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7 authors, including:

Camila Duarte Ferreira
Universidade Federal da Bahia

Alessandro de Oliveira Rios
Universidade Federal do Rio Grande do Sul

Janice Druzian
Universidade Federal da Bahia

Itaciara Larroza Nunes
Federal University of Santa Catarina

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ORIGINAL PAPER

Physicochemical Characterization and Oxidative Stability of Microencapsulated Crude Palm Oil by Spray Drying

Camila Duarte Ferreira[1] · Elaine Janaína Linhares da Conceição[2] · Bruna Aparecida Souza Machado[3] · Vanessa Stahl Hermes[4] · Alessandro de Oliveira Rios[4] · Janice Izabel Druzian[1] · Itaciara Larroza Nunes[1,2]

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Abstract The aim of this study was to evaluate the possibility of crude palm oil microencapsulation by spray drying to preserve the oil's characteristics such as carotenoid content, antioxidant activity, fatty acid, and peroxide value and improve its technological process as thermal stability and oxidative stability for possible use as a food fortifier. Capsules were generated from emulsions with different wall material combinations and then dried at 180 °C. The best wall material combination was cassava starch with gum arabic because it provided good encapsulation efficiency and yield and moisture content. Thermogravimetric analysis and differential scanning calorimetry analyses indicated that the microcapsules had satisfactory thermal stability. The fatty acid profile and color parameters did not change with oil microencapsulation. However, total carotenoids, antioxidant activity, and peroxide value changed with encapsulation. In conclusion, crude palm oil remains an important source of bioactive compounds, such as pro-vitamin A, which have various functions in the body and these microcapsules can be used on food industry fortification.

✉ Camila Duarte Ferreira
camiladuartef@hotmail.com

[1] Faculty of Pharmacy, Federal University of Bahia, Campus Ondina, Salvador, Bahia 40170-290, Brazil

[2] Nutrition School, Federal University of Bahia, Canela, Salvador, Bahia 40110-150, Brazil

[3] Faculty of Technology, National Service of Industrial Learning/ Integrated Campus of Manufacturing and Technology (SENAI/ CIMATEC) - Avenue Orlando Gomes, n° 1845, Piatã, Salvador, Bahia 41650-010, Brazil

[4] Food Science and Technology Institute, Federal University of Rio Grande do Sul – UFRGS, Bento Gonçalves Avenue, n°9500, Porto Alegre, Rio Grande do Sul 91501-970, Brazil

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Introduction

Crude palm oil is derived from the fleshy mesocarp fruit of the oil palm (*Elaeis guineensis*) (Codex 2013). In 2014, palm oil was the most consumed oil worldwide, with a total production of 58.4 million tons. On a global scale, the largest producers of palm oil are Indonesia, Malaysia, and Thailand, accounting for just over 87 % of production in 2014. In Latin America, the largest palm oil producer is Colombia (FAS 2014) and, in Brazil, the production was approximately 275,000 t in 2012, ranking 13th among the countries producing crude palm oil (FAS 2013).

The major constituents of palm oil are triacylglycerols (95 %), composed of approximately 40.4 to 56.9 % saturated fatty acids and 43.0 to 62.5 % unsaturated fatty acids, all in the *cis* configuration (Gee 2007). Palmitic (35.0 to 47.0 %), oleic (36.0 to 47.0 %), and linolenic (6.5 to 15.0 %) acid are the major fatty acids of this oil. Furthermore, this oil has high levels of carotenoids, especially β-carotene (500–2000 μg/g) (Codex 2013). Carotenoids are commonly used as food additives and are strongly recommended due to their pro-vitamin A content and antioxidant activity. Furthermore, carotenoids are being investigated as promising candidates for the prevention of cancer, heart disease, and deleterious effects of aging (Ribeiro et al. 2011; Wang et al. 2014).

However, carotenoids are rather unstable substances because they are very sensitive to oxygen, light, and heat. In their natural form, they are insoluble in water and slightly soluble in oil at room temperature. Increasing the oil temperature increases the solubility of carotenoids, although water-soluble forms are obtainable by saponification of oleoresins. It has been established

that oxidation of carotenoid pigments depends on temperature and oxygen pressure as well as the structural properties of the pigment. Furthermore, peroxides are generated as products of lipid oxidation and carotenoids can bring health problems. It has been proposed that microencapsulation may improve carotenoid stability (Rascón et al. 2011).

Among many techniques, such as spray drying, spray cooling/chilling, extrusion, fluidized bed coating, coacervation, and liposome entrapment (Aghbashlo et al. 2013a; Fang and Bhandari 2010), spray drying is the most commonly used method to encapsulate food ingredients due to its low cost and the availability of equipment (Gharsallaoui et al. 2007).

A variety of food ingredients, especially oils, have been encapsulated using different encapsulating wall materials and encapsulation methods for various purposes. For example, encapsulation can afford protection from deterioration, preservation of functional characteristics, extended shelf storage stability, controlled release, targeted delivery, and/or alleviation of formulation and processing problems (Aghbashlo et al. 2013a; Aghbashlo et al. 2013b; Ahn et al. 2008; Domian et al. 2014; Drusch and Mannino 2009). Microencapsulated oil powder can be dry-blended with other dry ingredients, reconstituted as a stable emulsion in an aqueous solution or added directly to wet food products. A range of foods are reported to be able to be formulated with microencapsulated oils including beverages, dressings and sauces, baked goods, dairy products, and powdered products (Domian et al. 2014).

The selection of wall materials for spray drying is vital for efficient encapsulation. The most common wall materials are gum arabic, maltodextrin, emulsifying starches (Fernandes et al. 2014; Kanakdande et al. 2007; Krishnan et al. 2005), and proteins such as whey proteins, sodium caseinate, and gelatin. Among these materials, gum arabic is preferred because of its encapsulation efficiency and stability (Loksuwan 2007). Gum arabic produces stable emulsions with most oils over a wide pH range and forms a visible film at the oil interface.

Special attention has been given to the studies aiming at improving the encapsulation efficiency during spray drying of food flavors and oils by minimizing the amount of unencapsulated oil present at the surface of powder particles. Maximizing the encapsulation efficiency thus prevents lipid oxidation and volatile losses and extends the product's shelf life. The main factors that affect encapsulation efficiency of microencapsulated oils and flavors are the type of wall material, the properties of the core materials (i.e., concentration, volatility), the characteristics of the emulsion (i.e., total solids, viscosity, droplet size), and the conditions of the spray drying process (i.e., atomization type, inlet air temperature, air flow, humidity). Thus, it is important to optimize the drying process to obtain the minimal surface oil in the powder particles (Tonon et al. 2011).

Most studies of oil microencapsulation involve fish oil (Aghbashlo et al. 2013a; Aghbashlo et al. 2013b; Jafari et al. 2008; Kagami et al. 2003; Wang et al. 2011), though several previous studies investigated the encapsulation of olive oil (Calvo et al. 2012), linseed oil (Anh et al. 2008; Carneiro et al. 2013; Gallardo et al. 2013; Quispe-Condori et al. 2011; Tonon et al. 2011), sunflower oil (Domian et al. 2014), and palm oil (Dian et al. 1996). There is only one article available on refined palm oil microencapsulation (Dian et al. 1996), and it is available only on the carotenoids content from microencapsulated oil and the encapsulation efficiency over 2 weeks. Moreover, there are no published studies reporting the effects of microencapsulation on the oxidative stability, antioxidant activity, carotenoids identity, and fatty acid profile of crude palm oil.

The aim of the present study was to evaluate the possibility of crude palm oil microencapsulation by spray drying to preserve the oil's characteristics such as carotenoid amount, antioxidant activity, fatty acid, peroxide value, thermal stability, and oxidative stability. Favorable properties of spray-dried, microencapsulated palm oil would encourage future use for food fortification.

Materials and Methods

Materials

Crude palm oil was supplied by the Agropalma Group (Pará, Brazil). The wall materials were cassava starch (CS) (Cargill, São Paulo, Brazil); whey protein concentrate (WPC) (Kerry do Brasil, Minas Gerais, Brazil), which contained a minimum of 33 % (*w*/*w*) milk protein and a maximum of 6 % (*w*/*w*) milk fat; and gum arabic (GA) (Instantgum BA, Nexira, São Paulo, Brazil).

Emulsion Preparation

Six composite wall materials were prepared: 20 % (*w*/*w*) CS + 80 % (*w*/*w*) WPC; 20 % (*w*/*w*) CS + 80 % (*w*/*w*) GA; 50 % (*w*/*w*) CS + 50 % (*w*/*w*) GA; 20 % (*w*/*w*) GA + 80 % (*w*/*w*) WPC; 50 % (*w*/*w*) GA + 50 % (*w*/*w*) WPC; and 80 % (*w*/*w*) GA + 20 % (*w*/*w*) WPC. The wall materials were added to distilled water at 25 °C, and the mixture was stirred until completely dissolved. The wall material and oil concentrations (total solids) were fixed at 40 % (*w*/*v*) and 10 % (*w*/*v*), respectively. Emulsions were formed using a rotor-stator blender (TE-102, Ultra-Turrax Tecnal, São Paulo, Brazil) operating at 15,000 *g* for 5 min and were used as the feed liquid for spray drying (Aghbashlo et al. 2013b; Carneiro et al. 2013).

Microencapsulation by Spray Drying

The spray drying process was performed in a laboratory-scale mini spray dryer (MSDi 1.0, Labmaq, São Paulo, Brazil) with a nozzle atomization system and a 1.0-mm-diameter nozzle.

The operational conditions of the spray drying were as follows: inlet and outlet drying air temperature were respectively 180 and 90 °C; flow feed rate, 0.9 L h^{-1} (Fernandes et al. 2014); air pressure, 2 kgf/cm^2; and spraying air flow rate, 4 m^3 min^{-1}. Before each experiment, the dryer was run with distilled water for 15 min to achieve desirable steady-state conditions. The finished microcapsules into the product vessel were stored in an amber glass bottle for further analysis.

Powder Analysis

Moisture Content

The moisture contents of the microcapsules (3 g) were determined at 105 °C using a weighting balance with a built-in heating element (MOC-120 H, Shimadzu Corporation, São Paulo, Brazil) (Polavarapu et al. 2011).

Process Yield and Encapsulation Efficiency

Surface oil was based on the method described by Aghbashlo et al. (2013b) by mixing 15 mL hexane with 2 g dried microcapsule and shaking the mixture for 2 min at room temperature. The slurry was then filtered through a Whatman no. 1 filter paper; each filter paper with collected microparticles was rinsed three times with 20 mL hexane. The filtrate solution containing the extracted oil was transferred to an oven at 70 °C for 6 h for complete evaporation of the hexane. The surface oil of the microcapsule was computed by recording the initial and final weights of the solution container. Powder analyses were replicated three times. The process yield (PY), the actual encapsulated oil (AEO), and encapsulation efficiency (EE) were calculated by Eqs. 1, 2 and 3:

$$\mathrm{PY}(\%) = (\text{total recovery} \div \text{total solid sprayed}) \times 100 \quad (1)$$

Where:

Total recovery represents the total mass of microcapsules obtained after encapsulation and total solid sprayed represents the total mass of solids before encapsulation

$$\mathrm{AEO}(\mathrm{w}) = \text{total oil} - \text{surface oil} \quad (2)$$

Where:

Total oil represents the oil added initially in the particle formation mixture and surface oil represents the weight of oil on the surface of the microcapsule.

$$\mathrm{EE}(\%) = (\mathrm{AEOw} \div \text{total oil}) \times 100 \quad (3)$$

Where:

AEOw represents the weight of oil inside the microcapsule and total oil represents the oil added initially in the particle formation mixture.

Scanning Electron Microscopy

Microscopy was kindly performed at Oswaldo Cruz Foundation of Bahia (Fiocruz—Bahia—Brazil) on microcapsules with the best characteristics. Microcapsules were observed with a scanning electron microscope with energy dispersive X-ray (SEM) (JSM—6390LV, LEO Electron Microscopy, Oxford, England) operating at 3 nm resolution at 15 kV and at 4 nm resolution at 30 kV. The samples were fixed directly on door-metallic specimens (stubs) and then subjected to metallization (sputtering) with a thin layer of gold in a critical equipment Leica (EM CPD 030, Austria) at a coverage rate of 0.51 Å/s for 180 s, a current of 3.5 mA, 1 V and 2×10^{-2} Pa. After metallization, the samples were observed with 2500 × magnification. Image acquisition was performed by the LEO software, version 3.01 (Carneiro et al. 2013).

Thermogravimetric Analysis (TG-DTG) and Differential Scanning Calorimetry

Thermogravimetric curves (TG) and differential thermogravimetric curves (DTG) of crude palm oil (CPO), cassava starch (CS), and gum arabic (GA) encapsulated without oil (white—CS:GA), and microparticles containing crude palm oil (CPO:CS:GA) were kindly performed at the Chemical Institute by the Group of Energy and Materials Science (Federal University of Bahia—Bahia, Brazil). Each sample was wrapped in platinum micro-crucibles and pre-weighed on a thermobalance (Shimadzu, TGA 50 H, Brazil). The analysis conditions were sample mass, 11.5 mg; nitrogen gas flow rate, 50 mL/min; heating rate, 10 °C/min; and temperature range, 25 to 600 °C.

Differential scanning calorimetry (DSC) curves were obtained on a differential scanning calorimeter (Seiko, DSC 6220, Japan). Each sample was weighed on an analytical balance (Shimadzu, AY 220, Brazil) and packed in an aluminum micro-crucible with volume of 40 μL. An empty crucible was used as reference. In this analysis, the weight sample was 11.5 mg, the nitrogen gas had a flow rate of 50 mL/min, the heating rate was 10 °C/min, and the temperature range was 25 to 600 °C.

Encapsulated and Un-encapsulated Crude Palm Oil Chemical Characterization

To evaluate the influence of the microencapsulation process on the oil chemical composition, the crude palm oil was chemically characterized. Total carotenoids (TC), color parameters, peroxide value (POV), antioxidant activity (AA), major carotenoid identity, fatty acid profile, and oxidative stability were studied before (oil control) and after the microencapsulation process. The oil extraction of the powder was performed according to Partanen et al. (2008). For this purpose, 20 g of

microcapsuled crude palm oil was transferred to a 250-mL Erlenmeyer flask with a stopper, 200-mL distilled water was added, and then the sample was swirled in a shaker (TE 424, Tecnal, São Paulo) for 30 min. Subsequently, 40-mL isooctane and 20-mL isopropyl alcohol were added to the solution and the solution was centrifuged (4000 *g*, 4 min) (5702 R, Eppendorf, Germany). Finally, the supernatant was collected, filtered, and incubated in a 45 °C oven for 3 h to completely evaporate the solvent.

Total Carotenoids

Crude palm oil carotenoid quantification was performed on a spectrophotometer (UV-Vis Lambda 25, Perkin Elmer, Waltham, USA) by reading the maximum wavelength of absorption of β-carotene (450 nm) in petroleum ether and the concentration calculated considering an absorptivity ($A^{1\%}{}_{1\ cm}$) of 2592 (Rodriguez-Amaya and Kimura 2004).

$$\text{Total carotenoids}\left(\frac{\mu g}{g}\right) = [\text{Ab} \times 100000 \div 2595] \div W_{oil} \quad (4)$$

Where:

Ab represents the oil absorbance and W_{oil} represents the oil weight.

Major Carotenoids Identification by HPLC

The carotenoid extract was prepared according to Zeb and Murkovic (2013). Carotenoids were extracted from crude palm oil (the oil control) and from the oil microcapsule (5 mg samples). The oil was dissolved in 5 mL of acetone and sonicated for 20 s. The samples were then kept at −20 °C for 24 h. The triacylglycerols crystallized and the carotenoids moved into the acetone fraction. The samples were then quickly filtered. This method removes approximately 90 % of the lipids. Saponification was avoided in order to reduce the formation of artifacts (e.g., hydrolysis of epoxides).

High-performance liquid chromatography (HPLC) analysis was performed using a HPLC system (Agilent 1100 Series, Germany) equipped with a quaternary solvent pumping system G1311A-DE14917573 (Agilent, 1100 Series, Germany) and a UV-Vis detector G1314B-DE71358944 (Agilent 1100 Series, Germany). A C30 reversed-phase polymeric column (250 mm × 4.6 mm × 3 μm i.d.; YMC, Japan) was used. The wavelength was adjusted to 450 nm. The mobile phase was a linear gradient of water/methanol/methyl *tert*-butyl ether (J. T. Baker-Mallinckrodt, USA) starting at a ratio of 5:90:5. The ratio was changed to 0:95:5 in 12 min, then to 0:89:11 by 25 min, then finally to 0:75:25 by 40 min at a flow rate of 1.0 ml/min at 33 °C. The final solvent ratio was maintained until the completion of the 60-min run. (Nunes and Mercadante 2007; Zanatta and Mercadante 2007). Standard curves were constructed from all-*trans*-β-carotene (5-50 μg/ml), all-*trans*--α-carotene (2-25 μg/ml), and cryptoxanthin (4-100 μg/ml) (7235–40–7, Sigma-Aldrich, USA). The limits of quantification (LOQ) and detection (LOD) were 10.89×10^{-2}mg/kg and 6.53×10^{-2}mg/kg for all-*trans*-β-carotene; 3.51×10^{-2}mg/kg and 2.11×10^{-2}mg/kg for cryptoxanthin; and 3.28×10^{-2}mg/kg and 1.97×10^{-2}mg/kg for all-*trans*-α-carotene. Areas under peaks were compared with calibration curves. Results were expressed in μg of carotenoids per g sample.

Color Parameters

Color determinations were made using a Minolta colorimeter (CR-400, Minolta, Osaka, Japan) with an illuminant D_{65} and observer angle of 2°. Color data are presented as CIELab coordinates, which define the color in a three dimensional space. L* is an approximate measurement of luminosity, which is the property according to which each color can be considered as equivalent to a member of the gray scale, between black and white, taking values within the range 0–100; a* takes positive values for reddish colors and negative values for the greenish ones, whereas b* takes positive values for yellowish colors and negative values for the bluish ones. C* is chroma $[(a^{*2} + b^{*2})^{1/2}]$ and is 0 at the center of a color sphere and increases according to the distance from the center. Finally, h_{ab} is the hue angle [*tan*-1(b*/a*)] (Andreu-Sevilla et al. 2008).

Peroxide Value (POV)

Crude palm oil was subjected to peroxide value determination based on the AOCS method (AOCS, 1993). The peroxide value was computed as follows by Eq. 5:

$$\text{POV}\left(\frac{\text{meq}}{\text{Kg}}\right) = [(S-B) \times N \times 1000] \div W \quad (5)$$

Where:

S is the titration of the sample (in mL); *B* is the titration of blank (in mL); *N* is the normality of the sodium thiosulfate solution; and *W* is the weight of sample (in g).

Antioxidant Activity (AA)

Measurement of 2,2-diphenyl-1-picryl hydrazyl (DPPH) radical scavenging activity was performed according to the methodology described by Brand-Williams et al. (1995). The DPPH solution (100 μM) was prepared in ethyl acetate, homogenized, and kept in the dark for 30 min to allow the formation of free radicals. The samples were weighed (approximately 100 mg) in test tubes on an analytical balance (M214A, Bel Engineering, Italy). DPPH was added in

4000 μL increments, followed by vortex mixing for 10 s. The absorbance readings were performed in a UV-Vis spectrophotometer (Lambda 25, Perkin Elmer, USA) at a wavelength of 515 nm after 30 min. To evaluate the radical scavenging activity, the percent of inhibition was obtained, according to the equation by Mensor et al. (2001):

$$\mathrm{AA}(\%) = (\mathrm{Aa}-\mathrm{Ab}) \times 100 \div \mathrm{Ac} \quad (6)$$

Where:

Aa = absorbance of the DPPH solution without addition of sample; Ab = absorbance of the mixture of solution of DPPH and sample; Ac = absorbance of the blank solution without DPPH.

Palm Oil Fatty Acid Profile by Gas Chromatography

Fatty acids profile was determined by the capillary column gas chromatographic method applied to the oil methyl esters (Joseph and Ackman 1992). The amount of total fatty acids (sum of free and bounded fatty acids) of each oil was obtained by transesterification into the corresponding methyl esters (fatty acid methyl esters—FAME), through saponification with NaOH in methanol, followed by methylation with BF3 catalyst (12 % in methanol). The FAME were extracted with iso-octane and stored in an inert atmosphere (N) in freezer at −18 °C. The FAME separation was performed on a gas chromatograph (3800, Varian, USA) equipped with a flame ionization detector and a fused silica capillary column (58 FFAP, Elite-WAX, USA) (30 m × 0.32 mm × 0.25 mm). The analysis parameters were injector temperature of 250 °C and detector temperature of 280 °C. The following thermal program was used: 150 °C for 16 min, then increasing 2 °C/min up to 180 °C, held for 25 min, following an increase of 5 °C/min up to 210 °C, held for 25 min more. Helium was used as carrier gas at 1.3 ml min^{-1}. Nitrogen gas was used as make up gas (30 ml min^{-1}); flow of hydrogen gas, and synthetic air were provided at 30 and at 300 ml min^{-1}, respectively. The injections were performed in duplicate for each extraction in volume of 1 μl. FAME were identified by comparing their retention times with those of authentic standards (189–19, Sigma-Aldrich, USA). The quantification of fatty acids, expressed in milligrams per gram of lipids, was performed by adding internal standard (C23:0, Sigma, USA) and calculating the extracted lipids according to Eq. 7. Reported yields were averaged from three replicate extractions (Nascimento et al. 2013):

$$\mathrm{Concentration}(\mathrm{mg/g}) = (A_x \times W_{\mathrm{is}} \times CF_x) \div (A_{\mathrm{is}} \times W_s \times CF_s) \times 1000 \quad (7)$$

Where:

A_x is the area of methyl ester fatty acid peek in the chromatogram of the sample; W_{is} is the weight (in milligrams) of internal standard added to the sample; CF_s is the conversion factor of fatty acid methyl ester to fatty acid; A_{is} is the area of internal standard methyl ester of fatty acid peek in the chromatogram of the sample; W_s is the sample weight (in milligrams); CF_x is the correction factor response of each fatty acid methyl ester ionization detector, relative to C23:0.

Oxidative Stability Test

The prepared microcapsules were stored at 45 °C for 5 weeks in an incubator in order to accelerate the oxidation process. Aliquots (250.0 g) of each sample were poured into each PYREX glass vessels. Samples were taken at intervals for encapsulation efficiency; peroxide value (POV) and total carotenoids were determined weekly. Crude palm oil was used as control (Carneiro et al. 2013).

Statistical Analysis

Moisture content, process yield, and efficiency encapsulation were evaluated in triplicate by analysis of variance (ANOVA) and Turkey's test $p < 0.05$ using SPSS (ver. 15). A paired t test ($p < 0.05$) using SPSS (ver.15) was used for the analysis of total carotenoids, carotenoid identification, color parameters, peroxide value, antioxidant activity, fatty acid profile, and oxidative stability test before and after encapsulation. All these experiments were replicated fivefold.

Results and Discussion

Moisture Content of Microcapsules

The core material retention during microencapsulation by spray drying is affected by the composition and the properties of the emulsion and by the drying conditions. In order to obtain good microencapsulation efficiency and even if the wall material is suitable, optimal spray drying conditions must be used. The main factors in spray drying that must be optimized are feed temperature, air inlet temperature, and air outlet temperature. In fact, feed temperature modifies the viscosity of the emulsion, its fluidity, and thus, its capacity to be homogenously sprayed. When the feed temperature is increased, viscosity and droplets size should be decreased but high temperatures can cause volatilization or degradation of some heat-sensitive ingredients. The rate of feed delivered to the atomizer is adjusted to ensure that each sprayed droplet reaches the desired drying level before it comes in contact with the surface of the drying chamber (Gharsallaoui et al. 2007).

The characteristics of the generated microcapsules are reported in Table 1. The moisture content of the capsules varied from 0.74 to 2.79 %. This finding was somewhat different

Table 1 Characteristics of the generated crude palm oil microcapsules using different wall materials at 180 °C

Wall material			Moisture content (%)	Process yield (%)	Encapsulation efficiency (%)
CS (%)	GA (%)	WPC (%)			
20	–	80	2.26 ± 0.105[a]	28.66 ± 0.781[c]	93.47 ± 2.406[a]
20	80	–	2.35 ± 0.115[a]	40.97 ± 2.055[a]	96.53 ± 0.504[a]
50	50	–	2.79 ± 0.100[a]	56.96 ± 3.091[b]	92.77 ± 2.909[ab]
–	20	80	1.64 ± 0.978[a]	54.54 ± 2.902[b]	92.99 ± 1.938[a]
–	50	50	2.58 ± 0.394[a]	39.10 ± 1.102[a]	94.15 ± 1.060[a]
–	80	20	0.74 ± 0.780[b]	47.03 ± 1.945[d]	97.89 ± 0.112[ac]

CS cassava starch, *GA* gum arabic, *WPC* whey protein concentrate (derived from milk)

Different letters in the same column indicate significant differences ($p < 0.05$)

from the moisture content of encapsulated rosemary essential oil reported by Fernandes et al. (2014) (1.40 to 3.56 %) that used combinations of gum arabic, modified starch, maltodextrin, and inulin as wall materials and used inlet drying air temperature of 180 °C. Aghbashlo et al. (2013b) also reported slightly higher moisture contents (1.41 to 4.36 %) of microencapsulated fish oil with wall material combinations of whey protein concentrate, whey protein isolated, skimmed milk powder, and sodium caseinate and 140 °C (4.36 %), 160 and 180 °C (1.41 %) as the inlet drying air temperatures. The slight discrepancies have several explanations. For example, the air inlet temperature used in this study was 180 °C, which is slightly higher than that in Aghbashlo et al. (2013a).

In general, the capsules did not show significant differences with respect to the moisture content when made with different wall material combinations. One exception was that the microcapsules made with GA:WPC (80:20) had a significantly lower moisture content ($p < 0.05$) compared to other combinations (Table 1). The relatively low moisture content of the capsules is promising for shelf stability because a high moisture content seems to promote fat oxidation (Dian et al. 1996). According to Aghbashlo et al. (2013b), Drusch et al. (2007), and Wang et al. (2011), a high inlet temperature of 180 °C accelerates the evaporation rate, resulting in microcapsules with low moisture.

There are other factors that can influence the moisture microcapsules, such as emulsion viscosity. Emulsion viscosity and particle size distribution have significant effects on microencapsulation by spray drying. High viscosities interfere with the atomization process and lead to the formation of elongated and large droplets that adversely affect the drying rate (Gharsallaoui et al. 2007).

Process Yield and Encapsulation Efficiency

As presented in Table 1, the process yield ranged from 28.66 to 56.96 %. There are few studies involving oil encapsulation and the process yield. Calvo et al. (2012) and Nunes and Mercadante (2007) both obtained a maximum process yield of approximately 51 % with extra virgin olive oil in a maltodextrin and modified starch capsule, and lycopene in a gum arabic and sucrose capsule, respectively. Low temperatures do not promote proper drying, though the drying temperature was not a problem in this study.

Encapsulation efficiency varied significantly between wall material combinations ($p < 0.05$) and ranged from 92.77 to 97.89 %. These results are above the levels reported by Aghbashlo et al. (2013a) (59.05–85.67 %), Aghbashlo et al. (2013b) (40.59–81.94 %), and Gallardo et al. (2013) (25.5–91.4 %). Thus, the particles in this study likely exhibit greater protection against lipid oxidation, given that there is less surface oil.

Encapsulation efficiency determines the degree of oil protection and is dependent upon numerous factors; the two most frequently cited factors are inlet air temperature and wall material (Gallardo et al. 2013). The temperature used for drying microcapsules in this study, 180 °C, may have contributed to the high efficiencies that was observed. According to Aghbashlo et al. (2013b), high inlet temperatures can contribute to fast formation of the microcapsules and a firm membrane that reduces migration of the oil to the encapsulated surface. Moreover, the wall material gum arabic is generally used as a thickening agent in foodstuffs, showing a ramified structure with long chains, which can be responsible for its higher viscosity and contributed for the high efficiency (Carneiro et al. 2013).

Furthermore, the wall material combinations WPC + CS, CS + GA, and GA + WPC, in relation to the oil amount used, may have contributed to our high observed encapsulation efficiency. This outcome occurred because, in general, the ratio of wall material relative to the core should be between 2 and 4 and, in this study, it was 4:1 (wall material:oil). A ratio lower than 2 can lead to increased surface oil, while a ratio greater than 4 results in a capsule with a very low content of encapsulated oil. A low content of encapsulated oil is typically not desirable for food applications (Gallardo et al. 2013).

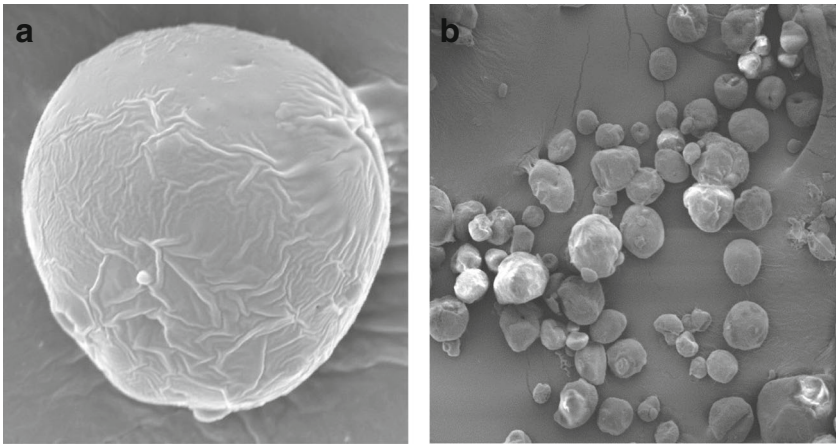

Fig. 1 SEM image of crude palm oil microencapsulated by spray drying with 50 % CS and 50 % GA as wall materials in two different magnification: 2500× (**a**) and 300× (**b**)

Microcapsules with 80 % GA and 20 % WPC showed the highest efficiency. It is argued that the presence of the disaccharide lactose in the concentrated whey protein may alter wall properties, thus facilitating wall formation and reducing oil retained on the inner surface of the particles. According to Aghbashlo et al. (2013b), the lactose glass phase increases the hydrophilic nature of the wall matrix and limits the diffusion of the solvent through the wall. The development of nitrogenous polymers and melanoidins, as a result of the reaction between the amino groups of proteins and the carbonyl groups of lactose (the Maillard reaction), may also contribute to formation of the wall. In a previous study, protein-carbohydrate conjugates formed by the Maillard reaction stabilized fish oil microcapsules by changing the physical properties of the wall (Aghbashlo et al. 2013b). Furthermore, according to Gharsallaoui et al. (2007), lactose in its amorphous state acts as a hydrophilic sealant that significantly limits the diffusion of oil through the hydrophobic wall core, thus leading to high levels of microencapsulation efficiency.

In general, the values obtained for efficiency met or exceeded those reported in other studies. The microcapsule with CS:GA—50:50 demonstrated the highest process yield ($p < 0.05$). Furthermore, the addition of 50 % cassava starch to the wall material provides a significant economic benefit when considering production on an industrial scale because the CS is cheaper than most other wall materials (all of the materials used in this study). In addition, with cassava starch-encapsulated palm oil, the potential exists to increase the commercial value of both CS and crude palm oil.

SEM Image

Figure 1 shows the SEM image of crude palm oil microcapsules produced with 50 % CS and 50 % GA by spray drying at an air inlet temperature of 180 °C. The encapsulate has a spherical shape without visible cracking, and these characteristics indicate that the capsules are less permeable to gasses, oxidative processes, and undesirable oil leakage to the particle surface. Furthermore, they showed different diameters ranging from 12–32 μm. Carneiro et al. (2013), Drusch et al. (2007), and Gallardo et al. (2013) microencapsulated linseed oil, fish oil, and linseed oil, respectively, and observed similar microcapsule morphology.

Thermogravimetric Analysis (TG-DTG) and Differential Scanning Calorimetry (DSC)

Thermogravimetric curves (Fig. 2a, b) show crude palm oil thermal analysis decomposition between 217 and 495 °C, with approximately 1.5 % residue (Fig. 2a). When

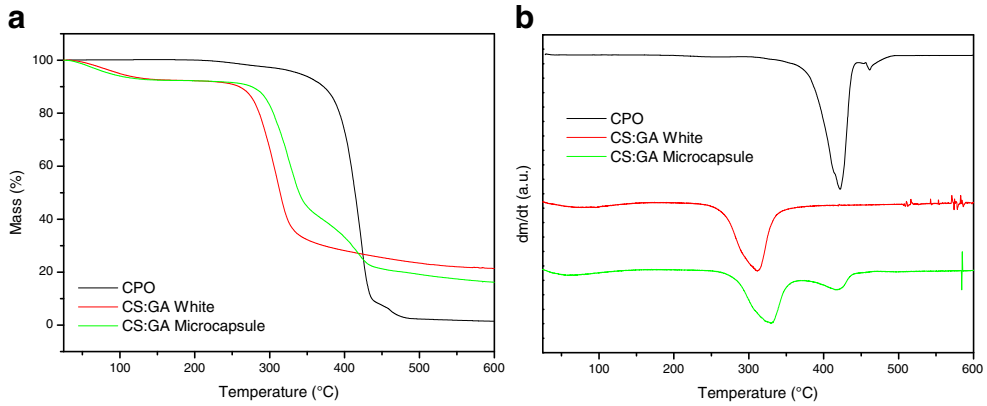

Fig. 2 TG (**a**) and DTG (**b**) scans of crude palm oil (*CPO*) and cassava starch (*CS*): gum arabic (GA) encapsulated without oil (*white*) and with crude palm oil

microencapsulated with cassava starch and gum arabic and spray dried, the decomposition temperature increased to the range of 244 to 569 °C (Fig. 2a, b) with a residue percentage of approximately 16 % (Fig. 2a). Without oil, the CS/GA decomposition was in the range of 250 to 492 °C (Fig. 2a, b) with a residue of approximately 22 % (Fig. 2a), indicating that the microcapsules increased the thermal stability of pure crude palm oil. Fernandes et al. (2014) found that gum arabic as a wall material increases the glass transition temperature (Tg) of oil in studies of oil microencapsulation. The increase in Tg is because encapsulation increases the maximum molar mass (from 47,000 to 3,000,000 g mol^{-1}), and Tg is positively associated with molar mass. Thus, gum arabic as an encapsulating material provides increased microcapsule thermal resistance, which makes it a promising wall material for applications in the food industry.

Phase transitions can be obtained from DSC curves from the peak temperatures. As shown in Fig. 3, crude palm oil has an endothermic peak at 422 °C, corresponding to oil evaporation. Comparing the calorimetric curve of crude palm oil microcapsules with the materials without oil, it was observed that the presence of crude palm oil influences the thermal microspheres performance. Microcapsulated palm oil showed an endothermic event at 72 °C, while the wall material alone showed an endothermic event at 82 °C, thus demonstrating similar thermal behavior and probable water evaporation between these endothermic events because these materials are hygroscopic. Therefore, it appears that the microspheres obtained by the spray drying process retained the thermal performance of the carbohydrates used as wall materials.

There was a little change in the crude palm oil thermal resistance, which suggests no modification or interaction between crude palm oil and carbohydrates such as wall materials used in the crude palm oil microcapsule structure.

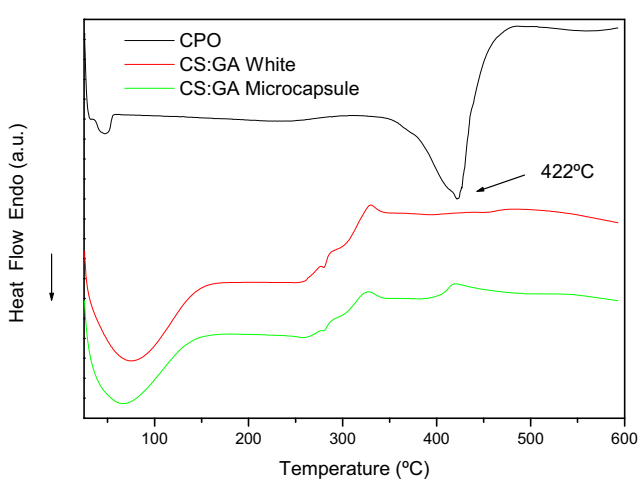

Fig. 3 DSC scans of crude palm oil (*CPO*) and cassava starch (*CS*): gum arabic (GA) encapsulated without oil (*white*) and with crude palm oil

Microencapsulation Effects on the Crude Palm Oil Characteristics

Total Carotenoids, Major Carotenoids Identification, Color Parameters, Peroxide Value, and Antioxidant Activity

Average carotenoid content found in crude palm oil before and after the encapsulation was 608.39 ± 32.94 μg/g and 600.52 ± 16.05 μg/g, respectively (Table 2), indicating that the spray drying processing conditions preserved the bioactive compounds and furthermore were within the range established by Codex (2013) (500–2000 μg/g). Similar values for the carotenoid content in crude palm oil without heating were found by Almeida et al. (2013) (578.26 ± 5.99 μg/g), Baharin et al. (2001) (632 ± 15.5 μg/g), and Choo et al. (2005) (550 ± 10 and 600 ± 20 μg/g). Dian et al. (1996) reported 215.18 μg/g carotenoids in microencapsulated refined palm oil, while their crude palm oil control contained 358.3 μg/g carotenoids.

The major carotenoids in the crude palm oil before and after encapsulation were all-*trans*-β-carotene and all-*trans*--α-carotene. However, there was a significant reduction of these carotenoids when subjected to microencapsulation ($p < 0.05$). All-*trans*-β-carotene and all-*trans*-α-carotene were measured in the following concentrations, respectively: 233.44 ± 21.40 μg/g and 88.78 ± 10.65 μg/g for crude palm oil (control) and 170.50 ± 17.15 μg/g and 67.37 ± 6.93 μg/g for the oil extracted from the microcapsule.

Despite the well-known phenomenon of carotenoid degradation, the mechanisms involved have not been elucidated. In contrast, for lipid oxidation, the different reactions and the initial, intermediate, and final products are known.

According to Rodriguez-Amaya and Kimura (2004), knowledge of underlying mechanisms of oxidative reactions and degradation of carotenoids is necessary not only to avoid the loss of these beneficial compounds during processing and storage of food but also to assess the implications in biological processes. Studies performed by Aust et al. (2003) indicated that lycopene degradation products enhance cell-cell communication via gap junctions, and this process is implicated in the protective mechanisms of carotenoids against cancer.

For crude palm oil, b*, C*, and h_{ab} coordinates before and after encapsulation were statistically different ($p < 0.05$) (Table 2). In general, the oil retained its luminosity (i.e., L* was maintained), and showed the same redness (i.e., a* was maintained), perhaps indicating preservation of carotenoids after microencapsulation. However, encapsulation led to a reduced b* value, signifying less yellow.

The peroxide value increased significantly ($p < 0.05$) due to microencapsulation (Table 2). The POV of palm oil extracted from capsules was 11.16 ± 0.00 meq/Kg oil while the POV of crude palm oil before encapsulation was 3.56 ± 0.19 meq/Kg oil. The increase in POV can be explained by the high oil

Table 2 Total carotenoids, color parameters, peroxide values, and antioxidant activity characteristics of the crude palm oil (CPO) when encapsulated with 50:50 CS and GA as wall materials

	Total carotenoids (μg/g)	Color parameters					Peroxide value (meq/Kg)	Antioxidant activity (%)
		L*	a*	b*	C	h_{ab}		
CPO before encapsulation—control	608.39 ± 32.94[a]	34.96 ± 0.31[a]	17.97 ± 0.24[a]	28.88 ± 0.43[a]	34.02 ± 0.49[a]	58.11 ± 0.10[a]	3.56 ± 0.19[a]	56.83 ± 2.49[a]
CPO after encapsulation	600.52 ± 16.05[a]	33.51 ± 0.70[a]	16.89 ± 1.82[a]	26.48 ± 1.52[b]	32.45 ± 1.29[b]	50.98 ± 0.26[b]	11.16 ± 0.00[b]	29.25 ± 1.13[b]

Different letters in the same column indicate significant differences ($p < 0.05$)

temperature during the drying process. Aghbashlo et al. (2013b) explained that the higher the processing temperature, the higher the amount of generated peroxides due to the rapid oxidation of lipids from the intensive energy present at higher drying temperatures. Importantly, crude palm oil after encapsulation remained within the parameters set by Codex (2013) for this analysis (15 meq/kg oil), indicating the quality of the oil was preserved.

Percent inhibition of DPPH• by palm oil was significantly reduced with microencapsulation ($p < 0.05$) (Table 2). This result is possibly due to the increase of the peroxide value because the latter indicates a higher degree of oxidation of the oil and also due to the reduction of antioxidants such as vitamin E (Ramadan et al. 2006). Furthermore, although total carotenoids did not change, the spray-dryer heat could have promoted isomerization of *trans* carotenoids to their less common *cis* forms. Isomerization results in some loss of color and pro-vitamin A activity, which ultimately reduces antioxidant activity.

Arana-Sánchez et al. (2010) microencapsulated essential oregano oil and obtained an increase in antioxidant activity in the oil after encapsulation. They attributed this increase to changes in the composition of pure oils in the microencapsulation process, given that there was less degradation of the oils. The inlet temperature that they used for microencapsulation (105 °C) was lower than that used in this study, which may account for the difference in results.

Fatty Acid Profile

The fatty acid (FA) profile was evaluated to assess the effects of the microencapsulation process (i.e., microcapsule emulsion and oil inclusion) on the oil composition according to the different wall components. In general, few differences were observed among the un-encapsulated oil and the oil from the microcapsule model (Table 3). Only the levels of palmitic acid and oleic acid showed significant differences after the oil encapsulation. However, all fatty acids found before and after encapsulation were within the standards published by Codex (2013). Calvo et al. (2012) reported that fish oil microencapsulated in a wall material of basic protein retained high concentrations of monounsaturated fatty acids. In addition, they reported that wall material composed of carbohydrates could also protect encapsulated mono and polyunsaturated fatty acids. This factor may explain the reduction of oleic acid after the crude palm oil encapsulation. In addition, this result may be explained in terms of the structure of the FAs. Generally, the greater the number of double bonds in the FA, the greater the ease of its oxidation, for example, by oxygen or light (Polavarapu et al. 2011).

Table 3 Characteristics of encapsulated and un-encapsulated (control) crude palm oil on the fatty acid profile

Fatty acid (mg/g)	Crude palm oil before encapsulation—control	Crude palm oil after encapsulation
Lauric acid (C12:0)	0.48 ± 0.06[a]	0.00 ± 0.06[a]
Myristic acid (C14:0)	0.79 ± 0.04[a]	0.79 ± 0.10[a]
Palmitic acid (C16:0)	40.57 ± 0.26[a]	40.89 ± 0.15[b]
Palmitoleic acid (C16:1)	0.12 ± 0.01[a]	0.13 ± 0.00[a]
Stearic acid (C18:0)	4.81 ± 0.04[a]	4.77 ± 0.06[a]
Oleic acid (C18:1)	43.84 ± 0.18[a]	43.29 ± 0.26[b]
Linoleic acid (C18:2)	8.86 ± 0.16[a]	8.67 ± 0.04[a]
Linolenic acid (C18:3)	0.23 ± 0.02[a]	0.22 ± 0.01[a]
Eicosadienoic acid (C20:0)	0.31 ± 0.03[a]	0.30 ± 0.03[a]

Different letters in different columns indicate significant differences ($p < 0.05$)

Oxidative Stability Test

Capsules were stored for 5 weeks at 45 °C and their residual encapsulated oil (the amount of oil retained within the capsules), peroxide value, and total carotenoids were monitored (Fig. 4). The residual encapsulated oil decreased from 92.77 ± 0.37 % to 90.62 ± 1.21 % (Fig. 4a); the peroxide value of encapsulated oil increased from 11.16 ± 0.00 meq/kg oil to 12.54 ± 0.00 meq/kg oil ($p < 0.05$) (Fig. 4b); and total carotenoids (Fig. 4c) of encapsulated oil decreased from

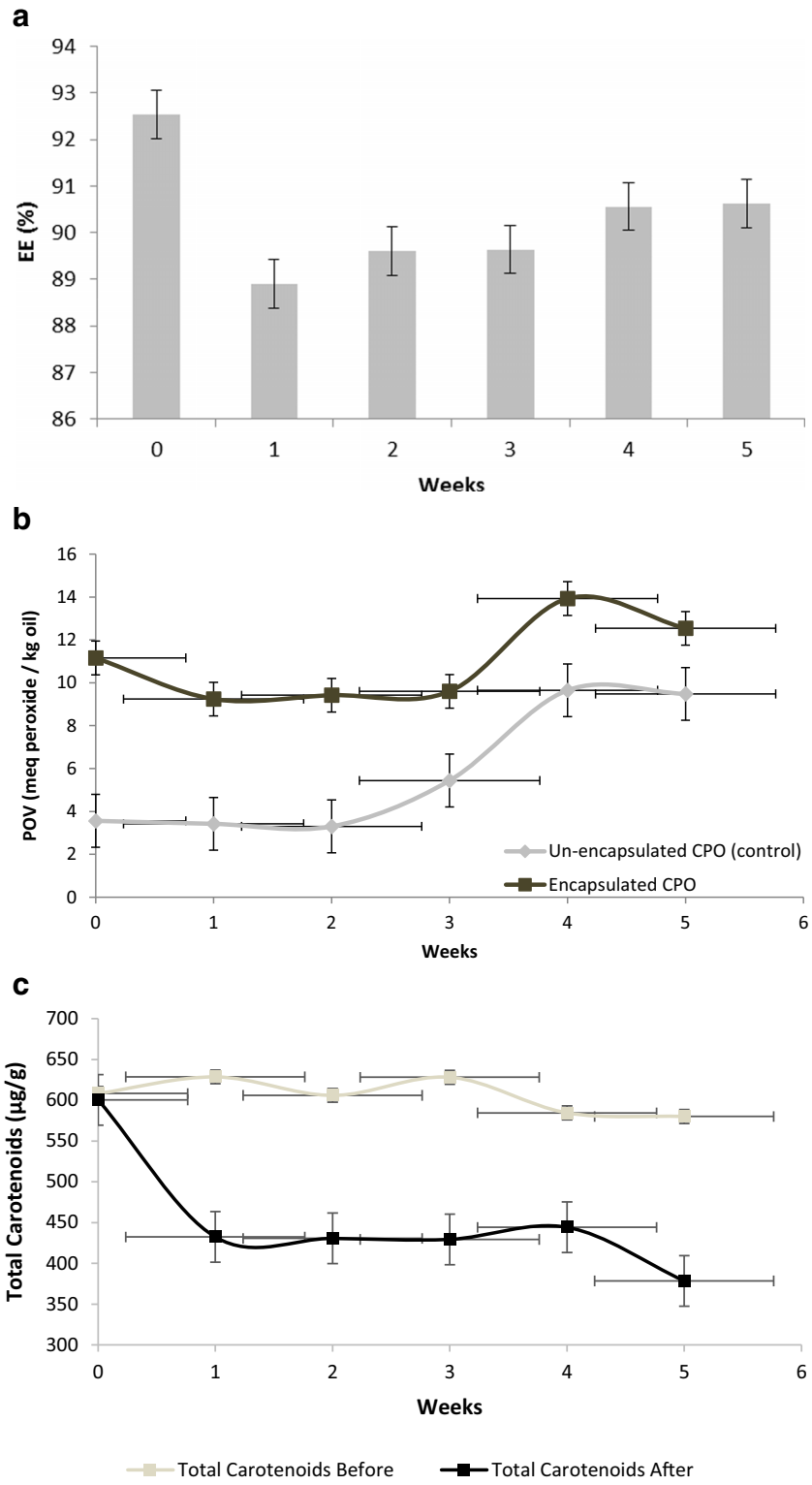

Fig. 4 The effect of storage time on the encapsulation efficiency (**a**), peroxide value (**b**), and total carotenoids (**c**) of microencapsulated crude palm oil. In **a**, *different letters* indicate significant differences between the weeks ($p < 0.05$)

600.52 ± 2.67 μg/g to 378.44 ± 10.67 μg/g ($p < 0.05$). Thus, 63.02 % of carotenoids were retained in the microcapsules.

Ahn et al. (2008) assessed the peroxide value and the values of encapsulation efficiency of encapsulated flaxseed oil at accelerated storage conditions at 60 ± 1 °C for 30 days and observed a reduction in carotenoids and an increase of peroxides with storage time. Moreover, Aghbashlo et al. (2013b) corroborated their findings under accelerated storage conditions of 25 °C ± 1 °C for 4 weeks with fish oil. Although the encapsulation efficiency decreased in week 1, this reduction was not significant at weeks 2 and 3. Tonon et al. (2011) reported the lowest peroxide value of 0.017 meq/kg oil and the highest encapsulation efficiency (91.97 %) when investigating the effect of emulsion composition and inlet drying air temperature on the microencapsulation of flaxseed oil.

Oil can be released to the surface of the microcapsule during storage, leading to a poorer oil protection against oxidation. This release may be related to physical and chemical changes of the capsule wall and molecular diffusion of oil. The released oil, when in contact with oxygen, is much more susceptible to oxidation than its encapsulated form. However, with increasing storage time, the amount of permeated oxygen from the wall to the inside of the particle dramatically increases, and therefore, the peroxide formation can occur in the interior of the capsule (Aghbashlo et al. 2013b, Wang et al. 2011, and Ahn et al. 2008).

Despite these results, the POV values after the encapsulation process remained within the maximum limit set by Codex (2013), which is 15 meq/kg oil. However, as observed in thermal analysis, the microcapsules withstood very high temperatures. Thus, although there was a significant reduction in carotenoids in the oxidative stability test, compared to other oils, crude palm oil remains an important source of carotenoids and pro-vitamin A activity. Therefore, these microcapsules can be applied to fortify foods which, for example, are not subjected to heating and oxygen.

Regarding the differences found with respect to the oil before (control oil) and after encapsulation, in microcapsules, carotenoids reduced (608.39 ± 32.94 μg/g—580.16 ± 58.16 μg/g—control oil) (600.52 ± 16.05 μg/g—378.44 ± 40.37 μg/g—after encapsulation) and peroxides increased (3.56 ± 0.19 meq/kg oil—9.48 ± 0.46 meq/kg oil—control oil) (11.16 ± 0.0 meq/kg oil—12.54 ± 0.0 meq/kg oil—after encapsulation) more than in the control oil possibly the question of porosity of the microcapsules. When the material is porous, such as microcapsules, there is a space among the particles and they are filled by air, then carotenoids reduced over the dust as it acted in the deactivation of more oxygen. In oil, the penetration of oxygen is slower. However, when microencapsulated, the oil becomes dispersible in water, allowing mixing it in foods, especially solid without sensory changes. Therefore, the use of oil microencapsulated is very important for the food industry.

Carotenoids act by sequestering reactive oxygen species, such as the peroxide radical (ROO●) and singlet oxygen ($^1O_2$) (Ribeiro et al. 2011; Rodriguez-Amaya and Kimura 2004). Changes in these compounds can be attributed to degradation by heat, which can cause carotenoid isomerization and oxidation (Andreu-Sevilla et al. 2008).

In **b** and **c**, *different letters* indicate significant differences between un-encapsulated and encapsulated crude palm oil for each storage time ($p < 0.05$). *EE* encapsulation efficiency, *POV* peroxide value.

Conclusion

Spray drying is a suitable method to encapsulate crude palm oil within cassava starch and gum arabic wall materials. The presence of these wall materials in a 50:50 blend, specifically, improved the encapsulating capability. This technology promotes satisfactory results of process yield and encapsulation efficiency, fatty acid profile, color parameters, and total carotenoids but decreased the antioxidant activity and increased the peroxide value. Thermal analyses revealed a good resistance of crude palm oil to encapsulation. Although there was a reduction of carotenoids in the oxidative stability test, they acted as excellent antioxidant in the stability test and, furthermore, compared to other oils, crude palm oil remains an important source of bioactive compounds and has the potential to be applied in the food fortification industry, such as cassava flour, ready-made blends, chocolate drink, and yogurt. Another possibility is to market the palm oil microcapsules for them to be used in foods already ready for consumption.

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