J Therm Anal Calorim (2011) 104:169–175
DOI 10.1007/s10973-010-1165-2

Comparison of olive, corn, soybean and sunflower oils by PDSC

Jorge López-Beceiro · Ramón Artiaga · Carlos Gracia · Javier Tarrío-Saavedra · Salvador Naya · José Luis Mier

ISBCXVI Special Issue

Abstract Vegetable oils of different types and qualities are widely used in homemade cooking and food industry. Most of the safety concerns were related to possible oxidation processes produced at the relatively high temperatures used when frying. Thus, the thermal stability to oxidation is an important parameter for edible oils. Oils from the Arbequina, Picual, Hojiblanca and Cornicabra olive varieties, corn, soybean and sunflower are studied in this work by means of pressure differential scanning calorimetry (PDSC). The general aim of this work is to evaluate the thermooxidative stability of these vegetable oils by the ASTM onset oxidation temperature (OOT) method. In addition, the ability of some parameters to identify different oils and some relations between the chemical composition and the OOT results are investigated.

Keywords Oxidation stability · Vegetable oil · PDSC · OOT

Introduction

Vegetable oils of different types and qualities are widely used in homemade cooking and food industry. Apart from their different organoleptic properties, different performance is provided by the different types of oil. There is also an ongoing debate on the health properties of the food processed with different kinds of oil. Corn, olive, soybean and sunflower oils are products widely used in the cooking as seasoning or frying agent. Moreover, it can produce significant changes in the healthfulness and salubriousness of food when the same oil is used repeatedly to fry. Most of the safety concerns were related to possible oxidation processes produced at the relatively high temperatures used when frying [1]. The factors that favour the alterations of the oil during the frying process are: high temperatures, reaction with the oxygen, higher oil/air contact surface, presence of water detached by the food, long time of process, presence of metallic pollutants, radiations (UV radiation), pollution by chemical species from the food. Lipid oxidation is not only responsible for unpleasant flavours in foods but can also produce harmful reactive oxygen species (ROS) that may lead to carcinogenesis, mutagenesis and ageing in humans. Corn oil and sunflower oil have a high content of linoleic acid (poliinsaturated), meanwhile oleic acid (monoisaturated) is the predominant fatty acid in olive oil. The levels of saturated fatty acids (palmitic acid and estearic acid) in sunflower oil are lower than the others. Besides, vegetable oils composition have phospholipids, acilglycerides and non-glycerides compounds as vitamin E (tocopherols and tocotrienols), vitamins A and D, carotenoids, sterols, methyl sterols and squalene. Vegetable oils normally contain large amounts of tocopherol especially the alpha, beta and gamma isomers. Some of these components, e.g. tocopherols (particularlyc-tocopherol), phospholipids (at less than 100 mg/kg), carotenoids (at low levels), squalene, and certain sterols, were reported to be beneficial to oil stability during frying [2]. Although different chemical compositions were reported for the same types of oil, in general, the reports agree in what are the major and minor components of each type of oil. The composition may also

J. López-Beceiro (✉) · R. Artiaga · J. Tarrío-Saavedra · S. Naya · J. L. Mier
Escola Politécnica Superior, University of A Coruña, Avda. Mendizábal s/n, 15403 Ferrol, Spain
e-mail: jlopezb@udc.es

C. Gracia
TA Instruments, Avda. Europa, 21. Parque Empresarial La Moraleja, 28108 Alcobendas, Madrid, Spain

vary depending on the extraction and refinement procedures [3]. Table 1 shows the chemical composition retrieved from the USDA National Nutrient Database for Standard Reference-22 [4]. Although, in this case, no distinction was made respect to the olive varieties, it can be taken as an indication in order to compare olive with other edible oils. Classification of monovarietal olive oils based on their chemical composition was accomplished [5]. It was also found that factors such as the climate, the soil, the extraction technology and the stage of ripeness probably influence the chemical composition of olive oils [6].

Synthetic antioxidants are widely used to avoid the oxidation. These may include butylated hydroxyanisole (BHA), tertiary butyl hydroquinone (TBHQ), 2,4,5-trihydroxybutyrophenone (THBP), di-tertbutyl-4-hydroxymethylphenol (IONOX-100), propyl gallate (PG), octyl gallate (OG), nordihydroguaiaretic acid (NDGA) and 4-hexylresorcinol (4HR) [7].

The thermal and thermooxidative properties of the oils are related to the fatty acid composition and the antioxidants content that avoids the oxidative reactions and possible interaction between the major and minor chemical components. Among oxidative alterations, the formation of reactive free radicals that rapidly reacted with the atmospheric oxygen to produce primary and secondary oxidation products was frequently observed in vegetable oils [8].

The thermal and thermooxidative properties can be evaluated by thermal analysis techniques such as thermogravimetry (TG) [9, 10] and differential scanning calorimetry (DSC) [11–13]. TG and time derivative TG (DTG) curves can be used to estimate the quality of edible oils by determining the kinetic parameters (activation energy of

Table 1 Chemical composition of sunflower, soybean, corn and olive oil, retrieved from the USDA National Nutrient Database for Standard Reference-22 [4]

	Common name	Sunflower mid-oleic	Soybean	Corn
Total fat/g		100	100	100
Saturated fat/g		9.0	15.6	12.9
14:0	Myristic acid	57	0	24
16:0	Palmitic acid	4219	10455	10580
17:0	Margaric acid	37	34	67
18:0	Stearic acid	3564	4436	1848
20:0	Arachidic acid	297	361	431
22:0	Behenic acid	836	366	0
Monounsaturated fat/g		57.3	22.8	27.6
16:1 undifferentiated	Palmitoleic acid	95	0	114
16:1 *c*		95	N.A.	114
17:1		N.A.	0	N.A.
18 undifferentiated	Oleic acid	57024	22550	27335
18:1 *c*		57024	22550	27335
20:1	Gadoleic acid	211	233	129
Polyunsaturated fat/g		29.0	57.7	54.7
18:2 undifferentiated	Linoleic acid	28925	50960	53510
18:2 n-6 *cc*		28703	50422	53510
18:2 *tt*		N.A.	533	N.A.
18:2 i		219	N.A.	286
18:03	Linolenic acid	37	6789	1161
18:3 n-3 *ccc*		37	6789	1161
Total trans fatty acids/g		0.2	0.5	0.3
Total trans-polyenoic fatty acids/g		0.2	0.5	0.3
Total omega-3 fatty acids		37	6789	1161
Total omega-6 fatty acids		28925	50422	53510
Tocopherols		41.08	94.64	14.30

Contents are indicated in mg, except when /g is indicated. Each fatty acid isomer is referred by its numerical designation. The first number of this designation indicates how many carbon atoms are in the fatty acid molecule, and the number after the colon indicates the number of double bonds. Omega-3 and omega-6 isomers include "n-3" and "n-6" markings, and the letters *c* and *t* are used to indicate whether the double bonds are in *cis* or *trans* configurations. 18:2i accounts for *cis*, *trans* and *trans*, *cis* isomers of 18:2

the thermal decomposition), influence of the antioxidants and the oxidative induction period. DSC is applied to estimate the energy of the exothermic and endothermic reactions involved in the oxidative thermal decomposition, and to study the crystallization processes, specific heat and glass transition temperatures. Previous TG–DSC studies showed that extra virgin olive oils showed a complex multistep decomposition pattern with the first step that exhibited a quite different profile among samples [9].

In the last year two DSC methods have aroused high interest: high pressure oxidation induction time (OIT) [14] and high pressure oxidation onset time (OOT) [15]. OIT method (ASTM E1858) [16] calculates the time of slow oxidation, called induction time, which precedes the rapid oxidation process. The use of pressure differential scanning calorimetry (PDSC) has the additional advantage of reducing evaporation from the sample and it gets results in less time than conventional DSC. The OOT method (ASTM E2009) [17] measures the degree of oxidative stability of the substance at a given heating rate, usually constant, and environment. These experiments can also be made under ambient or high pressures such as in the OIT case. The higher the OIT or OOT values the higher the oxidation stability. The aim of this work is to study, by the OOT method, the thermooxidation of four common vegetable oils used in cooking. The results could be taken as an indication of the thermooxidative stability in actual frying conditions. Moreover, the heat flow curves obtained by the OOT method or some of the parameters associated to these curves could be used to identify different vegetable oils.

Experimental

Soybean, corn, sunflower and four mono-varietal olive oils were studied by PDSC. All of them are Spanish commercial oils. The olive varieties were: picual, arbequina, hojiblanca and cornicabra. Mixtures of arbequina and picual were also prepared to evaluate possible interactions.

The PDSC tests were carried out in a TA Instruments pressure cell mounted on a Q2000 modulated DSC, with the following conditions: open aluminium pan, a heating rate of 10 °C min^{-1} from room temperature to 300 °C, sample mass in the 3–3.30 mg range, and an oxygen pressure of 3.5 MPa, with a flow rate of 50 mL/min according to the ASTM E2009 method. The experiments were manually stopped once the end of the exotherm was reached.

Thermal behaviour

Figure 1 shows an overlay of the different DSC plots obtained in the OOT experiments covering the range of temperatures where the oxidation exotherms start. The variability between replicates of a given sample is not so big to prevent a good distinction between samples. According to the OOT values, presented in Fig. 2, the oils can be ordered with respect to the stability to oxidation, in decreasing order, as follows: picual, cornicabra, hojiblanca, arbequina, corn, soybean and sunflower. The OOT values of arbequina and corn are relatively close. Nevertheless, as shown in Fig. 1, once the exothermic reaction was initiated, it proceeds much faster in the case of corn, indicating a higher stability of arbequina. Thus, a criterium that may complement the OOT values could be the slope of the exotherm. Table 2 shows the maximum slope of heat flow versus time (slope max) obtained in each case, the temperature at that point of maximum slope (T at max slope) and the slopes of the heat flow curves vs temperature in the range from 5 to 10 W/g (slope between 5 and 10).

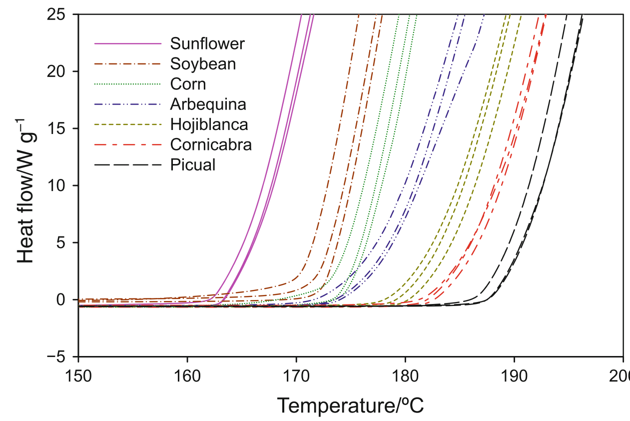

Fig. 1 Overlay of the different DSC plots obtained in the OOT experiments covering the range of temperatures where the oxidation exotherms start

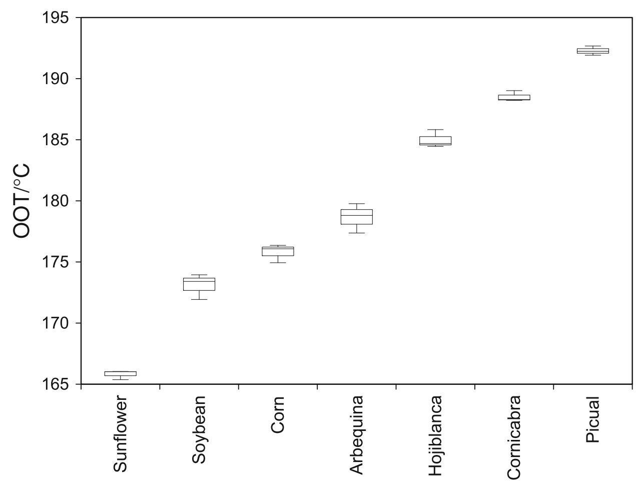

Fig. 2 Box-plot indicating the OOT values and the range of variation for the different oil samples

Table 2 Parameter values obtained from the DSC traces obtained in the OOT tests of different edible oils

	Sunflower	Soybean	Corn	Arbequina	Hojiblanca	Cornicabra	Picual
OOT/°C	165.81	173.10	175.79	178.65	184.99	188.51	192.28
Slope max/W g^{-1} s^{-1}	3.40	13.13	8.89	1.57	4.22	6.04	11.21
T at max slope/°C	174.69	185.09	189.14	188.23	199.34	202.98	206.06
Slope between 5 and 10/W g^{-1} °C^{-1}	2.79	3.91	3.56	2.08	2.28	2.25	2.76

Table 3 Some chemical components of monovarietal olive oils

	Arbequina	Hojiblanca	Cornicabra	Picual
16 (palmitic)	14300	9000	8400	9900
18 (stearic)	2100	3300	2600	3200
18 *c* (oleic)	75300	75200	78700	77800
18:2 *cc* (linoleic)	8500	9500	7500	5000
18:03 (linolenic)	600	700	600	700

Contents are indicated in mg. Extracted from [5]

The reaction rate is related to the slope of the exotherm, which is higher in the case of sunflower and corn. Table 3 shows some chemical components of monovarietal olive oils [5]. The common names for fatty acids are shown in the first column. Considering the compositional values presented in Table 1 and the slope values presented in Table 2, the linoleic acid content seems to be related to the lower slope presented by the olive curves with respect to sunflower, soybean and corn. The lower OOT value of sunflower is due to his higher linoleic acid content. It can be also observed in Fig. 1 that corn and arbequina traces present a shape at the beginning of the exotherm, which is different from that presented by the other samples. That shape is an indication of an oxidizing process, previous to the main oxidation, which can be related to the higher palmitic acid content of arbequina and corn. The higher stability to oxidation of picual and cornicabra is probably due to their low contents in linoleic acid. Figure 3a shows an overlay of the traces obtained from arbequina and picual samples as well as from two picual–arbequina mixtures. The oxidation of arbequina starts at lower temperature than picual, but its slope is lower, indicating a slower reaction, and no overheating is observed. Picual presents a very sharp exotherm and a very important overheating, reaching 284 °C. That overheating explains that the long tails observed in the case of arbequina is not observed for picual. It is also interesting that the overheating presented by picual is not observed in any of the arbequina–picual mixtures, indicating that some stabilizing effect is produced by arbequina. Figure 3b plots the OOT values obtained from picual, arbequina and two mixtures of them. A linear trend is observed so that the OOT increases with the picual content. It indicates that no oxidative interaction is produced between the two types of oil.

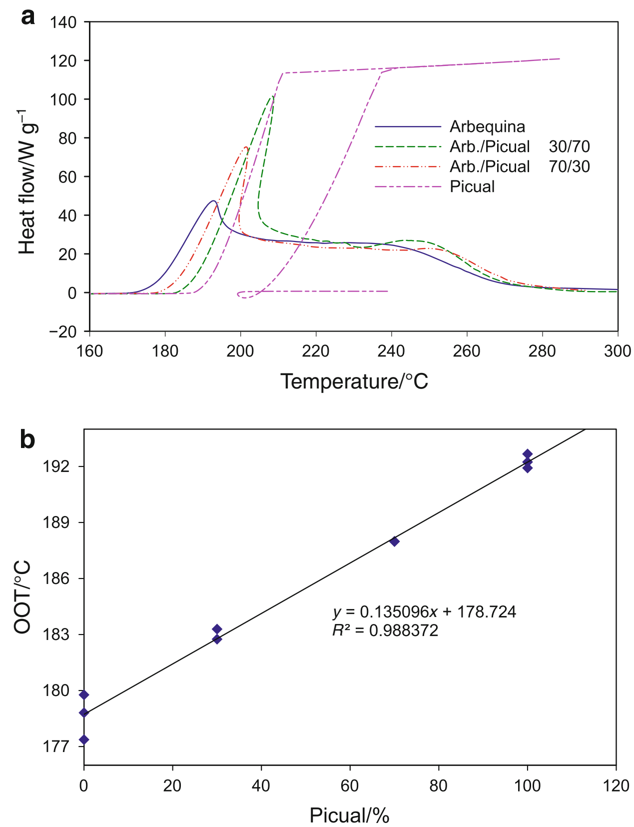

Fig. 3 Overlay of the typical PDSC traces (**a**) and the OOT values (**b**) obtained from picual, arbequina and two mixtures of them

Classification

It is important to note that all the statistical tools mentioned below have been implemented using the R and SPSS statistical packages. According to the F test (one way ANOVA) [18], the variable OOT is different for at least one oil type studied (p-value = 4.28e−015 is less than the significance level equal to 0.05), therefore the oil class factor significantly influences the response OOT. The same has occurred while testing the other variables: p-value (maximum slope of heat flow versus time) = 3.07e−

Table 4 Mean values of OOT in the homogeneous subsets for the oil class factor. Obtained by applying the Tukey test (with $\alpha = 0.05$)

Oil class	*N*	Different groups						
		1	2	3	4	5	6	7
Sunflower	3	165.81						
Soy	3		173.10					
Corn	3			175.79				
Arbequina	3				178.65			
Hojiblanca	3					184.99		
Cornicabra	3						188.51	
Picual	3							192.27
Significance		1.00	1.00	1.00	1.00	1.00	1.00	1.00

N is the number of replicates

Table 5 Confusion matrix using seven different oil classes obtained by the FLD method

Method	Estimated	Actual						
		Arbeq.	Corn	Cornic.	Hojibl.	Pic.	Soy	Sunfl.
FLD	Arbequina	100	0	0	0	0	0	0
$p = 0.9986$	Corn	0	99	0	0	0	0	0
	Cornicabra	0	0	99	0	0	0	0
	Hojiblanca	0	0	1	100	0	0	0
	Picual	0	0	0	0	100	0	0
	Soy	0	1	0	0	0	100	0
	Sunflower	0	0	0	0	0	0	100

007 < 0.05, *p*-value (temperature at that point of maximum slope) = 7.10e−013 < 0.05 and *p*-value (slopes of the curves in the 5–10 W/g range) = 1.31e−009 < 0.05. In addition, it has been proven that OOT variable is also different for each studied oil type, using the Tukey test (see Table 4) [18]. Table 4 shows the OOT means for each different group found by Tukey test. Each group statistically different from the others corresponds to one different oil class. However, the other variables found no significant differences between some levels. Therefore, the OOT variable discriminates between the oil varieties better than the other ones.

The results support the idea that the OOT can be a feature from which it is possible to classify the different oil types, as it was done on the basis of chemical composition data in other works [5, 19]. Thus, a supervised classification [20] of the oils is performed, using the OOT and the other parameter values shown in Table 2. The Fisher linear discriminant analysis method (FLD) [20, 21] is used for classifying the different parameter vector corresponding to each oil type. A parametric bootstrap resampling [22] has been done to increase the sample size, thus the discriminating power of OOT and other variables described above can be tested, using a simulated sample with the same characteristics than the actual one. The parametric bootstrap is implemented for generating new values from OOT and the other variables, assuming that are distributed according a normal distribution where the mean is the sample mean and the variance is the sample variance. The variance and the sample mean for each variety from the actual data are estimated and after 100 resampling are performed for each one. The cross-validation method technique is used for the validation of the empirical model. It works by leaving out one parameter vector (consist of the variables displayed in Table 2); then a model is trained with the remaining parameter vectors and, finally, the developed model is used for classifying the characteristic vector left out. This is repeated until all the vectors have been left out once [23, 24]. Then, the percentage of correct classification is calculated. The results are presented in Table 5. The number of simulated samples correctly classified is shown in the matrix diagonal. According to these results (probability of correct classification equal to 0.9986), the OOT and the other characteristics (maximum slope of heat flow versus time, temperature at that point of maximum slope and slopes of the heat flow curves versus temperature in the

Table 6 Parameter values of the chemical composition-OOT relation observed for different oils

	Parameter Estimation	Standard error	*t* statistic	*p* value
Intercept	1.25e+02	4.25e+00	29.301	2.49e−15
Oleic	1.06e−03	7.97e−05	13.305	4.55e−10
Linoleic	1.46e−03	1.63e−04	8.931	1.29e−07
Palmitic	−1.29e−03	2.15e−04	−6.029	1.75e−05
Oleic-linoleic interaction	−2.98e−08	4.94e−09	−6.032	1.74e−05

5–10 W/g range) allow for classification of all the samples. Thus, the OOT value is a very convenient parameter, not only to evaluate the thermooxidative stability, but also for classification purposes.

OOT-chemical composition relation

Since classification of monovarietal olive oils based on their chemical compositions was reported [5] and, as demonstrated in this work, the OOT parameter also allows for classification of olive and other oils, it would make sense to investigate a possible relation of the chemical composition with the OOT. The independent chemical variables selected for this investigation were palmitic, stearic, oleic, linolenic and linoleic acids. The method consists of doing a linear regression where the response variable is the OOT and the independent variables are assumed continuous (no factors). The resulting model variables have been chosen according to the criteria of statistical significance (t and F tests) and coefficient of determination, beginning with the more complicated models and ending with the simplest [25]. Table 6 shows the estimated linear regression parameters, their standard error, the values of t statistic and the resulting p-values. These results indicate that the OOT values can be estimated principally from the oleic, linoleic and palmitic acids contents, and from the interaction between oleic and linoleic acids. All the input variables are highly significative (p-values < 0.05), reaching an adjusted determination coefficient of $R^2 = 0.956$.

Conclusions

The onset oxidation temperature is an adequate parameter for distinguishing between olive, corn, soybean and sunflower oils. It also allows to distinguish between different varieties of olive oils. Accordingly, the samples can be ordered with respect to the stability to oxidation, in decreasing order, as follows: olive picual, olive cornicabra, olive hojiblanca, olive arbequina, corn, soybean and sunflower. Although the OOT values of corn and arbequina oils are very close, the DSC curves show that the oxidizing process is much faster in the corn case, which is reflected in the slope of the exotherm.

The contents in palmitic, oleic and linoleic acids are related to the OOT and thermal stability of different vegetable oils.

Different OOT values can be obtained by mixing different oils so this parameter, by itself, cannot be used to distinguish between mixtures and single variety samples. Even considering the whole OOT traces, some mixtures of arbequina and picual cannot be distinguished from hojiblanca or cornicabra.

The OOT parameter allows for classification of the sunflower, soybean, corn and the four monovarietal olive oils considered in this work.

A relation was found between some chemical components and the OOT results. Particularly, linolenic, oleic and palmitic acid greatly influence the thermooxidative stability.

Acknowledgements The first, second, fourth and fifth authors acknowledge the Spanish Ministerio de Ciencia e Innovación for the provision of funds MTM2008-00166.

References

1. Vorria E, Giannou V, Tzia C. Hazard analysis and critical control point of frying—safety assurance of fried foods. Eur J Lipid Sci Technol. 2004;106:759–65.
2. Kochhar SP. The composition of frying oils. In: Rossell, editor. Frying. Improving quality. Cambridge, UK: Woodhead Publishing Limited; 2001. p. 87–114.
3. Trade Standard applying to olive oils and olive-pomace oils. In:COI/T.15/NC No3/Rev.4. International Olive Council. 2009. http://www.internationaloliveoil.org/downloads/NORMAEN1.pdf. Accessed 10 Sep 2010.
4. U.S. Department of Agriculture, Agricultural Research Service. USDA National Nutrient Database for Standard Reference, Release 22. In: Nutrient Data Laboratory. 2009. http://www.nal.usda.gov/fnic/foodcomp/Data/SR15/dnload/pk260w32.exe. Accessed 11 Sep 2010.
5. Aranda F, Gomez-Alonso S, Rivera del Alamo RM, Salvador MD, Fregapane G. Triglyceride, total and 2-position fatty acid composition of Cornicabra virgin olive oil: comparison with other Spanish cultivars. Food Chem. 2004;86:485–92.
6. Aparicio R, Luna G. Characterisation of monovarietal virgin olive oils. Eur J Lipid Sci Technol. 2002;104:614–27.
7. Qin LX, Chao J, Yan SY, Li YM, Gang CX. Analysis of synthetic antioxidants and preservatives in edible vegetable oil by HPLC/TOF-MS. Food Chem. 2009;113:692–700.
8. Albi T, Lanzón A, Guinda A, León M, Pérez-Camino MC. Microwave and conventional heating effects on thermoxidative degradation of edible fats. J Agric Food Chem. 1997;45:3795–8.
9. Vecchio S, Cerretani L, Bendini A, Chiavaro E. Thermal decomposition study of monovarietal extra virgin olive oil by simultaneous thermogravimetric/differential scanning calorimetry: relation with chemical composition. J Agric Food Chem. 2009;57:4793–800.

10. Dweck J, Sampaio CMS. Analysis of the thermal decomposition of commercial vegetable oils in air by simultaneous TG/DTA. J Therm Anal Calorim. 2004;75:385–91.
11. Pambou-Tobi NP, Nzikou JM, Matos L, Ndangui CB, Kimbonguila A, Abena AA, Silou T, Scher J, Desobry S. Comparative study of stability measurements for two frying oils: soybean oil and refined palm oil. Adv J Food Sci Technol. 2010; 2:22–7.
12. Vittadini E, Lee JH, Frega NG, Min DB, Vodovotz Y. DSC determination of thermally oxidized olive oil. J Am Oil Chem Soc. 2003;80:533–7.
13. Ostrowska-Ligeza E, Bekas W, Kowalska D, Lobacz M, Wroniak M, Kowalski B. Kinetics of commercial olive oil oxidation: dynamic differential scanning calorimetry and Rancimat studies. Eur J Lipid Sci Technol. 2010;112:268–74.
14. Kodali DR. Oxidative stability measurement of high-stability oils by pressure differential scanning calorimeter (PDSC). J Agric Food Chem. 2005;53:7649–53.
15. Erhan SZ, Sharma BK, Perez JM. Oxidation and low temperature stability of vegetable oil-based lubricants. Ind Crop Prod. 2006; 24:292–9.
16. American standard test method for determining oxidation induction time of hydrocarbons by differential scanning calorimetry, vol. 14.02. West Conshohocken, PA: ASTM International E1858-08; 2008.
17. American standard test method for oxidation onset temperature of hydrocarbons by differential scanning calorimetry, vol. 14.02. West Conshohocken, PA: ASTM International E2009-08; 2008.
18. Maxwell SE, Delaney HD. Designing experiments and analyzing data. A model comparison perspective. 2nd ed. New Jersey: Lawrence Erlbaum Associates; 2004.
19. Nasiruddin Khan M, Sarwar A, Farooq Wahab M. Chemometric assessment of thermal oxidation of some edible oils. Effect of hot plate heating and microwave heating on physicochemical properties. J Therm Anal Calorim. 2010;102:369–74.
20. Peña D. Análisis de datos multivariantes. Madrid: McGraw-Hill; 2002.
21. Hernández Orallo J, Ramírez Quintana MJ, Ferri Ramírez C. Introducción a la minería de datos. Madrid: Pearson-Pentice Hall; 2008.
22. Efron B, Tibshirani R. An introduction to the bootstrap. Boca Raton: Chapman & Hall/CRC; 1993.
23. Ferraty F, Vieu P. Nonparametric functional data analysis: theory and practice. Springer series in statistics. Berlin: Springer; 2006.
24. López-Granados F, Peña-Barragán JM, Jurado-Expósito M, Francisco-Fernández M, Cao R, Alonso-Betanzos A, Fontenla-Romero O. Multispectral classification of grass weeds and wheat (*Triticum durum*) using linear and nonparametric functional discriminant analysis and neural networks. Weed Res. 2008;48: 28–37.
25. Peña D. Regresión y diseño de experimentos. Madrid: Alianza Editorial; 2007.