

The Canadian Society for Bioengineering
The Canadian society for engineering in agricultural, food, environmental, and biological systems.



La Société Canadienne de Génie Agroalimentaire et de Bioingénierie
La société canadienne de génie agroalimentaire, de la bioingénierie et de l'environnement

Paper No. CSBE17101

Stability of palm olein oil with different antioxidants during repeated frying of churros (Spanish fried dough pastry)

R. Castro-Lopez

J.A. Gómez-Salazar

A. Cerón García

M.E. Sosa-Morales

Departamento de Alimentos, División de Ciencias de la Vida, Campus Irapuato-Salamanca, Universidad de Guanajuato. Carretera Irapuato-Silao km 9, Irapuato, Gto., MEXICO 36500
r.castrolopez@ugto.mx; msosa@ugto.mx

**Written for presentation at the
CSBE/SCGAB 2017 Annual Conference
Canad Inns Polo Park, Winnipeg, MB
6-10 August 2017**

ABSTRACT The antioxidants are substances added in low concentrations can delay or prevent the oxidation of fats and oils. They may be natural or synthetic; synthetic antioxidants are being restricted due to potential harmful to consumers. Antioxidants are useful not only during oil storage, also for repeated frying operations in fast-food restaurants and snacks industry. The objective of this work was to study the stability of palm olein oil using the antioxidants BHT and ascorbyl palmitate, during the repeated frying of churros. Churros are sweet snacks defined as deep-fried dough pastry, very popular in Spain and Mexico. Dough was prepared and churros were formed in strips by a manual simple extruder. Churros were fried in batches of 0.08 kg for 3.5 min at 180°C, 25 batches of churros were fried per day. For olein palm added with 200 ppm of BHT, peroxide values (PV) increased from 1.95 meq/kg in fresh palm olein to 18.45 meq/kg after six days of usage. Free fatty acids (FFA) increased from 0 to 0.54%. Both values are within the limits of Mexican regulations for fats and oils, being maximum 20 meq/kg for PV and 3% for FFA. For olein with BHT / A. palmitate (200/100 ppm) the same performance was performed in six days whereas in four days, similar results were obtained for palm olein added with natural antioxidant ascorbyl palmitate at 100 ppm. Therefore, a better yield was obtained when using BHT at 200 ppm as antioxidant for the repeated frying of churros.

Keywords: Antioxidant, Ascorbyl palmitate, BHT, Repeated frying.

Papers presented before CSBE/SCGAB meetings are considered the property of the Society. In general, the Society reserves the right of first publication of such papers, in complete form; however, CSBE/SCGAB has no objections to publication, in condensed form, with credit to the Society and the author, in other publications prior to use in Society publications. Permission to publish a paper in full may be requested from the CSBE/SCGAB Secretary: Department of Biosystems Engineering E2-376 EITC Bldg, 75A Chancellor Circle, University of Manitoba, Winnipeg, Manitoba, Canada R3T 5V6 or contact bioeng@csbe-scgab.ca. The Society is not responsible for statements or opinions advanced in papers or discussions at its meetings.

INTRODUCTION Fried products are frequently consumed, and represent a profitable business for those who market them. Wheat flour is one of the main ingredients in bread making. Bakery products are divided into baked goods and fried products such as donuts and wheat flour churros (Gómez-Pallarés *et al.*, 2006). In repeated frying, the oil is continuously exposed to air and light for prolonged periods, the food is brought into contact with the hot oil at high temperatures, between 150 and 200°C. Vigorous formation of bubbles is generated by the evaporation and expansion of the water vapor present in the food in contact with the hot oil, conditions that favor the decomposition of the oil (Santacruz-Vazquez *et al.*, 2011).

Lipolysis also known as hydrolytic rancidity is one of the chemical transformations that the oils undergo in their structure, which can reduce their nutritive value, produce volatile compounds that also impart unpleasant odors and flavors. Lipolysis is a reaction catalyzed by lipase enzymes that enter action by processes at high temperatures, such as the fry that causes triglycerides to break down into glycerol (Lercker and Carrasco, 2010). To prevent or delay the degradation of the oil in storage, commercial antioxidants are added. The mechanisms seek to provide higherer stability to the oil. Synthetic antioxidants such as butylhydroxyanisole (BHA), butylhydroxytoluene (BHT), tertbutylhydroquinone (TBHQ), may have a high toxicity potential (Hou, 2003). To overcome these deficiencies, more research is focused on natural antioxidants such as ascorbyl palmitate, tocotrienols and tocopherols (vitamin E), spice extracts, among others (Guo *et al.*, 2016). The objective of this work was to study the stability of palm olein oil using different antioxidants (BHT and ascorbyl palmitate), during the repeated frying of churros.

MATERIALS AND METHODS

Repeated frying process The frying process was performed with commercial palm olein prepared with 200 ppm BHT as a synthetic antioxidant (Treatment 1), with ascorbyl palmitate with 100 ppm (Treatment 2), a combination of both antioxidants in the same concentrations (Treatment 3), and a control without any antioxidant (Treatment 4), donated by the company Aarhus Karlshamn Mexico (AAK, Morelia, Michoacán, Mexico). The frying process with each treatment was carried out with 3 L of palm olein using a domestic electric fryer (Tefal, Mexico City). The frying process consisted of several cycles. One cycle consisted of 25 batches of 80 g of wheat flour churros fried at 180°C for 3 min, 30 s. Before starting each cycle, the palm olein level was checked and the volume needed to maintain a constant level was added (fresh palm olein was added). This replacement was carried out to simulate the practices developed in fast food establishments. The repeated frying process was stopped as soon as the maximum levels of peroxides established by Mexican standards were reached.

Determination of peroxide index This was determined according to the Mexican standard NMX-F-154-SCFI-2010. Using 1 g of KI and 1 g of olein, 30 ml of glacial acetic acid-chloroform solution (3: 2 v/ v) were added. Then, 0.5 ml of a 5% KI solution and 30 ml of distilled water were added and heating in a water bath for 1 min. 2.5 ml of 2% starch solution was added and the final solution was titrated with 0.01 N sodium thiosulfate solution. This same procedure was performed in the sweet wheat flour churros after each frying cycle to determine the peroxides in the food.

Determination of p-anisidine The value of p-anisidine was performed instrumentally with the help of a CDR FoodLab Junior equipment (Italy).

Determination of free fatty acids (FFA) content FFA were determined following the official Mexican standard NMX-F-101-SCFI-2012. A sample (5 g) of palm olein was combined with 50 ml of isopropyl alcohol and several drops of phenolphthalein (1% alcoholic solution) and titrated with 0.1 N NaOH.

Determination of viscosity The viscosity of the palm olein was determined according to DIN 51519. A sample (7.1 ml) of the oil was taken at 40°C and a Brookfield viscometer (LV DV-II +) was measured at 100 rpm using the small sample adapter for reduced volumes and needle number 21, the result is expressed in cp.

Color Determination Color determination was performed in an instrumental way following the methodology reported by Magariños and Bauzá (2003) with a Color Flex EZ colorimeter (45/0 LAV Standard Box) obtaining the factors L^* , a^* , and b^* of the CIELAB system. Once the instrument was calibrated, the sample filtered and tempered at 25 ° C was poured into the glass cuvette and the values a^* , b^* and L^* were read. The net color difference, ΔE , was calculated with the expression:

$$\Delta E = \sqrt{L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (1)$$

Where L^* , a^* and b^* are parameters after determined frying cycles, while L_0^* , a_0^* and b_0^* are the parameters for the fresh palm olein.

Statistical analysis Results were analyzed by analysis of variance (ANOVA) using Statgraphics ® software (Centurion XVI). A Tukey test was performed with a confidence level of 95%.

RESULTS AND DISCUSSION

Peroxide Value. The value of peroxides is one of the most used techniques to determine the quality of the oils, since the increase of this value is directly related to the degree of oxidation of the oil, in this case the palm olein. This value is influenced by food type. The control (without antioxidants) presented a lower performance (20.45 meq/kg in two days) in comparison with the palm olein with antioxidants. Palm olein with ascorbyl palmitate (100 ppm) as natural antioxidant did not show a good performance as BHT (200 ppm), which had good performance with six days of usage (18.45 meq/kg). The combination of antioxidants BHT (200 ppm)/A. Palmitate (100 ppm), had a high performance as well. In other studies, the use of natural antioxidants has had the same performance as synthetic antioxidants. Guo *et al.* (2016), reported rosemary extract and tea polyphenols as a natural antioxidant had the same performance than BHA and TBHQ when potato chips are fried.

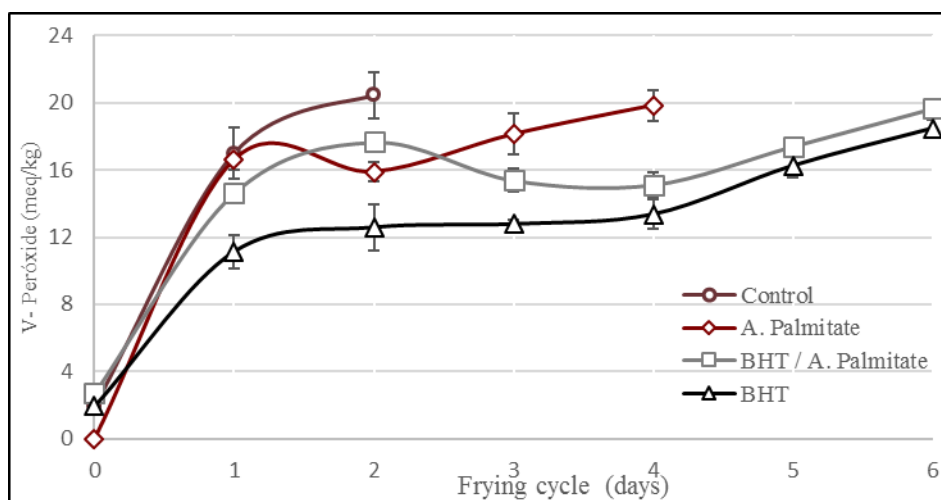


Figure 1. Value of peroxides in palm olein without antioxidants (Control) and with different antioxidants during the repeated frying of sweet churros of wheat flour.

P-Anisidine value The value of *p*-anisidine is a very used quality parameter because it forms part of secondary oxidation in which the determination of peroxides is no longer reliable. P-anisidine values increased as the repeated frying increase (Fig. 2). Similar trend was obtained by Guo et al. (2016).

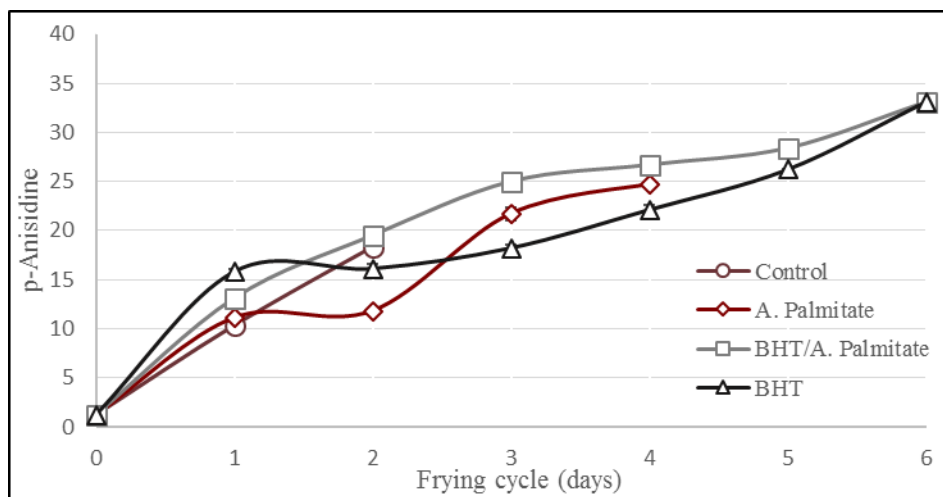


Figure 2. Increase in the value of p-Anisidine. In palm olein without antioxidants (control) and with different antioxidants during the repeated frying of sweet churros of wheat flour. There is no significant difference between treatments $p < 0.05$

Free fatty acids Free fatty acids are produced by the hydrolysis of triglycerides by combining steam, oxygen and water that attacks the ester bond to produce monoglycerides and diglycerides (Choe and Martin 2007). Free fatty acids (FFA) increased from 0 to 0.54% in palm olein with BHT (200 ppm), while in palm olein with Ascorbyl Palmitate (ppm) it reached up to 0.42% in only four days. The same behavior is presented in the case of control and palm olein with the combination of natural and synthetic antioxidants (100 and 200 ppm respectively). These results are in agreement with those obtained by Jaswir et al., (2000), regarding the trend and behavior using citric acid and rosemary extract as a natural antioxidant (Fig. 3).

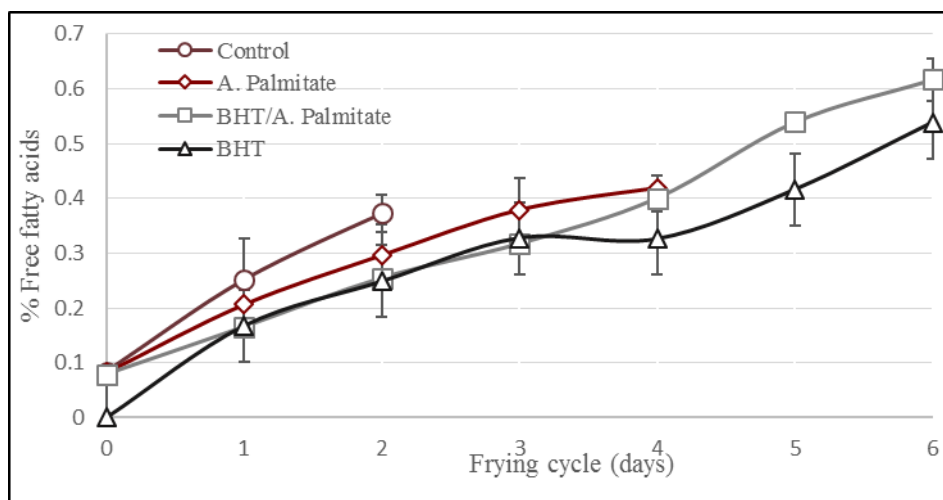


Figure 3. Free fatty acids in palm olein without antioxidants (control) and with different antioxidants during the repeated frying of sweet churros of wheat flour.

Viscosity The viscosity is a parameter that has also been used to observe the changes in the quality of the oils during the frying, since as the deterioration increases, the viscosity also increases, for all four treatments an increase could be observed, although it should be noted in the case of control the change was minimal (42.5 - 43 cp), a similar case in the other treatments, as can be seen in figure 4. The treatment with BHT (200 ppm) is different from the others with a $p < 0.05$, it should be mentioned that Del Carmen Flores-Alvarez, et al., (2012) obtained similar results in which there was no significant change in the fish nuggets frying, with 50 to 52 cp changing the viscosity.

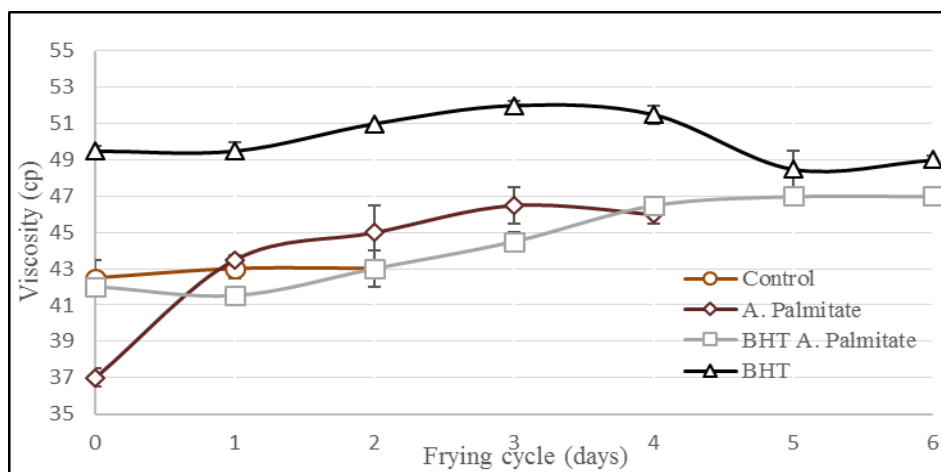


Figure 4. Viscosity of palm olein without antioxidants (control) and with different antioxidants during the repeated frying of sweet churros of wheat flour.

Parameter CIELab in the palm olein during the frying of the wheat flour churros The changes in the color of the palm olein during the frying of the wheat flour churros can be observed in table 1, where the parameter L^* tends to decrease its initial value, as the fry days increase, being in the palm olein with BHT and in the control where the greatest change can be observed with a $p < 0.05$, the decrease in the L^* value during the frying process indicates that the oil is getting darker, caused by the remains of the churros de wheat flour, in which the Maillard reaction is carried out by the sugar and protein content (Maskan 2003). The change to a reddish color (Parameter a^*) as well as the increase of yellow color (Parameter b^*) was more noticeable in palm olein with BHT with a significant difference ($P < 0.05$) followed by the control, these results are consistent with that obtained by Cardoso-Ugarte et al., (2013) where essential oil of basil (200 ppm) was used in palm olein and an antioxidant control, being the control that showed the greatest difference in the parameter L^* (88.2 To 48.3) at control differential (53.9 to 53.2).

Peroxide in churros of wheat flour The value of peroxides was evaluated in the wheat flour churros after each cycle, observing that in the churros that were fried in the control and palm olein with BHT (200 ppm) reaching values of 19.43 and 22.61 meq / kg respectively, while in the churros that were fried in the olein with A. Palmitate (100 ppm) and BHT / A. Palmitate (200/100 ppm) values of 10.15 and 12.92 meq / kg were obtained. Therefore, although the olein with A. Palmitate did not yield the same yield as with BHT, the food maintained low levels of peroxide (Fig. 5). The results using A. Palmitate as a natural antioxidant concur with that obtained by Cardoso-Ugarte et al., (2013) where in fish nuggets fried with a mixture of oils (palm olein and canola oil) was obtained from 1.5 to 10.7 meq/kg using TBHQ (200 ppm) as a synthetic antioxidant, but not with BHT as a synthetic antioxidant, where the maximum permissible value of peroxides by Mexican standards was reached in wheat flour churros.

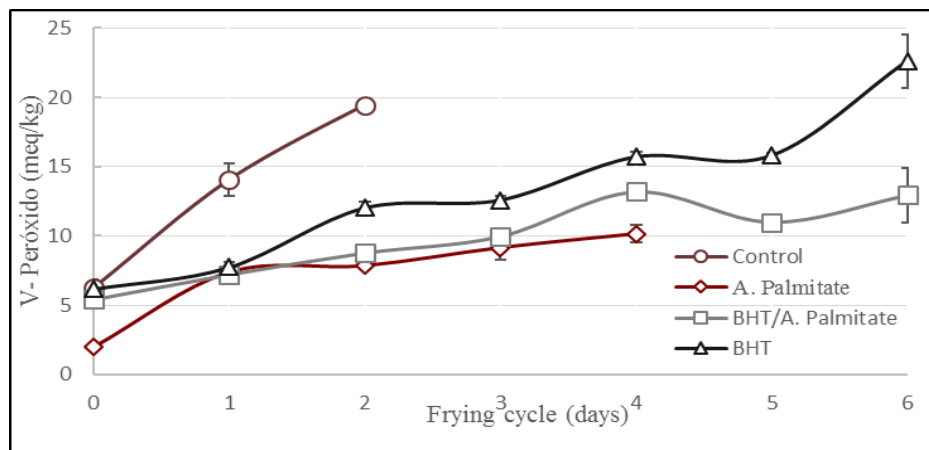


Figure 5. Peroxides values in churros from different batches during the repeated frying in palm olein with different antioxidants.

Table 1. Color of the palm olein during the repeated frying of sweet wheat flour churros.

BATCH	CONTROL	A. PALMITATE (100ppm)	BHT/ A. PALMITATE (200/100 ppm)	BHT (200 ppm)	
L*	0	74.05 ±0.78 ^a	74.97 ±0.04 ^a	74.34 ±0.13 ^a	75.07 ±0.06 ^a
	1	73.89 ±0.02 ^a	73.81 ±0.23 ^a	74.02 ±0.07 ^a	70.82 ±0.74 ^b
	2	69.71 ±0.81 ^b	74.51 ±0.04 ^c	64.40 ±0.38 ^a	63.82 ±1.48 ^a
	3	-	74.12 ±0.04 ^b	72.45 ±0.95 ^{ab}	71.25 ±1.20 ^a
	4	-	73.95 ±0.09 ^d	71.74 ±0.60 ^a	71.70 ±0.87 ^a
	5	-	-	72.64 ±0.19 ^b	67.65 ±0.95 ^a
	6	-	-	72.46 ±0.12 ^b	67.63 ±1.41 ^a
a*	0	-6.17 ±0.09 ^d	-6.32 ±0.01 ^c	-5.30 ±0.07 ^b	-6.77 ±0.02 ^a
	1	-4.35 ±0.19 ^d	-4.42 ±0.10 ^d	-4.82 ±0.06 ^a	-3.40 ±0.07 ^c
	2	-3.15 ±0.11 ^b	-5.11 ±0.02 ^a	-2.04 ±0.06 ^c	-2.20 ±0.26 ^c
	3	-	-4.44 ±0.01 ^a	-3.34 ±0.44 ^b	-3.68 ±0.20 ^b
	4	-	-4.58 ±0.06 ^a	-2.38 ±0.18 ^b	-3.98 ±0.18 ^c
	5	-	-	-2.32 ±0.06 ^a	-2.63 ±0.25 ^a
	6	-	-	-2.73 ±0.08 ^a	-2.34 ±0.31 ^a
b*	0	45.84 ±0.30 ^c	44.35 ±0.08 ^b	48.45 ±0.49 ^d	40.87 ±0.14 ^a
	1	52.35 ±0.75 ^b	52.27 ±0.44 ^b	48.82 ±0.12 ^a	51.72 ±0.37 ^b
	2	53.11 ±0.39 ^c	48.56 ±0.22 ^a	52.70 ±0.30 ^c	51.16 ±0.36 ^b
	3	-	51.70 ±0.04 ^a	53.90 ±1.20 ^b	52.77 ±0.35 ^{ab}
	4	-	52.14 ±0.07 ^a	56.37 ±0.27 ^b	52.79 ±0.42 ^a
	5	-	-	57.09 ±0.55 ^b	53.70 ±0.33 ^a
	6	-	-	55.33 ±0.23 ^b	54.73 ±0.26 ^a
ΔE for the last batch	9.26 ±0.58^b	8.11 ±0.10^a	7.61 ±0.31^a	16.37 ±0.49^c	

Means containing different letters in the same parameter row are significantly different ($P < 0.05$).

CONCLUSION Palm olein with 200 ppm of BHT had the best performance for the repeated frying of sweet wheat churros among the studied treatments. On the other hand, Ascrobyl Palmitate resulted in low peroxides values in the wheat flour churros. More antioxidants may be studied in order to extend the performance of palm olein for repeated frying operations.

Acknowledgements. Thanks CONACYT for the support of a scholarship to carry out the postgraduate studies. Also, thanks EDUCAFIN for the support to attend this conference.

REFERENCES

- DIN 51519. Oil- Viscosity. German Institute for Standardization. Available from: http://www.widman.biz/Seleccion/din_51519.html Accessed: 2016 Nov
- Del Carmen Flores-Álvarez, M., Molina-Hernández, E. F., Hernández-Raya, J. C., & Sosa-Morales, M. E. (2012). The effect of food type (fish nuggets or French fries) on oil blend degradation during repeated frying. *Journal of Food Science*, 77(11).
- Cardoso-Ugarte, G. A., Morlán-Palmas, C. C., and Sosa-Morales, M. E. (2013). Effect of the addition of basil essential oil on the degradation of palm olein during repeated deep frying of French fries. *Journal of food science*, 78(7).
- Choe E, Min DB. 2007. Chemistry of deep-fat frying oils. *J Food Sci* 72(5): R77–R86.
- Gómez-Pallarés, M., León, A.E. And Rossel, C.M. (2006). Of such flours such breads: grains, flour and bread products in Latin America. (1st Ed., P. 31). Cordoba, Argentina: Báez Ediciones.
- Guo, Q., Gao, S., Sun, Y., Gao, Y., Wang, X., & Zhang, Z. 2016. Antioxidant efficacy of rosemary ethanol extract in palm oil during frying and accelerated storage. *Industrial Crops and Products*, 94, 82-88.
- Hou, D.X., 2003. Potential mechanism of cancer chemoprevention by anthocyanin. *Curr. Adv. Mol. Med.* 3, 149–159.
- Jaswir, I., Man, Y. B. C., & Kitts, D. D. 2000. Synergistic effects of rosemary, sage, and citric acid on fatty acid retention of palm olein during deep-fat frying. *Journal of the American Oil Chemists' Society*, 77(5), 527-533.
- Lercker, G. Carrasco, A. 2010. The culinary process of frying and the use of olive oil in it. The virgin olive oil: treasure of Andalusia. Ed. Unicaja Foundation, Malaga-Spain, Cap. 10, pp. 312-323.
- Magariños, C., Bauzá, M. 2003. Determination of the color of virgin olive oils. *Journal of the Faculty of Agricultural Sciences (UNCuyo)*, 35 (2), 71-76
- Maskan M. 2003. Change in color and rheological behavior of sunflower seed oil during frying and after adsorbent treatment of used oil. *Eur Food Res Technol* 218(1):20–5.
- NMX-F-223-SCFI-2011. Food-comfortable vegetable oil-specifications. Official Journal of the Federation. Available from: http://dof.gob.mx/nota_detalle_popup.php?codigo=5204623 Accessed: 2016 Oct. (In Spanish)
- NMX-F-154-SCFI-2010. Foods-oils and vegetable fats or animals-determination of peroxide value-test method. Official Journal of the Federation. Available from: http://dof.gob.mx/nota_detalle.php?codigo=2033523&fecha=11/04/2005. Accessed: 2016 Oct. (In Spanish)
- NMX-F-101-SCFI-2012. Foods-oils and vegetable fats or animals-determination of free fatty acids-test method. Official Journal of the Federation. Available from: http://www.dof.gob.mx/nota_detalle.php?codigo=5268346&fecha=17/09/2012 Accessed: 2016 Oct. (In Spanish)
- Santacruz-Vázquez, C., Santacruz-Vázquez, V., Luna Cerón, H. (2011). Determination of morphometric changes from the fractal dimension and its relation to the physicochemical parameters of a wheat flour product in laminar form during the immersion frying process. *Surfaces and Vacuum*. 24 (4) 145-152.
- Suaterna Hurtado, A.C. 2009. Food frying: frying oil. *Perspectives on Human Nutrition*, 11 (1), 39-53.