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Changes in oxidative stability, composition and physical characteristics of oil from a non-conventional source before and after processing

Cambios en la estabilidad oxidativa, composición y características físicas de aceite de fuente no convencional antes y después de su procesamiento

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Abstract

The growing demand for vegetable oils has led to the study of unconventional sources. Buffalo gourd (*C. foetidissima* Kunth) could be an alternative one. Refining process effect on oil´s composition and physicochemical characteristics, was determined. Oil extraction was carried out by soxhlet method and refining through combined methods. A yield of 34% crude oil was obtained, fatty acid % and peroxide index decreased and no changes for K_{232} and K_{270} coefficients were detected. Color varied with refining (L * from 78.36 to 87.51, b * from 18.52 to 11.31). According to fatty acid profile, unsaturated predominated: 73.26% and 63.28%, respectively. No foreign functional groups were detected, according to the FTIR analysis, the viscosity changed from 0.045 to 0.062 Pa*s and the oxidative stability decreased markedly in the refined oil. In the sensory test, no difference was identified between fritters obtained with refined buffalo gourd seed oil and those made with commercial canola oil. Due to the composition and characteristics observed, both crude and refined oil could be an alternative for consumption.

Keywords: color, fatty acids, infrared spectrum, oxidative stability, viscosity.

Resumen

La creciente demanda de aceites vegetales ha orillado al estudio de fuentes no convencionales. La calabacilla loca (*C. foetidissima* Kunth) resulta una fuente alternativa. Se determinó el efecto de la refinación en la composición y características fisicoquímicas de este aceite. El rendimiento de aceite crudo fue de 34%, los índices de % de ácidos grasos y de peróxidos disminuyeron, no hubo cambios para coeficientes K_{232} y K_{270}, se detectaron diferencias en color (*Luminosidad* de 78.36 a 87.51, coordenada b* de 18.52 a 11.31) y en el contenido de fenoles totales. Predominaron los ácidos grasos insaturados: 73.26% en aceite crudo y 63.28% en el refinado, sin detectarse grupos funcionales ajenos, de acuerdo con el análisis FTIR. La viscosidad cambió de 0.045 a 0.062 Pa*s y la estabilidad oxidativa disminuyó en el aceite refinado. En la prueba sensorial no se identificó diferencia entre frituras obtenidas con aceite refinado de calabacilla loca y las hechas con aceite comercial de canola. Los resultados indicaron que tanto el aceite crudo como el refinado podrían ser una alternativa de consumo.

Palabras clave: ácidos grasos, color, espectro infrarrojo, estabilidad oxidativa, viscosidad.

1 Introduction

Vegetable oils are organic compounds obtained from seeds or other parts of plants whose tissues accumulate as energy source and where they also take an important role in the cells' functioning and structure (Saldaña and Martínez-Monteagudo, 2013). These are esters formed by the union of fatty acids with glycerol. They constitute the most stable compounds, are not easily degradable, do not dissolve in water and their density is lower than it. Vegetable oils chemical composition corresponds, in most cases, to a mixture of 95% triglycerides and 5% free fatty acids, sterols, waxes and other minor components (FAO, 2012).

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In human diet, lipids are important for being an energy supply, in addition they are precursors of other molecules, such as various hormones; while in the food industry its importance lies in its lubricating properties, its flavor, its properties as heat transmitters, as a vehicle of various ingredients and many other functions (Orsavova *et al*., 2015; Sánchez-Paz *et al*., 2018).

As Seale *et al*. (2017) reported, in recent years, an increasingly growing demand for vegetable oils for food industry and domestic use has developed, due to its multiple functions and applications in the food, cosmetic, pharmaceutical and even biofuel production industries (Pardauil *et al*., 2011), which has increased per capita consumption (Dorni *et al*., 2017); this has led to the search for new sources of this multifunctional raw material.

In recent decades, several unconventional sources have been explored in the world that have shown their potential to complement or increase the supply of edible vegetable oils in the market. One of those unconventional sources is buffalo gourd (*C. foetidissima* Kunth), a plant that grows wild in the semi-desert regions of North America(Lira-Saade *et al*., 2009), which is an interesting source to be exploit due to the few agronomic care demanded, because of its seeds high oil content (up to 36%), as reported in previous studies (Stevenson *et al*., 2007), although the oil of other cucurbit seeds has also been studied, such as *Cucurbita pepo* L., *Cucurbita moschata* and *Cucurbita maxima* reported by Seymen *et al*. (2016) and Shaban and Sahu (2017). However, it is not enough to obtain the crude oil, but its refining and characterization is necessary, so that it can be evaluated as a valid proposal of edible vegetable oil (Grasso, 2013).

The refining process, including the heating to which most commercial edible vegetable oils are subjected during the production process, can cause alterations in their structure and composition (Valantina *et al*., 2015; Bazina & He, 2018), eliminating components that could favor or affect their chemical stability, such as natural antioxidants(Al-Juhaimi *et al*., 2018), which would also impact their sensory properties, that are transmitted to the food processed with them and would affect their acceptance by the common consumer; however, it is a necessary process for impurities elimination that creep into solvent extraction and that could generate alterations in the composition and properties of the oil during storage, so this work is focused on assessing the effect of refinement in the chemical composition, oxidative stability and physical characteristics of buffalo gourd seed oil (*C. foetidissima* Kunth), to subsequently carry out a sensory evaluation using buffalo gourd refined oil in a frying process (potato chips) as a model food to be used against those made with vegetable oil of accepted consumption, in order to explore the viability of its consumption as an alternative raw material in the food industry, or to orientate its use towards another type of industry.

2 Materials and methods

2.1 Buffalo gourd seeds oil obtention (BGSO)

Buffalo's gourd fruit collection (*C. foetidissima* Kunth) was carried out in a property "Jagüey de Ferniza" in the municipality of Saltillo, Coahuila, México, located in the coordinates 25° 14' 2.313" N, 101° 0' 27.753" W, and 25° 13' 45.716" N, 100° 49' 25.324" W, at 2500 masl, in august 2017, seeds were extracted and washed with running potable water up to mucilage removal; they were then dried by natural convection in the sun in cotton inter-cloth for 2 days, until a ≈ 15% humidity was achieved. They were then ground in a blender OsterTM Profesional BPST02-B00 (Sunbean Mexicana, SA de CV, México, D.F.) at medium speed for 15 s, and the greatest amount of husk (fiber) was removed through a mesh No. 60. The resulting material was washed to remove water soluble compounds and dried in a forced convection oven NovatechTM (Avante Tecnología, SA de CV, Tlaquepaque, Jalisco, Méx.) a 40 ± 1 °C for 24 h. The oil was extracted using the first part of the AOAC method 920.39 (Latimer, 2012), using ACS anhydrous petroleum ether as solvent. A part of the product was stored in amber airtight bottle at 6 ± 1 ºC, and the rest was subjected to a physicochemical refining process.

2.2 BGSO Refining

This process was carried out as established by Grasso (2013), with modifications. 500 mL of 3% NaOH and 25 g of crude oil were placed in a 1 L Erlenmeyer flask, followed by heating under reflux for 30 min; subsequently, it was decanted to remove saponified free fatty acids. The oil was washed 5 times with 150 mL of distilled water at 75 ºC and filtered through Whatman No. 1 filter paper by adding 25 g of anhydrous sodium sulfate reagent to remove moisture.

Finally, the micelle was distilled to obtain the pure oil phase. For deodorization and bleaching, in the flask used for distillation of the micelle, 7% w / w activated carbon was added. The mixture was subjected to 85 °C for 30 min, with gentle stirring. It was filtered hot in a glass funnel and Whatman No. 1 filter paper. The sample was cooled to room temperature and stored in a labeled amber bottle and sealed at 6 ± 1 ºC.

Both oils underwent the following tests:

2.3 *Fatty acids % determination, peroxide index, extinction coefficient (K_{232} and K_{270}), total phenols and color*

All these determinations were made at room temperature. The quantification of fatty acids % and peroxide index was carried out in accordance with regulation 2568/91 / EEC, referred by Pérez-Arquillué *et al*. (2003). Total polyphenol content was determined by methodology referred by these same authors with modifications, using gallic acid for the standard curve, and expressing the results in mg of gallic acid per kg of oil. The extinction coefficient was determined according to the method reported by Paz-Antolín & Molero-Meneses (2000), using the equation $\mathbf{K}_\lambda = \mathbf{D}_\lambda/\mathbf{C}$, in which $\mathbf{K}_\lambda$ represents the specific extinction coefficient for each wavelength (232 and 270nm, respectively), $\mathbf{D}_\lambda$ absorbance value, from spectrophotometer lecture, and **C** is the oil's dissolution concentration in g/100 mL.

Color difference was analyzed using a MinoltaTM CR300 triestimulus colorimeter model (Konica Minolta Holding, Inc., Tokyo, Japan), programmed for the CIE $L*a*b*$ color coordinate system (Hunter, 1958); The equipment was previously calibrated according to the manufacturer's instructions. Three readings were taken per sample. The hue angle (H°) was calculated from the color variables of the system used, according to the equation: $H° = \tan^{-1}(b*/a*)$, referred by Elodio-Policarpo *et al*. (2019).

2.4 *Determination of the fatty acid profile by gas chromatography*

Fatty acids esterification was performed according to the methodology reported by Haas *et al*. (2003), with modifications. 1 μL of diluted esterified sample (1:10 in ACS hexane) was injected into a Perkin Elmer® AutoSystem XL gas chromatograph with a FID detector at 300 °C, using a Alltech® EC-100 capillary column of 30m × 0.32mm × 0.25 μm and a heating ramp from 90 to 240 ºC with an increase of 5 °C/min for 15 min. The analysis time was 31 min. Nitrogen was used as a carrier gas. The identification and quantification of fatty acids was made by comparing the chromatographic characteristics of the unknown peaks with those of the standard Sigma-SUPELCO® FAME mix C4 - C24 (Fig. 2a).

2.5 *FTIR analysis*

It was performed at room temperature on a Spectrum Two infrared spectrophotometer (Perkin Elmer Inc., Waltham, Massachusetts, USA) equipped with a universal ATR module (attenuated total reflectance) with diamond crystal. Sufficient sample was placed in the detector. The vibrational transition frequencies were reported in wave numbers (cm^{-1}) within the mid-infrared. An average of 30 scans were recorded with a resolution of 4 cm^{-1} in the region of 450 to 4000 cm^{-1}.

2.6 *Viscosity determination*

The method described by Besbes *et al*. (2004), with modifications was followed. An AR1500 controlled stress rheometer (TA Instruments, New Castle, U.S.A.) with 20 mm stainless steel cone geometry and 4° angle was used. The GAP was adjusted to 90 μm, 200 μL of sample were placed on the Peltier plate and subjected to a constant cut-off rate of 100 s^{-1} for 300 s at 25 ± 1 ºC. The results were reported in Pa*s with respect to time.

2.7 *Oxidative stability determination by differential scanning calorimetry (DSC)*

It was carried out as reported by Tan *et al*. (2002) in a DSC4000 equipment (PerkinElmer Inc., Waltham, USA). Isotherms' temperatures were programmed at four temperatures: 110, 120, 130 and 140 ºC, with a flow of purified oxygen (99.8%) of 50 mL / min. For each isotherm, BGSO samples of 5 ± 0.5 mg weighed in aluminum trays without cover were used, which were placed in DSC chamber. The oxidative induction times ($\mathbf{t}_0$) were taken at the intersection point of the baseline extrapolation and the curve's tangent for each temperature treated (Fig. 4), according to what is referred to by Pardauil *et al*. (2011) and, finally, the linear regression equations were determined. As these last authors concluded in their study, the oxidative stability determination method by DSC was the most appropriate to evaluate this quality parameter in oils

and fats since small amounts of sample are required, it is also highly sensibly, accurate and rapid in results obtention, as well as been highly correlated with data obtained with other methods of wide application for this purpose, such as Rancimat.

2.8 Sensory analysis

Potato slices of alpha variety with a thickness of 1.2 + 2 mm were prepared, washed and drained, keeping a moisture content not exceeding 75%, and subjected to frying in refined BGSO, at 180 ± 2 °C, and as a control a parallel system was prepared using commercial canola oil (CCO) refined brand canoil® (Aceites, Grasas y Derivados SA de CV, Zapopan, Jalisco, Mexico), purchased at a local supermarket, under the same process conditions.

The fritters obtained in both processes were seasoned with 3 g of table salt per 100 g of fritters and subjected to paired preference test and triangular or discrimination test, using a panel of 68 untrained judges, in order to emulate best possible to a group of consumers of the adult-young segment (18 to 24 years old), one of the population groups with the highest consumption of fried foods (Esquivel-Ramírez *et al*., 2014; Topete-Betancourt *et al*., 2019).

2.9 Statistical analysis

Experiment was performed in a completely randomized design, with the exception of sensory analysis, the determinations were performed in triplicate, and the results were analyzed using Fisher's ANOVA and minimum significant difference test (LSD) with 95% confidence level in Aphelion® Statgraphics X64 software.

Sensory evaluation data analysis was carried out according to the 1 and 5% significance tests for the tail test, as described by Ramírez-Navas (2012)

3 Results and discussion

3.1 BGSO obtention

Obtained yield for crude BGSO was 34%, with respect to the raw's materia total mass, once the extraction process was concluded. This yield was lower than that reported for seed oils of other cucurbitaceae species, such as *Cucurbita pepo* and *Cucurbita maxima*, although this depends on many factors, such as growing and climatic conditions, among others (Seymen *et al*., 2016), and it should be considered that the sample studied corresponded to seeds collected in the wild. However, this yield was similar to that reported for this same species by Lira-Saade *et al*. (2009).

3.2 Fatty acids % determination, peroxide index, extinction coefficient (K_{232} and K_{270}), total phenols and color difference

Crude BGSO presented higher acidity and peroxides index than that refined (Table 1), so, in these aspects, refining process seems to have caused a positive change, although the values obtained for the peroxide index are below to the maximum specified in the current reference standard (NMX-F-475-SCFI-2011), and the acidity index was slightly above that specified in the same standard, which could have been a consequence of dragging of components other than fatty acids due to the extraction method used (organic solvent drag). On the other hand, the changes in the extinction coefficients K_{232} and K_{270} (Table 1) were not significant ($P \leq 0.05$), which evidenced the absence of oil decomposition products during the refining and bleaching process, referred to peroxides and hydroperoxides which are related to these coefficients; this is consistent with Paz-Antolin & Molero-Meneses (2000) reports, who evidenced that these coefficients practically do not vary unless vegetable oil reaches 100 °C, a fact that in this study did not occur, since the highest temperature proved in this study was between 85-90 °C during the bleaching process.

Regarding to total phenols (Table 1), a lower content of them was detected in refined BGSO compared to the crude one ($P \leq 0.05$), which suggests this type of antioxidant compounds were lost during refining process, and might deprive it of protection against oxidation by exposure to promoters, such as air, light, high temperatures, or their combination, as Seymen *et al*. (2016) concluded in their research on pumpkin seed oil (*Cucurbita pepo* L.).

Table 1. Parameters(1) evaluated in crude and refined BGSO.

BGSO	% oleic acid	Peroxide index (mEq/kg)	K_{232}	K_{270}	Total polyphenols(2)
Crude	0.16±0.00[b]	0.24±0.02[b]	0.34±0.03[a]	2.49±0.05[a]	49.3±0.38[b]
Refined	0.09±0.00[a]	0.12±0.02[a]	0.35±0.03[a]	2.52±0.01[a]	31.6±0.22[a]

(1)Means ± experimental error, different letters indicate significant statistical differences between oils (Fisher LSD test, $P \leq 0.05$).
(2)Expressed in mg equivalent of gallic acid per Kg of oil.

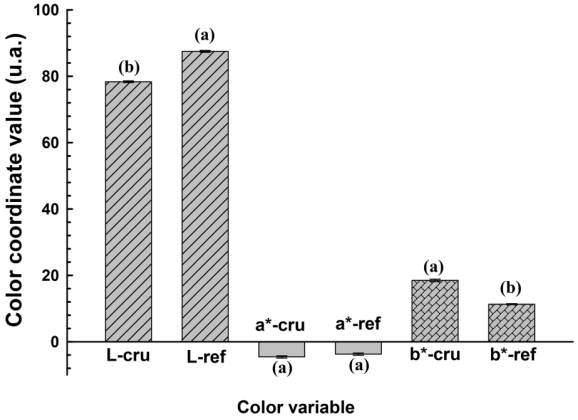

Fig. 1. Color in $L*a*b*$ system of crude and refined oil (different letters indicate significant differences between oils from the Fisher LSD test (Fisher LSD test, $P \leq 0.05$)).

Figure 1 shows changes in oil color before and after refining. The brightness value ($L*$) increased 10% after refining, as a result of pigment removal; the chromatic variable $a*$ did not show significant differences ($P \leq 0.05$) after the refining process, unlike the variable $b*$, which decreased up to 39% during processing. This result indicated a lighter and brighter greenish color, that is, optically cleaner, after having undergone the refining process. Regarding the hue angle (H°), no significant difference was detected between the crude oil, with 76,158 ± 0.9º, and the refined one, with 71,782 ≤ 1,646°, according to Fisher's LSD test ($P \leq 0.05$); which could show that no volatile compounds were formed during processing, as reported by Elodio-Policarpo *et al*. (2019).

Color determination values indicated that the variable $L*$ is 10% higher in refined oil compared to crude one, which was a possible result of pigments removal during bleaching phases, as described by Besbes *et al*. (2005). Tsaknis *et al*. (1997) reported lower $L*$ values in oils extracted from pumpkin seeds different species (*C. pepo* and *C. maxima*), in variable $a*$ reported negative digits, which is indicative of a more intense green color. Choe & Min (2006) indicated that the presence of green color in oils can be caused by the presence of residual chlorophylls, depending on the origin botanical source, whose presence can take an oxidizing role, according to the same authors.

3.3 Fatty acid profile analysis

Figure 2 shows the correspondence of the fatty acids detected in each sample, contrasted with the standard (FAME) used for its identification and quantification. The predominant fatty acids in BGSO are oleic (C18: 1) and linoleic (C18: 2), as well as traces of other (Table 2). In general, for the most of the fatty acids presents, including caprylic acid (the only of short chain present), the refining process had a significant decrease effect ($P \leq 0.05$); Even the lignoceric acid, present in the crude oil, was completely removed. Only γ-linolenic acid obtained a marginal increase, probably derived from the loss of mass corresponding to other fatty acids. The change in the concentrations of both saturated and unsaturated fatty acids after the refining process was attributed to the saponification reaction of free fatty acids during the neutralization process with sodium hydroxide, similar to what Svengroš (1995) reported. On the other hand, heat treatments during refining could also cause a decrease in unsaturated fatty acids (Besbes *et al*., 2005).

The main fatty acids present in BGSO, oleic and linoleic, are considered essential fatty acids, for which various health benefits have been reported, in addition to facilitating their use in processes such as hydrogenation (Dorni *et al*., 2018). On the other hand, those same unsaturations make them vulnerable to rapid oxidation if they are not protected with an antioxidant. (Al-Juhaimi *et al*., 2018).

Table 2. Main fatty acids of crude and refined oil, and total of satured and unsatured fatty acids on each oil.

Main fatty acids	Crude oil (%)	Refined oil (%)
Caprylic acid (C8:0)	0.90±0.012[b]	0.74±0.023[a]
Palmitoleic acid (C16:1)	1.85±0.043[b]	1.30±0.056[a]
Heptadecanoic acid (C17:0)	0.82±0.023[b]	0.68±0.072[a]
Cis-10-heptadecenoic acid (C17:1)	0.21±0.012[a]	0.17±0.026[b]
Helaidic acid (C18:1n9t)	0.88±0.015[b]	0.54±0.043[a]
Oleic acid (C18:1n9c)	12.65±0.029[b]	9.44±0.075[a]
Linoleic acid (C18:2n6c)	55.93±0.038[b]	50.16±0.156[a]
γ-linolenic acid (C18:3n6)	0.85±0.020[a]	0.90±0.041[a]
Linolenic acid (C18:3n3)	0.89±0.020[b]	0.74±0.038[a]
Lignoceric acid (C18:2)	0.41±0.012[b]	0.00±0.000[a]
Total satured fatty acids	**2.13±0.000[a]**	**1.42±0.095[a]**
Total unsatured fatty acids	**73.26±0.020[b]**	**63.28±0.344[b]**

[(1)]Means ± experimental error, different letters indicate significant statistical differences between oils (Fisher LSD test, $p \leq 0.05$).

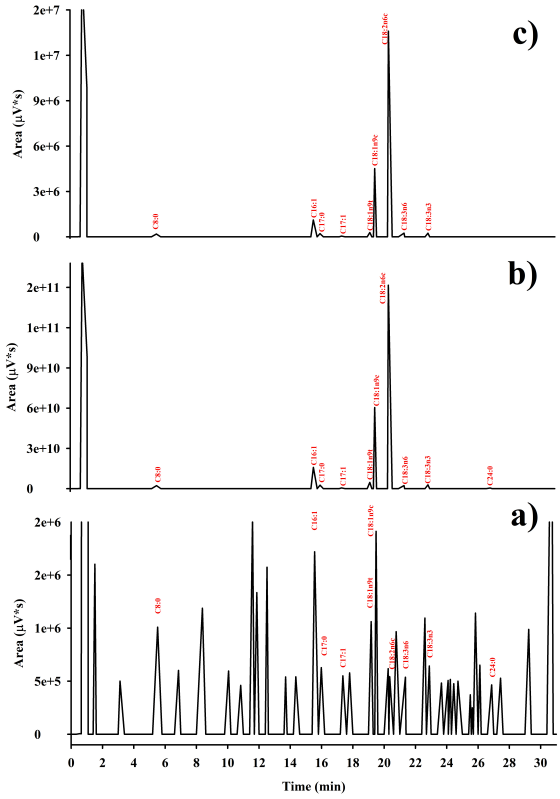

Fig. 2. Chromatograms obtained by GC of FAME standar (a), BGSO crude (b), and BGSO refined (c).

The polyunsaturated fatty acids present in trace amounts (Table 2), are equally susceptible to oxidation, under the conditions that detonate it, the chain reaction of oxidative rancidity could originate. The profile obtained for the BGSO is similar to that reported in edible rapeseed, soybean and sunflower oils (Dorni *et al*., 2018), as well as in the seed oil of other pumpkin species (Nederal, *et al*., 2014; Seymen *et al*., 2016; Shaban & Sahu, 2017) and different from the oil of other oilseeds, such as the fruits of some palm species (Ramírez-Niño *et al*., 2018) or that of sweet almonds (Hernández & Zacconi, 2009), where other saturated fatty acids, such as lauric (C: 12) and myristic (C: 14), are the main ones in their composition. Nederal *et al*. (2014) concluded that the processing of pumpkin seeds (*C. pepo* L.) to obtain oil influenced the composition of their fatty acid profile. Another factor that affects this is the natural antioxidants present in the seeds, such as those found in other pumpkin species, such as *Cucurbita moschata* and *C. maxima* (Seymen *et al*., 2016).

3.4 Infrared spectrum analysis (FTIR)

In the resulting infrared spectrum, both for the raw and refined BGSO (Fig. 3), a tension band corresponding to the C=C bond at 3004 cm^{-1}, corresponding to the unsaturated fatty acids present in the oils, was visualized, in addition to two bands at 2924 and 2856

cm^{-1}, associated with tension of the symmetric CH and asymmetric CH bonds in CH_2. Further back, at 1744 cm^{-1}, a band associated with the extension movement of the C=O bond, typical of triglyceride bonds, was shown. Between 1452 and 1228 cm^{-1} several bands were observed corresponding to the flexion of C-H bonds in CH_2 and CH3; and at 1156 cm^{-1} a tension vibration corresponding to the C-O link was located, as well as at 1104 cm^{-1} tension vibration O-CH_2 was located, as well as a band at 712 cm^{-1}, corresponding to the flexion of (CH_2) n with n> 4, typical of carbon skeletons of considerable length. There were no noticeable changes in the intensity of the bands of 3600 to 3400 cm^{-1}, which would evidence the presence of hydroperoxides, and also in the bands present between 1800 and 1700 cm^{-1}, related to carbonyls, as referred by Elodio-Policarpo *et al*. (2019), which seems to correspond to the stability of the extinction coefficients determined K_{232} and K_{270}. This information revealed that there were no significant changes in the molecular structure of buffalo gourd seed oil after refining, considering the absence of functional groups outside those of fatty acids, which is consistent with the results obtained for K_{232} and K_{270} extinction coefficients, as well as the peroxide index values obtained for both oils, where significant changes were not detected either.

These results corresponded to the IR spectrum of other vegetable oils such as olive, sweet almond (Hernández & Zacconi, 2009), corn and sesame (Fadzlillah *et al*., 2014), as well as those of soybean oil, sunflower and grape seed (Vasconcelos *et al*., 2015). According to the latter authors, the failure to detect other types of bonds in the molecular structure of the samples studied is indicative of the purity of the oils obtained.

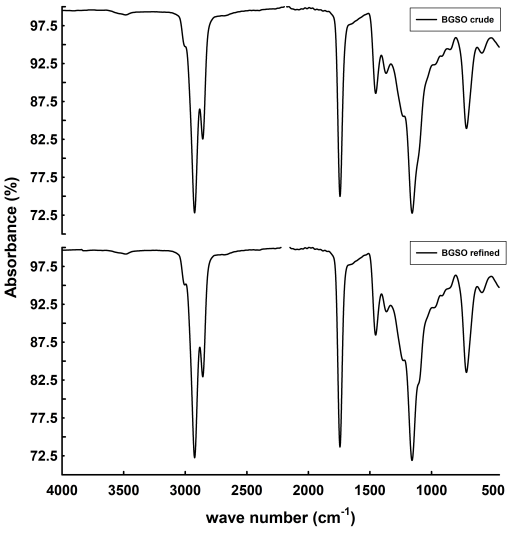

Fig. 3. FTIR spectras of crude and refined oil.

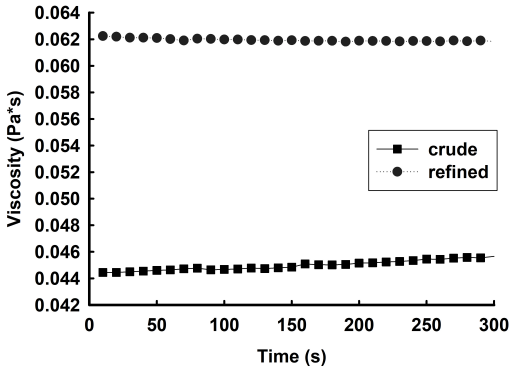

Fig. 4. Crude and refined oil viscosity at room temperature (25 °C) and constant speed.

3.5 Viscosity determination

Regarding the viscosity of both fluids (Fig. 4), it was found that the behavior of the raw and refined BGSO was independent of the strain rate gradient during the evaluation time at room temperature (25 ± 1 °C), which suggested a Newtonian behavior, such as the one described by Masoliver i Marcos *et al*. (2017).

On the other hand, the change in viscosity values between raw and refined BGSO was evident: the oil was significantly more viscous ($P \leq 0.05$) after the refining process. This difference in viscosity is due to the fact that, at room temperature, this attribute depends on the oil's molecular structure, decreasing with the unsaturation of fatty acids (Besbes *et al*., 2004; Masoliver i Marcos *et al*., 2017). It is also likely to be due to the lower friction between the fatty acid chains (Sidique *et al*., 2010), this could be due to an increase in the concentration of saturated fatty acids in relation to unsaturated fatty acids after the refining process (Table 2).

Refined BGSO viscosity value corresponds to that of seed oils from other cucurbits, as reported by Tsaknis *et al*. (1997). Sidique *et al*. (2010) also found similar values of this parameter at room temperature for soybean oils (0.0611 Pa), sunflower (0.062 Pa) and canola (0.0671 Pa). This could be as a result of the similar proportion of saturated and unsaturated fatty acids in their composition, according to the origin plant.

3.6 Oxidative stability

The regression equations obtained for the oxidative induction times ($\mathbf{t_0}$) in crude and refined BGSO were adjusted to a temperature-dependent logarithmic behavior with an adjustment of 99.9%. A significant difference ($P \leq 0.05$) was observed between both oils (Table 3), since in the refined oil these times were significantly reduced with respect to those obtained for crude oil (Fig. 5), which trend to zero as temperature increased.

The difference in oxidative stability behavior between raw and refined BGSO could be a consequence of the loss of natural antioxidant, such as tocopherols, polyphenols and carotenoids, present in virgin oils, as reported by Al-Juhaimi *et al*., (2018), having unsaturated fatty acids unprotected against oxygen action in the case of refined oil, where antioxidants were removed during extraction and refining. Marques da Silva *et al*. (2016) reported that vegetable oils extracted using hot solvents tend to be less stable due to thermal degradation during prolonged exposure to heat, coupled with residual chlorophylls acting as sensitizers of the oxidative process, as reported by Choe & Min (2006), although in crude oils chlorophylls and carotenoids have a synergistic relationship with fatty acids to protect against the oxygen action, as reported by Plazola-Jacinto *et al*. (2019).

Refined buffalo gourd oil's seeds oxidative induction times ($\mathbf{t_0}$) at 120 °C were compared against other vegetable oils, and were similar to those of soybean, sunflower and peanut oils, superior to safflower and grapes seed oil (Saldaña & Martínez-Monteagudo, 2013), and lower than others, such as corn, olive, canola, coconut and sesame seeds (Tan *et al*., 2002). At 130 °C, according to the referred studies for refined buffalo gourd seed oil resulted in a longer oxidative induction time with respect to sunflower, safflower and grapeseed oils, and inferior for olive, corn, peanut, soy, canola, coconut and sesame. The latter is probably due to the presence of antioxidants added during the production of commercial oils, whether natural, such as tocopherols, or artificial oils, such as butylhydoxyanisole (BHA) and butylhydroxytoluene (BHT), which contribute to the oxidative stability of processed oils (Villanueva *et al*., 2017), which could explain the reason for buffalo gourd seed refined oil exhibited lower oxidative induction times at 120 and 130 °C compared to most of the reported oils, since it does not contain added antioxidants; on the other hand, buffalo gourd seeds crude oil presented longer oxidative induction times at both temperatures compared to most of the reported oils; this is consistent with the presence of phenols in its composition, which could be functioning as natural antioxidants in BGSO, as reported by Seymen *et al*. (2016).

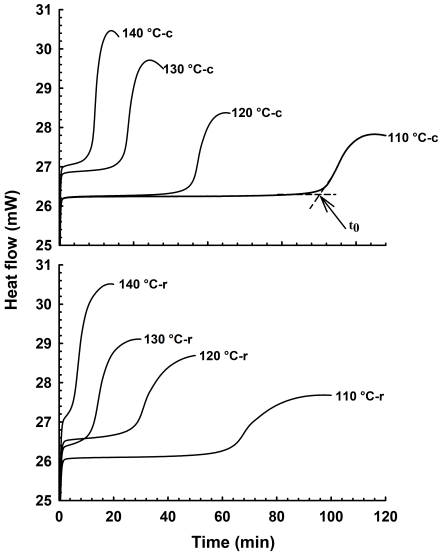

Fig. 5. Oxidative induction time (DSC) at different temperatures for crude (c) and refined (r) oil.

Table 3. Oxidative induction times at different temperature for crude and refined oil.

Treatment	t_0[(1)] (min)				Regression equation	$r^{2(3)}$
	110 °C	120 °C	130 °C	140 °C		
Crude oil[(4)]	180.25±1.86[a]	89.59±0.43[a]	43.45±0.38[a]	21.95±0.07[a]	$T^{(2)} = 183.76 - 14.2*\ln(t_0)$	0.99
Refined oil[(4)]	62.43±0.25[b]	27.13±0.14[b]	11.36±0.11[b]	4.81±0.02[b]	$T^{(2)} = 158.39 - 11.68*\ln(t_0)$	0.99

(1) $\mathbf{t_0}$: oxidative induction time.
(2) **T**: temperature of DSC analysis.
(3) $\mathbf{r^2}$: coefficient of determination.
(4) Means ± experimental error, different letters indicate significant statistical differences between times (t_0) at same temperature (Fisher LSD test, $p \leq 0.05$).

3.7 Sensory analysis

After submitting the fritters obtained to the scrutiny of the judges, for the preference test it was found that consumers were indifferent to choose between fries made with BGSO and those with CCO, with a level of significance of 5 and 1%, according to the test of a tail (Ramírez-Navas, 2012).

As for the triangular test, where it was sought that the judges identify the frying made with BGSO, a positive identification was not achieved even at a 0.01% level of significance. Cabreriso *et al*. (2017) also found that the development of flavors due to volatile compounds or degradation products of the oils used to fry potatoes, is not identified by the judges in those fritters made in the first hours of oil use. This seems to be due to the logic of the low development of the degradation found for the oils used in this study. In addition, as mentioned by Ciappini *et al*. (2016) in his study: consumers do not have tools beyond their own senses to identify the differences between the products made with the different oils, and it is clear that these are not enough to detect the difference between the products that were submitted to evaluation.

Conclusions

Buffalo gourd oil processing presented different impacts on its composition and properties: fatty acids % and peroxides index were improved, there were no changes in the extinction coefficients, but it does cause pigment loss, which produces an oil of a brighter and clearer color, although this also seems to mean the loss of phenolic compounds; loss of saturated and unsaturated fatty acids occurs, its viscosity increases, no alterations in its chemical structure were detected and oxidative induction times decrease after the refining process, mainly due to the loss of possible antioxidant compounds, since the FTIR did not reveal activating compounds that will accelerate the lipid oxidation reaction. Raw BGSO has a healthy profile for possible human and / or animal consumption, and possible antioxidant compounds, in addition to maintaining its oxidative stability. Finally, the development of undesirable flavors was not detected after the oil processing, since the sensory test indicated that consumers did not detect a difference between fried foods obtained with BGSO and those made with CCO. BGSO could be an unconventional alternative for frying processes, but also for other applications.

Nomenclature

BGSO	buffalo gourd seed's oil
CCO	commercial canola oil
FID	flame ionization detector
FAME	fatty acids methyl esters
FTIR	Fourier transform infrared spectroscopy
ATR	Total attenuated reflectance
IR	infrared
GAP	sample tickness (μm)
DSC	differential scanning calorimetry
ANOVA	one-way analysis of variance
LSD	Fisher minimum significant difference test
$\mathbf{t_0}$	oxidative induction time (min)
T	temperature of DSC analysis (°C)
$\mathbf{r^2}$	coefficient of determination

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