Table 3. All rate constants increased with temperature. Globally, the all-E-carotenoids were more stable than the Z-forms. The LYC rate constants were the lowest (S-Min, from 0.46 to  $0.95 \times 10^{-3}$  kg/mg-day, S-Max, from 0.25 to  $0.31 \times 10^{-3}$  kg/mg-day, UnS-Min, from 0.11 to  $0.22 \times 10^{-3}$  kg/mg-day) which indicates that LYC was the most stable carotenoid in



**Fig. 5.** Variation of dimensionless concentrations ( $C/C_0$ ) of different carotenoids in papaya chips packaged under air conditions during the storage at four temperatures (● 15 °C, ○ 25 °C, ▼ 35 °C, △ 45 °C): (a) S-Min (palm oil, 24% lipids), (b) S-Max (palm oil, 29% lipids), (c) UnS-Min (soy oil, 24% lipids). Lines represent modeled data (— 15 °C, .... 25 °C, -- 35 °C, -.- 45 °C). BCX, all-E-β-cryptoxanthin; BC, all-E-β-carotene; LYC, all-E-lycopene; Z-BC, Z-β-carotene; Z-LYC, Z-lycopene. Values are expressed as the means  $\pm$  standard deviation at each storage time ( $n = 3$ ).

papaya chips during storage, regardless of the treatment. BCX and BC presented similar degradation rate constants for S-Max and UnS-Min treatments. Nevertheless, in chips obtained by S-Min, rate constants for BCX (from  $1.84$  to  $11.63 \times 10^{-3}$  kg/mg-day) were higher than those for

BC (from  $1.21$  to  $7.40 \times 10^{-3}$  kg/mg-day).

No isomers (Z-BC and Z-LYC) were produced during storage, certainly because of the low temperature. Isomerization is a reaction assumed to be sensitive to temperature that does not occur at



**Table 3**

Second-order rate constants and theoretical half-life of different carotenoids in papaya chips packaged under air conditions during the storage at four temperatures.

Treatments*	$k \times 10^{-3}$ (kg/mg·day)				$t_{1/2}$ (days)			
	15 °C	25 °C	35 °C	45 °C	15 °C	25 °C	35 °C	45 °C
BCX, all-E- $\beta$ -cryptoxanthin								
S-Min	1.84 (0.21)	2.44 (0.34)	7.70 (0.86)	11.63 (2.35)	54	41	13	8
S-Max	1.12 (0.17)	1.86 (0.25)	2.26 (0.43)	4.68 (0.57)	90	54	45	21
UnS-Min	0.77 (0.13)	1.28 (0.24)	2.43 (0.51)	3.99 (0.82)	150	91	48	29
BC, all-E- $\beta$ -carotene								
S-Min	1.21 (0.25)	1.51 (0.21)	4.77 (0.55)	7.40 (1.09)	72	58	18	12
S-Max	1.20 (0.14)	2.05 (0.22)	2.08 (0.37)	5.36 (0.89)	74	43	42	16
UnS-Min	0.61 (0.16)	1.26 (0.29)	3.86 (0.72)	6.08 (1.18)	156	75	24	16
LYC, all-E-lycopene								
S-Min	0.46 (0.05)	0.57 (0.09)	0.70 (0.07)	0.95 (0.13)	22	18	14	11
S-Max	0.25 (0.03)	0.27 (0.02)	0.25 (0.03)	0.31 (0.04)	33	30	32	26
UnS-Min	0.11 (0.01)	0.10 (0.01)	0.14 (0.04)	0.22 (0.05)	94	104	75	49
Z-BC, Z- $\beta$ -carotene								
S-Min	4.39 (0.68)	6.29 (0.96)	12.93 (1.65)	24.68 (4.91)	33	23	11	6
S-Max	2.65 (0.31)	4.48 (0.47)	5.75 (0.87)	16.25 (2.20)	50	29	23	8
UnS-Min	3.47 (0.42)	7.10 (1.27)	7.49 (0.84)	17.37 (3.39)	37	18	17	7
Z-LYC, Z-lycopene								
S-Min	2.14 (0.35)	2.88 (0.50)	7.95 (1.08)	16.94 (3.51)	19	14	5	2
S-Max	1.30 (0.17)	2.09 (0.29)	2.66 (0.36)	4.17 (0.61)	32	20	16	10
UnS-Min	0.72 (0.14)	1.06 (0.18)	2.37 (0.44)	4.01 (0.55)	67	45	20	12

\* Treatments: S-Min, saturated oil and minimum lipid content (palm oil with 24% lipids); S-Max, saturated oil and maximum lipid content (palm oil with 29% lipids); UnS-Min, unsaturated oil and minimum lipid content (soy oil with 24% lipids). Standard error is expressed in brackets ( $n = 3$ ).

temperatures lower than 100 °C (Colle et al., 2010a). Among the Z-carotenoids present after frying, Z-BC showed the highest degradation rate constants for all treatments (S-Min, from 4.39 to 24.68  $\times 10^{-3}$  kg/mg·day, S-Max, from 2.65 to 16.25  $\times 10^{-3}$  kg/mg·day; UnS-Min, from 3.47 to 17.37  $\times 10^{-3}$  kg/mg·day).

Fig. 6 shows the rate constants of reference ( $k_{ref}$ ) and the activation energies ( $E_a$ ) for the different carotenoids in PCs. All CTs followed Arrhenius temperature-dependency pattern (most models with  $R^2 > 0.95$ ). The rate constants of reference ( $k_{ref}$ ) varied from 1.80 to 4.80  $\times 10^{-3}$  kg/mg·day for BCX, from 2.20 to 3.00  $\times 10^{-3}$  kg/mg·day for BC, from 0.10 to 0.70  $\times 10^{-3}$  kg/mg·day for LYC, from 5.10 to 9.50  $\times 10^{-3}$  kg/mg·day for Z-BC, and from 1.70 to 5.20  $\times 10^{-3}$  kg/mg·day for Z-LYC. Approximately, the BCX and BC were degraded 7–18 and 4–23-fold faster than LYC, respectively. However, when comparing the Z-isomers, the  $k_{ref}$  of Z-BC was 2–4-fold superior to the values obtained for Z-LYC. This indicates that isomerization has a more dramatic effect on lycopene degradation, which is the main carotenoid in papaya.

$E_a$  were 40–48 kJ/mol for BCX, 45–52 kJ/mol for BC, 5–21 kJ/mol for LYC, 43–60 kJ/mol for Z-BC, and 29–63 kJ/mol for Z-LYC. Lycopene was thus less sensitive to an increase in temperature than the other carotenoids in its all-E-conformation. However, when isomerized, Z-LYC tends to have a similar sensitivity to temperature than Z-BC. The  $E_a$  values of BC and LYC in the papaya chips were in accordance with those previously reported by Achir et al. (2015) in thermally treated grapefruit juice (45  $\pm$  10 kJ/mol for BC, and 26  $\pm$  10 kJ/mol for LYC); (Colle et al., 2013) also found similar activation energies in a tomato emulsion during a heat treatment, 45 and 28 kJ/mol for BC and LYC, respectively.

Because this study did not analyze the degradation products especially from oxidation reactions, it is not possible to deepen the reaction mechanism, but some authors have studied and proposed some mechanisms. In the case of  $\beta$ -carotene, the oxygen can attack this molecule either on the  $\beta$ -ring or on the chain. This radical attack followed by homolytic internal substitution gives the epoxides, which appear as initial products. The stable final products, the apocarotenones and apocarotenals, could be formed from the epoxides (Mohamed, Hashim, Rahman, & Zain, 2001; Pénicaud et al., 2011). If the attack of the oxygen molecule is done on the chain of  $\beta$ -carotene, in chain epoxides

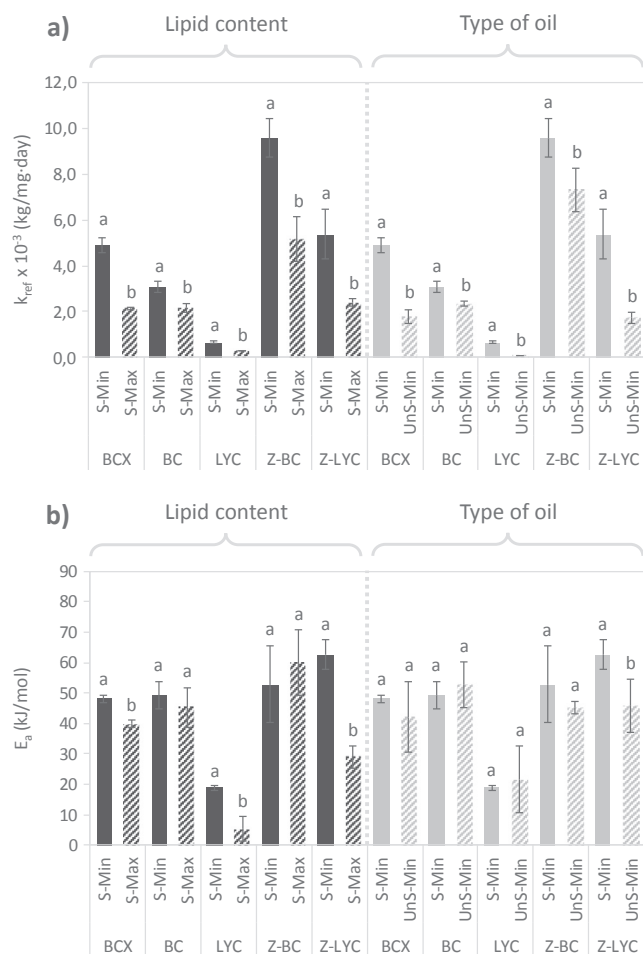
are formed, especially on *cis* isomers, due to the higher availability of the  $\pi$ -electrons in these *cis* forms (Pénicaud et al., 2011). Oxidation of lycopene occurs on both the isolated double bonds and the terminal double bonds of the conjugated double bond system, followed by rearrangements, resulting in many lycopene epoxides (Rodríguez & Rodríguez-Amaya, 2009). Kobori, Wagner, Padula, and Rodríguez-Amaya (2014) found that interaction of oxygen with the lycopene molecule is manifested by a high abundance of the compounds 6-methyl-5-hepten-2-one, geranial, 2,3-epoxy-geranial and rose oxide. For  $\beta$ -cryptoxanthin, information about oxidation mechanisms is scarce. For instance, in a model system two oxidation products derived from this carotenoid affected by non-iodine-catalyzed illumination were identified, 5,6-epoxy- $\beta$ - $\beta$ -carotene-3-one and  $\beta$ - $\beta$ -carotene-3-one (Li, Xiao, Zhang, & Liu, 2015).

#### 3.4. Effect of lipid content (24% versus 29%) and type of oil (soy versus palm) on carotenoid degradation in papaya chips packaged with air during storage

According to data shown in Table 3, degradation was faster in the S-Min treatment (chips with palm oil and 24% lipid content) whatever the carotenoid and its configuration (all-E and Z- forms). In S-Max samples (chips with palm oil and 29% lipid content) the degradation rate constants of Z-BC were the lowest. Moreover, it was found that LYC, Z-LYC and BCX were more stable in the chips obtained with the UnS-Min treatment (chips with soy oil and 24% lipid content). Table 3 also shows the theoretical half-life ( $t_{1/2}$ ) of each individual carotenoid that was calculated as representative of the second-order kinetic reaction according to the Eq. (4).

$$t_{1/2} = \frac{1}{kC_0} \quad (4)$$

The  $t_{1/2}$  is dependent on initial carotenoid concentration. For the same reactivity, the highest  $C_0$  the lowest  $t_{1/2}$ . For each carotenoid as temperature increased,  $t_{1/2}$  values decreased in a consistent manner with faster reactions accompanied by higher rate constants (Table 3). The increase in storage temperature from 15 to 45 °C caused a reduction of the  $t_{1/2}$  of 4.2–6.3, 4.5–10.0 and 1.3–2.1-fold for BCX, BC and LYC,



**Fig. 6.** Arrhenius parameters (at a reference temperature of 30 °C) of carotenoids in papaya chips packaged under air conditions during the storage at different temperatures (15–45 °C): (a)  $k_{ref}$ , (b)  $E_a$ . Bars are expressed as the means  $\pm$  standard deviation ( $n = 3$ ). For each carotenoid means with the same letter are not significantly different (Student's  $t$ -test,  $p < 0.05$ ). BCX, all-E- $\beta$ -cryptoxanthin; BC, all-E- $\beta$ -carotene; LYC, all-E-lycopene; Z-BC, Z- $\beta$ -carotene; Z-LYC, Z-lycopene. S-Min, palm oil with 24% lipids; S-Max, palm oil with 29% lipids; UnS-Min, soy oil with 24% lipids.

respectively. The  $t_{1/2}$  values for LYC (the main carotenoid) at 25 °C (typical shelf storage temperature for this kind of product) were 18, 30 and 104 days for S-Min, S-Max and UnS-Min treatments, respectively. Moreover, their isomers (Z-LYC) presented  $t_{1/2}$  values of 14, 20 and 45 days for S-Min, S-Max and UnS-Min treatments, respectively. The lower  $t_{1/2}$  of lycopene in S-Min demonstrates that this carotenoid is more sensitive to degradation when papaya chips are obtained under S-Min conditions (palm oil and 24% lipid content) in comparison to the other treatments, S-Max and UnS-Min.

A comparison of Arrhenius parameters of different carotenoids in the papaya chips packaged with air was carried out in order to analyze the effect of lipid content (S-Min vs S-Max) and type of oil (S-Min vs UnS-Min) as shown in Fig. 6. When evaluating the effect of palm oil content in the papaya chips on carotenoid degradation, it was found that the  $k_{ref}$  values for the different CTs in S-Min (24% lipids) were significantly higher ( $p < 0.05$ ) compared to those obtained in S-Max (29% lipids). The  $k_{ref}$  values were  $\sim 1.4$ -fold higher for BC, and  $\sim 2$ -fold higher for BCX, LYC, Z-BC and Z-LYC (Fig. 6.a). This means that CTs are less stable during storage when papaya chips have a lower lipid content. A hypothesis to explain this behavior is that the presence of a higher lipid content in the chips could cause a protective effect by replacing the voids that are filled with air, thus reducing the oxidation of CTs.

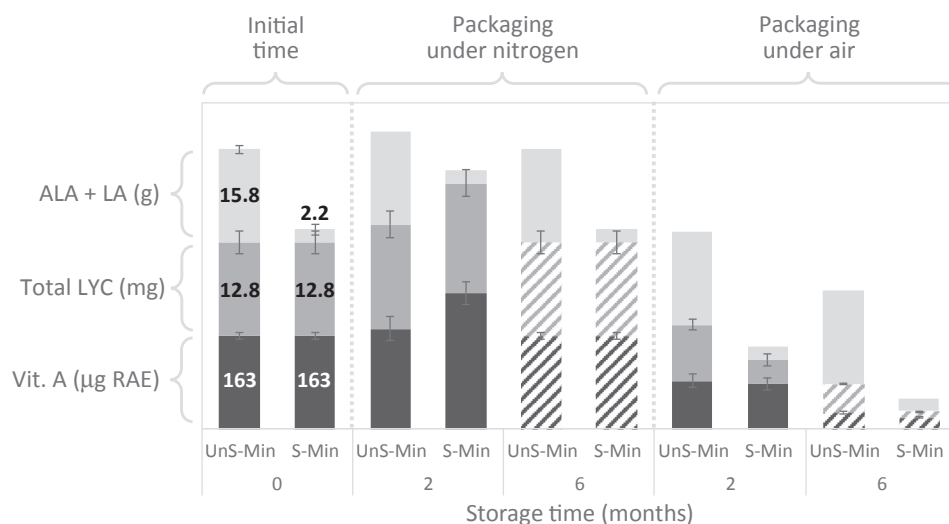
Fig. 6.b shows that BCX, LYC and Z-LYC in the chips with higher lipid content (S-Max) had significantly lower activation energies ( $p < 0.05$ ). When increasing the lipid content, the values of  $E_a$  decreased from 48 to 40 kJ·mol<sup>-1</sup>, from 19 to 5 kJ·mol<sup>-1</sup> and from 63 to 29 kJ·mol<sup>-1</sup> for BCX, LYC and Z-LYC, respectively.

Analyzing the effect of the type of oil (palm vs soy) in papaya chips with 24% lipids, it was observed that the  $k_{ref}$  values of all CTs were significantly higher ( $p < 0.05$ ) in S-Min compared to those in UnS-Min. The  $k_{ref}$  values were  $\sim 1.3$ -fold higher for BC and Z-BC,  $\sim 3$ -fold higher for BCX and Z-LYC, and  $\sim 7$ -fold higher for LYC (Fig. 6.a). The palm oil used in this study presented 54.45% and 45.55% of saturated and unsaturated fatty acids (UFA), respectively; while UFA represented 84.55% of soy oil (mostly linoleic acid, n-6) (Table 1). The greater retention of CTs in papaya chips with soy oil could be explained by several hypotheses: (1) competition for oxygen is generated between the double bonds of UFA present in soy oil and carotenoids, however, once these UFAs are oxidized, this oil could turn pro-oxidant, in this case further studies would be necessary to evaluate the lipid stability in PCs during long term storage; (2) the lower viscosity of soy oil during cooling compared to palm oil could favor deeper oil absorption inside the pores that are generated in the fried product, replacing the voids that are filled with air and thus reducing carotenoid oxidation. This alternative to saturated oil could be nutritionally interesting provided that the PCs are stored for a limited period and the soy oil is of good quality. Therefore, matrix lipid composition (lipid content and type of oil) affected kinetic parameters of CTs and demonstrated a protective role on CTs, especially for lycopene. In addition, more research shall be required to understand how differences in food matrix (type of oil, lipid content) can affect kinetic parameters of CTs.

### 3.5. Effect of packaging atmosphere (air versus nitrogen) and type of oil (soy versus palm) on the nutritional features of papaya chips during storage

The relationship between storage time and experimental data of vitamin A activity, total lycopene content and theoretical content of polyunsaturated fatty acids for papaya chips packaged with air and nitrogen are described in Fig. 7, depending on the type of oil. According to experimental data, PCs with an initial nutritional value of 163  $\mu$ g Retinol Activity Equivalent (RAE) (portion of 100 g) packaged under air conditions and stored for 2 months at an ambient temperature of 25 °C, which is the average storage temperature in the daytime under tropical temperatures, retained about 52 and 48% of this value for chips with soy oil (UnS-Min) and palm oil (S-Min), respectively. On the other hand, total lycopene content (sum of all-E and Z-isomers) in PCs packaged with air (initial content of 12.8 mg/100 g chips, fresh weight) retained about 60 and 26% of the initial total lycopene content after 2 months at 25 °C, for UnS-Min and S-Min, respectively. Fig. 7 shows also vitamin A activity and total lycopene for chips packaged with nitrogen based on experimental data. Provitamin A and lycopene were stable in chips packaged under N<sub>2</sub> conditions after 2 months of storage, as no degradation was observed.

Arrhenius model predictions of vitamin A and total lycopene in PCs after 6 months of storage (typical shelf-life of this kind of product) are also shown in Fig. 7. If PCs packaged with air were stored for 6 months at 25 °C, only 18 and 12% of initial RAE would be retained for UnS-Min and S-Min, respectively. About 31 and 7% of total lycopene would be retained if the chips were stored for 6 months at 25 °C. In chips packaged with nitrogen there would be no carotenoid degradation after 6 months by assuming a  $k_{ref}$  value of 0. Provitamin A and lycopene were more stable in the presence of soy oil in chips packaged with air. This is very interesting from a nutritional point of view, since the chips with soy oil would have a better nutritional composition providing essential fatty acids. The absence of air during vacuum frying may inhibit lipid oxidation in the product (Andrés-Bello et al., 2011). Lipid stability in fried products depends on the quality of the frying oil and process and storage conditions; for instance, Lee and Pangloli (2013) showed a lipid



**Fig. 7.** Vitamin A activity, total lycopene content and theoretical content of polyunsaturated fatty acids in 100 g portion of papaya chips packaged under air or nitrogen conditions during the storage at 25 °C. Solid bars: data based on experimental results. Stripe bars: data based on Arrhenius model predictions. Bars are expressed as the means  $\pm$  standard deviation ( $n = 3$ ). Vit A, Vitamin A activity: Retinol Activity Equivalent (RAE) estimate was calculated for a bioconversion of 12:1. RAE = [(all-E- $\beta$ -carotene/12) + (minor compounds/24)]  $\times$  unit (g). Minor compounds are Z- $\beta$ -carotene and all-E- $\beta$ -cryptoxanthin. Total LYC, Total lycopene content: it was calculated as the sum of all-E and Z-isomers in papaya chips, fresh weight. ALA + LA, alpha linolenic acid (n-3) + linoleic acid (n-6). S-Min, palm oil with 24% lipids; UnS-Min, soy oil with 24% lipids.

stability in potato chips fried in an unsaturated oil (mid-oleic sunflower oil) stored during 6 weeks at ambient temperature (22 °C). Assuming that there is a slight or minimal degradation of polyunsaturated fatty acids during a limited storage time, the chips with soy oil would exhibit a higher content of alpha linolenic and linoleic acids (total sum of 15.8 g/100 g chips, fresh weight) in comparison to chips with palm oil (2.2 g/100 g chips, fresh weight). Further studies are needed to verify the oxidation stability of fatty acids in vacuum-fried chips during storage. Globally, packaging under nitrogen conditions and the use of unsaturated oil may be considered for optimal carotenoid retention and for improving the nutritional properties of chips.

#### 4. Conclusions

The present study evaluated the reactivity of different CTs present in vacuum-fried papaya chips during storage, taking into account the lipid composition of matrix (type of oil and lipid content). Conservation of CTs in this kind of product during storage is of commercial and nutritional importance. Our results showed that there was a positive effect of packaging papaya chips with N<sub>2</sub> on carotenoid retention (under the tested conditions of temperature and time) allowing a minimal degradation of CTs. Degradation of carotenoids in the case of a packaging with air followed a second order kinetic model. Retention of all-E-carotenoids was higher than that of Z-carotenoids, and lycopene (the main carotenoid in papaya chips) was the most stable in comparison to the other CTs. The Arrhenius model correctly described the carotenoid degradation in papaya chips during storage at 15–45 °C. Vacuum frying allows the use of both saturated and unsaturated oils (due to the absence of oxygen and lower temperatures during the process) maintaining a high quality of the frying medium that favors a higher preservation of CTs during storage. Packaging under nitrogen conditions and the use of an unsaturated oil may be considered for optimal shelf life and carotenoid retention of these food products during storage. The data generated in this study brings new scientific knowledge about how important storage conditions and matrix composition are on carotenoid degradation.

In a more cognitive perspective, this study shows that the degradation kinetic is driven by oxygen. Therefore, further research is needed to understand the physical and chemical phenomena involved in carotenoid degradation during the storage of carotenoid-rich fried products. Regarding the uncertainty of analysis and the difficulty to have access to different degradation products in real matrices, a kinetic approach should be probably conducted in both a model medium and the real matrix.

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#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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