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Comparative Study of Vegetable Oils Oxidative Stability using DSC and Rancimat Methods

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A COMPARATIVE study was carried out to evaluate and compare the oxidative stability of vegetable oils (olive, corn and sunflower) in Egypt, through evaluation of accelerated oxidation at four different isothermal temperatures (110, 120, 130, 140 °C) using two different instruments: a differential scanning calorimeter (DSC) and a Rancimat instrument, taking into account the physicochemical quality characteristics and relationships between oxidative stability and fatty acid composition of oils. The Rancimat instrument was set at the four different isothermal temperatures with an air flow 20 L/h and measures the induction period (IP) of the selected oils. The differential scanning calorimetry (DSC) technique involved accelerated oxidation of oil samples in an air flow of 60 ml/min in DSC cell set at four different isothermal temperatures. A rapid increase in evolved heat was observed with the appearance of a sharp exothermic curve during initiation of the oxidation reaction. From the resulting exothermic curve, the onset of oxidation time (T_o) was determined graphically by the DSC instrument. There was an excellent correlation ($p<0.0001$) found between DSC (T_0) values and Rancimat (IP) measurements where the Pearson correlation coefficient (>0.98) between the two methods with coefficient of determination (R^2 >0.89) for DSC independent of the vegetable oil source, imply that DSC can be recommended as an alternative appropriate objective method for assessing the oxidative stability of vegetable oils because of its simplicity, absence of toxic chemicals, small amount of sample and time-saving nature and could be easily used for routine analysis in oils and fats industry.

Keywords: Vegetable oils, Oxidative stability, DSC, Rancimat, Comparative study

Introduction

Vegetable oils are fundamentally important in food and nutrition, for their essential fatty acids, phospholipids, carotenoids, natural antioxidants, and other physiologically active substances presented in different qualitative and quantitative proportions, depending on the type of oil and on the production technology with distinctive sensory performance and sometimes therapeutic property, in addition to their major function of providing energy [1, 2]. Vegetable oils are natural products obtained from oil-containing seeds, fruits, or nuts by different pressing methods, solvent extraction or a combination of these. Although vegetable oils naturally contain antioxidants such as tocopherols, tocotrienols, carotenoids, phenolic compounds and sterols, but they lack the sufficient oxidative stability. The oxidation of oil destroys essential fatty acids and produces low-molecular weight off-flavor compounds, toxic compounds and oxidized polymers

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which can cause apparent serious changes in the sensory and technological properties of the oil, reducing its shelf-life, and making the oil less acceptable to consumers or for industrial use. In order to overcome the stability problems of oils and fats, synthetic antioxidants; such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) are added to oils due to their high efficiency, high stability and low cost [3, 4].

Oxidative stability is one of the most important quality parameters of vegetable oils. It refers to the resistance of oils to oxygen and temperature and it is closely related to the triacylglycerol and fatty acid composition of oils, as well as some natural and added minor antioxidant components and numerous external factors. Oxidative stability is influenced by the chemical composition of the oil and action of various factors with pro- and anti-oxidant characteristics, and it can occur during oil processing and storage. Pro-oxidant factors include exposure to light, oxygen, heat, and the presence of trace elements in oils. These factors can accelerate lipid oxidation, decrease oxidative stability and consequently cause significant impacts on sensory properties, nutritional depreciation, and decrease in the shelf life. Besides, pro-oxidants can generate secondary oxidation products such as free fatty acids, peroxides, hydroperoxides, dienes, conjugated trienes, hydroxides and ketones that can cause toxicity and contribute to the development of heart disease, cancer and atherosclerosis [5-10].

The oxidation products have adverse effects on the human body; therefore, proper assessment of the oxidative stability is a decisive step in the safety assessment of oil [11]. Available methods used for evaluating oils oxidative stability include PDSC, Rancimat, Schaal oven test, GC and titration (determination of peroxide, *p*-anisidine value and calculation of the *Totox* indicator). Other methods are based on the measurement of antioxidant activity using DPPH, ABTS and DMPD reagents [12]. Spectrophotometric examination in the UV can provide information on the quality of oil, its state of preservation and changes brought about by technological processes and the presence of conjugated *diene* and *triene* systems resulting from oxidation processes and/or refining practices, NMR, vibrational techniques, fluorescence spectroscopy, spectrofluorimetry are also used [13, 14].

The Rancimat method is considered as an accelerated determination of oxidation by conductimetric method evaluating the stability by measuring the oxidation induction time, with the Rancimat apparatus which is capable of operating over a temperature range of 50 to 220ºC. During the analysis, Rancimat vessels containing 5g of oil samples are placed in an electric heating block, effluent air containing volatile organic acids from the oil sample is collected in a measuring vessel containing distilled water (60 mL). The conductivity of water is measured automatically as oxidation proceeded. Filtered, cleaned and dried air is allowed to bubble through the hot oil at 20 L/h. The induction period (IP) or the oxidation induction time (OIT) of the oil sample is then automatically recorded. OIT is the time taken until there is a sharp increase in conductivity, which is determined by the intersection of the baseline with the tangent to the conductivity curve. After each run, the glassware is rigorously cleaned to avoid any contamination that would catalyze the peroxidation. The tubes are thoroughly cleaned with acetone after each run and then washed off with washing liquid and hot water. The washed tubes are rinsed with distilled water and dried in the oven. Measuring vessels, electrodes and connecting tubes are cleaned several times with alcohol and distilled water [15-19].

Differential Scanning Calorimetry (DSC) belongs to thermoanalytical techniques which are increasing in importance for their fast and reliable monitoring oil quality with low levels of chemical waste. DSC evaluates the thermal oxidation behaviors of oils through precise recording of heat flow into and out of an oil sample. The heat flow is reported as a function of either time or temperature and plotted on the DSC thermograms, in which each peak is associated with a specific physical or chemical process. DSC has attracted the interest of the scientific community because only a small amount of sample is needed for the analysis without specific sample preparation and it is a repeatable method [20-23].

The aim of this study was to evaluate and compare vegetable oils oxidative stability using DSC and Rancimat methods, taking into account the physicochemical quality characteristics of the oils and the relationships between IP values and the fatty acid composition of the oils. For this study, three vegetable oils (olive, corn and sunflower) were used.

Materials and Methods

Materials

Vegetable oils from various plant origins were used. These were extra virgin olive oil (EVOO), refined-bleached-deodorized (RBD) corn and sunflower oils without antioxidants; RBD corn and sunflower oils with added antioxidant [175 mg/kg of Butylated hydroxyanisole (BHA)]. All solvents and chemicals used were of Analytical and HPLC grades obtained from Sigma Chemical Co. (USA).

Analytical determinations

Peroxide value (mequivalent of O_2/kg oil) was determined according to AOAC Official Method 965.33 [24]. Acidity or free fatty acid (oleic acid %) was determined according to ISO 660:2020 [25]. Natural conjugated constituents were determined by measuring UV absorption at specific wavelengths (232, 270 nm) in purified solvent according to ISO 3656:2011 [26]. Fatty acid composition was converted into methyl ester and determined by GC according to ISO 12966-2:2017 [27].

Oxidative stability of oils by Rancimat method

Oxidative stability of oils by Rancimat method was evaluated according to Gutiérrez [28] using Metrohm Rancimat 679 Analytical Instrument (Switzerland), utilizing a sample of 5 g ± 0.01 g, set at different constant temperatures (110, 120, 130, 140 °C) with an air flow of 20 L/h and measures the induction period IP (h) of the selected oil sample printed automatically. IP was recognized by a sharp change in the slope on the chart. A tangent was drawn from the slope to intersect an extension of the baseline; the distance of this intersection from the start was a measure of the induction time or IP in hours (converted to minutes in this study).

Oxidative stability of oils by DSC method

Oxidative stability of oils by DSC method was determined by a Setaram LABSYS evo DSC (France) under isothermal conditions where the accelerated oxidation of oil samples in an air flow of 60 ml/min in DSC cell set at isothermal temperatures (110, 120, 130, 140 °C). Oil samples of 20 mg ± 0.5 mg were weighed into open aluminium pans without lid (open crucibles) to allow the samples to be in direct contact with the air stream and placed in the equipment's sample chamber. The aluminium reference pan as identical as possible to the oil sample pan was left empty. The DSC oxidative induction time (T_0) of the oxidative reaction corresponded closely to the intersection of the extrapolated baseline and the tangent line (leading edge) of the exothermic curve and measured in minutes [29, 30].

Statistical Analysis

Peroxide value, free fatty acid, UV and fatty acid composition measurements were performed in triplicates and represented as means ± standard errors. Statistical analysis was performed using one way analysis of variance (ANOVA) followed by Duncan's Multiple Range Test (DMRT) with $p<0.05$ being considered statistically significant. Specific differences between treatments were determined by least significant differences (LSD) test. Pearson correlation coefficient and R^2 were used to compare the values of DSC (T_o) and Rancimat IP [31].

Results and Discussion

Physicochemical quality characteristics of the studied oils

Physicochemical quality characteristics (PV, FFA and UV) of the studied oils were listed in **Table 1.**

Table 1. Physicochemical quality characteristics of the studied oils

Quality parameter	EVOO	CO	SO	LSD
PV [meq O_2/kg oil]	3.86^{a}±0.02	2.43^{b}±0.015	2.08 ^{c}±0.03	0.045
FFA (%)	0.294^{a}±0.011	0.076^{b}±0.012	0.028^{c}±0.011	0.023
UV Abs_{232} (Diene)	1.399^{c}±0.001	1.910^{a}±0.001	1.701^{b}±0.001	0.002
UV Abs_{270} (Triene)	0.134^{c}±0.001	1.003^{a}±0.002	0.744^{b}±0.002	0.003

EVOO: Extra virgin olive oil, CO: Corn oil, SO: Sunflower oil
Mean values in the same column with different letters are significantly difference ($p<0.05$).
Values are means ± standard deviation of three determinations.

As expected in **Table 1**, EVOO, CO and SO showed a low peroxide values being 3.86, 2.43 and 2.08, respectively. It was clear that that obtained values were much lower than permitted maximum peroxide level stipulated by the Codex standards for olive oils and olive pomace oils [32] and Codex standards for named vegetable oils [33], which should not be over than 10 for vegetable oils. The low peroxide values of the studied oils indicated that these oils were not subjected to any serious rancidity

before extraction and that these oils were unoxidized and of high initial quality.

It was clear from the obtained data that the amount of free fatty acids formed by hydrolysis and oxidation were generally too small to affect the quality of the oils. It was 0.294, 0.076 and 0.028% for extra virgin olive, corn and sunflower oils, respectively. It was clear that the obtained values were much lower than the permitted maximum level stipulated by the Codex standards for olive oils and olive pomace oils [32] and Codex standards for named vegetable oils [33]. The observed low acidity indicated that the oils did not undergo hydrolytic processes and may have a long shelf life.

Absorbencies at 232 and 270 nm of EVOO, CO and SO indicated that EVOO had the lowest absorption band at 232 nm being 1.399 followed by that of SO (1.701) then that of CO (1.910). It was noticed that the UV absorbencies at 232 nm were correlated positively to linoleic acid ($C_{18:2}$) concentration in the oils. The small value in absorbency at 270 nm of EVOO (0.134) might be further contributed to its low concentration of linoleate coupled with surplus oxidative stability of this oil, and subsequently low relative rates of formation of ketonic and aldehydic oxidative products, as well as low formation of conjugated trienes. While, the more absorption at 270 nm caused by the other studied oils which exceeded that of EVOO, where CO (1.003) and SO (0.744) having higher values than that for extra virgin olive oil, might be attributed to their higher oxidative degradation of the polyunsaturated linoleate present in these oils at higher concentrations resulting in the increase formation of conjugated trienoic and ketodienes. The excess UV absorbance at 270 nm could be also explained by the higher amount of activated methylene groups in polyunsaturated fatty acids in these oils, especially sunflower oil than in extra virgin olive oil which are oxidized to form secondary oxidative products [14]. The initial characteristics of vegetable oils used in this study indicated that all the oils were of good quality.

Fatty acid composition of the studied oils

The fatty acids composition of EVOO, CO and SO were determined using GC, and the obtained results were represented along with useful relations from the fatty acid composition of oils in **Table 2.**

As expected in **Table 2**, all the studied oils had elevated amounts of total unsaturated fatty acids (ΣUSFA) ranged between 81.4872% in EVOO to 86.995% in SO. The most predominant USFAs were oleic and linoleic acids. From the composition point of view, EVOO had a high content (70.0302%) of monounsaturated oleic acid ($C_{18:1}$). However, CO and SO contained the lesser concentrations of oleic acid (32.94, 34.18%), respectively, while they had superior content of the polyunsaturated linoleic acid ($C_{18:2}$), its percentage reached 51.622, 52.91%, respectively. On the other hand, linoleic acid was found in low percentage in EVOO (8.88%). Concerning the saturated fatty acids (ΣSFA), their total ranged between 12.2729% in SO and 18.41% in EVOO. Palmitic acid was found to be the most prevalent acid in all the studied oils, its percentage was 15.356, 11.2009 and 7.73% for EVOO, CO and SO, respectively, followed by stearic acid; its concentration was 2.341, 2.179 and 3.3149% in the above respective oils. The fatty acid composition varies in different oils. In order to reveal the relation between the stability of the oils and their fatty acids, the main fatty acids (palmitic acid, oleic acid, linoleic acid and linolenic acid) in **Table 2** were selected to represent the fatty acid composition of each oil. The minor fatty acids were not considered because of their low content and ignorable contribution to the oxidation stability of vegetable oils [7].

Generally, edible oils with higher degree of unsaturation are more susceptible to lipid oxidation. The stability of different fatty acids and fatty acid methyl esters was mainly due to their chemical structure. Compositional features of fatty acid esters that influence the thermal oxidation properties include chain length, degree of unsaturation and branching of the chain. As is well known, oxidation mostly takes place in the double bonds; therefore, fatty acid esters of high unsaturation degree are more prone to oxidation. Consequently, unsaturated methyl esters, unsaturated fatty acids (or vegetable oils for that matter) are less stable than those with saturated carbon chains [7, 11, 29]. It was shown that SO had the greatest ΣUSFA (86.995) followed by CO (85.7716) then EVOO (81.4872) and these is the order of increasing stability. Also, it was observed from the results of the GC analysis of the tested oils, that EVOO which characterized with its high contents of monounsaturated fatty acid oleic and low contents in the polyunsaturated linoleic acid, makes this oil the most stable among the studied oils. Because the global proportion of unsaturated fatty acids is somewhat similar in these oils, this result was justified by a higher PUFA/MUFA ratio in CO (1.569) followed by SO (1.541) which are much higher than the ratio of EVOO (0.136). This may show a predictable behavior towards oxidation which correlates directly with PUFA/MUFA ratio. As shown in **Table 2**, the order of decreasing PUFA/MUFA ratio started by the highest value recorded for CO (1.569), followed by SO (1.541) and at least comes EVOO (0.136) with highest stability and lowest PUFA/MUFA ratio. This ratio may be listed as MUFA/PUFA, the inverse PUFA/MUFA

ratio, where instead of assigning the highest value for CO; the value was inversed to be the lowest one [34].

It was noticed that the relative ratios of palmitic acid over linoleic acid ($C_{16:0}/C_{18:2}$) and oleic acid over linoleic acid ($C_{18:1}/C_{18:2}$) were correlated with the relative ratio of monounsaturated fatty acids over polyunsaturated fatty acids (ΣMUFA / ΣPUFA) which were a helpful index for distinguishing oils under study. In addition, the ratio of linoleic acid over linolenic acid ($C_{18:2}/C_{18:3}$) was also helpful to distinguish the oil. SO with the lowest stability has the highest ratio (183.79) followed by CO (67.657) and at last comes EVOO with the lowest ratio (9.823) indicating its highest stability. Moreover, a very useful relationship was the summation of linoleic and linolenic acids over oleic acid [$(C_{18:2} + C_{18:3}) / C_{18:1}$], where CO recorded the highest value (1.5903) indicating its lowest stability, followed by SO (1.5564), then the lowest value that recorded for EVOO (0.1397) indicating its highest stability. According to the results obtained in the present study, fatty acid composition is the internal factor that has the greatest effect on the oxidative stability of oils [6, 35].

Table 2. Fatty acid composition % of the studied oils

Fatty Acid [%]	EVOO	CO	SO	LSD
$C_{12:0}$	*ND	*ND	0.077±0.001	-
$C_{14:0}$	0.063b±0.001	*ND	0.129a±0.001	0.006
$C_{16:0}$	15.356a±0.001	11.2009b±0.0001	7.73d±0.01	0.014
$C_{16:1}$	1.22a±0.01	0.1096c±0.0001	0.129b±0.001	0.011
$C_{17:0}$	0.061b±0.001	0.085a±0.001	0.047c±0.001	0.008
$C_{17:1}$	0.092a±0.001	0.034b±0.001	0.032b±0.001	0.008
$C_{18:0}$	2.341c±0.002	2.179d±0.02	3.3149b±0.002	0.158
$C_{18:1}$	70.0302a±0.015	32.94c±0.14	34.18b±0.18	0.292
$C_{18:2}$	8.88e±0.1	51.622d±0.2	52.91b±0.1	0.455
$C_{18:3}$	0.904a±0.001	0.763b±0.001	0.289d±0.001	0.008
$C_{20:0}$	0.472b±0.02	0.537a±0.01	0.257d±0.01	0.024
$C_{20:1}$	0.361a±0.01	0.303b±0.01	0.175d±0.01	0.019
$C_{22:0}$	0.117e±0.001	0.176d±0.01	0.718b±0.001	0.014
Σ SFA	18.41a±0.11	14.1779b±0.1	12.2729c±0.1	0.177
Σ USFA	81.4872d±0.3	85.7716c±0.5	86.995b±0.3	0.704
Σ SFA / Σ USFA	0.2259a±0.01	0.1653b±0.01	0.1411c±0.01	0.018
Σ MUFA	71.70a±0.2	33.39c±0.2	34.52b±0.22	0.498
Σ PUFA	9.784d±0.2	52.385c±0.2	53.199b±0.19	0.376
Σ PUFA / Σ MUFA	0.136c±0.01	1.569b±0.11	1.541b±0.12	0.161
Σ MUFA / Σ PUFA	7.328a±0.01	0.637c±0.01	0.649bc±0.01	0.016
$C_{16:0} / C_{18:2}$	1.729a±0.001	0.217b±0.001	0.146c±0.002	0.016
$C_{18:1} / C_{18:2}$	7.886a±0.11	0.638b±0.12	0.646b±0.11	0.197
$C_{18:2} / C_{18:3}$	9.823e±0.1	67.657d±0.17	183.079b±0.3	1.312
$\frac{C_{18:2} + C_{18:3}}{C_{18:1}}$	0.1397c±0.01	1.5903b±0.1	1.5564b±0.1	0.163

*ND: Not Detected, EVOO: Extra virgin olive oil, CO: Corn oil, SO: Sunflower oil, SFA: Saturated Fatty Acids, USFA: Unsaturated Fatty Acids, MUFA: Monounsaturated Fatty Acids PUFA: Polyunsaturated Fatty Acids
Mean values in the same column with different letters are significantly difference ($p<0.05$).
Values are means ± standard deviation of three determinations.

Oxidative stability of the studied oils

Determination of oxidative stability of oils is a tedious and time-consuming method when analyzed at room temperature, thus it is necessary to use accelerated test at high temperature to obtain the oxidative stability in a shorter time. In particular, accelerated oxidation tests increase the lipid oxidation rate by exposing the food to elevated temperatures, in the presence of excess quantities of air or oxygen.

When high temperatures are used to accelerate oil degradation, the oxidation reactions differ from the characteristic ones at lower temperatures. Therefore, it is advisable to compare the relative stability of various oils at different temperatures [36 - 38].

Oxidative stability values (minutes) of the studied oils at four different isothermal temperatures (110ºC, 120ºC, 130ºC, 140ºC) by Rancimat and DSC methods were listed in **Table 3.**

Table 3. Oxidative stability of the studied oils by Rancimat and DSC methods at different isothermal temperatures

Oil	Rancimat IP (min.)					DSC T_0 (min.)			
	110ºC	120ºC	130ºC	140ºC		110ºC	120ºC	130ºC	140ºC
EVOO	894.0	433.8	189.0	108.6		525.6	234.9	105.7	44.3
CO+ BHA	696.0	358.8	173.4	79.2		407.4	202.8	92.0	39.0
CO	420.0	252.0	113.4	54.0		245.4	123.2	60.0	28.5
SO+ BHA	342.0	174.0	92.4	45.0		198.0	90.1	41.5	23.2
SO	226.2	127.2	60.0	33.0		131.0	70.0	37.0	19.5

EVOO: Extra virgin olive oil, CO: Corn oil, SO: Sunflower oil

Oxidative stability of the studied oils by Rancimat Method

The Rancimat test is an official method that is recognized internationally. The Rancimat test measures resistance to accelerated oxidation (oxidative stability) which is a very important parameter for evaluating the quality of oils once it gives a good perception and estimation of the susceptibility to oxidation process. In the tables representing results of this study, IP was expressed in minutes instead of hours to be compared with onset time (T_o) of DSC which is represented in minutes.

The results of oxidative stability, in terms of measurement of induction periods (Rancimat, 20 L/h) at four different isothermal temperatures (110, 120, 130, 140ºC) of the tested oils (EVOO, CO, SO, CO+BHA and SO+BHA) were shown in **Table 3**. The data showed that EVOO had the highest induction period being 894, 433.8, 189, 108.6 min. at four different isothermal temperatures: 110ºC, 120ºC, 130ºC, 140ºC, respectively, indicating superior resistance to oxidation, followed by CO+BHA (696, 358.8, 173.4, 79.2 min.), CO (420, 252, 113.4, 54 min.), SO+BHA (342, 174, 92.4, 45 min.), SO (226.2, 127.2, 60, 33 min.) at four different isothermal temperatures: 110ºC, 120ºC, 130ºC, 140ºC, respectively. The highest resistance of EVOO to oxidation was due to lesser linoleate, higher percentage of oleate. The lowest induction period of SO was attributed to its lower antioxidant content and higher polyunsaturated fatty acid linoleic (52.91%) and the highest degree of unsaturation (ΣUSFA 86.995%) which allowed the oil to oxidize easily. As it is known that linoleic acid oxidizes 50 times faster than oleic acid.

Considering the measurement of oxidative stability by the Rancimat method for oils with added antioxidant (CO+BHA and SO+BHA) to study the effect of the added antioxidant [175 mg/kg of Butylated hydroxyanisole (BHA)] on the oxidative stability of oils, it was observed an overall increase in the IP of the oils with added antioxidant as CO+BHA and SO+BHA compared with CO and SO without added antioxidant, respectively. The differences between the values before and after the addition of the antioxidant BHA (175 mg/kg) reflect the antioxidant activity of BHA in the oils and also may be attributed to the synergistic effect of BHA with oils components.

The Rancimat test only gives a total estimation of the antioxidant potential of the oil, without information on the possible contribution of single compounds and their positive or negative interactions. Then, oxidative stability is not dependant on a single parameter, but is rather affected by the fatty acid composition and a complex pool of antioxidants and prooxidants.

Oxidative stability of the studied oils by DSC Method

A DSC measuring cell consists of a furnace and an integrated sensor with designated positions for the sample and reference pans. The sensor areas are connected to thermocouples or may even be part of the thermocouple. This allows for recording both the temperature difference between sample and reference side (DSC signal) and the absolute temperature of the sample or reference side. The result of a DSC

experiment is a curve of heat flow versus time. Due to the heat capacity (*cp*) of the sample, the reference side (usually an empty pan) generally heats faster than the sample side during heating of the DSC measuring cell; i.e., the reference temperature increases a bit faster than the sample temperature. The main property that is measured by DSC is heat flow, the flow of energy into or out of the sample as a function of time on the x-axis, and usually shown in units of mW (milliwatt) on the y-axis. Since a mW is a mJ/s (millijoule per second) this is literally the flow of energy in unit time. The actual value of heat flow measured depends upon the effect of the reference and is not absolute. What matters is that a stable instrumental response or baseline is produced against which any changes can be measured. The starting point of the curve on the y-axis may be chosen as one of the starting parameters, and it should be set at or close to zero. Two different conventions exist for the display of the heat flow curve: one show endotherms in the downward direction, the other upward assigned for exotherms.

The oxidative stability determined by DSC method as T_o (oxidative induction time) values were determined by the intersection of an extrapolated baseline and the tangent line (leading edge) of an exothermic peak. The dynamic DSC curve of oil sample is given where the exothermic peak related to auto-oxidation process of unsaturated fatty acids is observed. From the DSC curve, the oxidative induction time or onset time (T_o, DSC) at which the auto-oxidation process begins is determined. The onset time is usually taken as a parameter characterizing the oxidative susceptibility of oils.

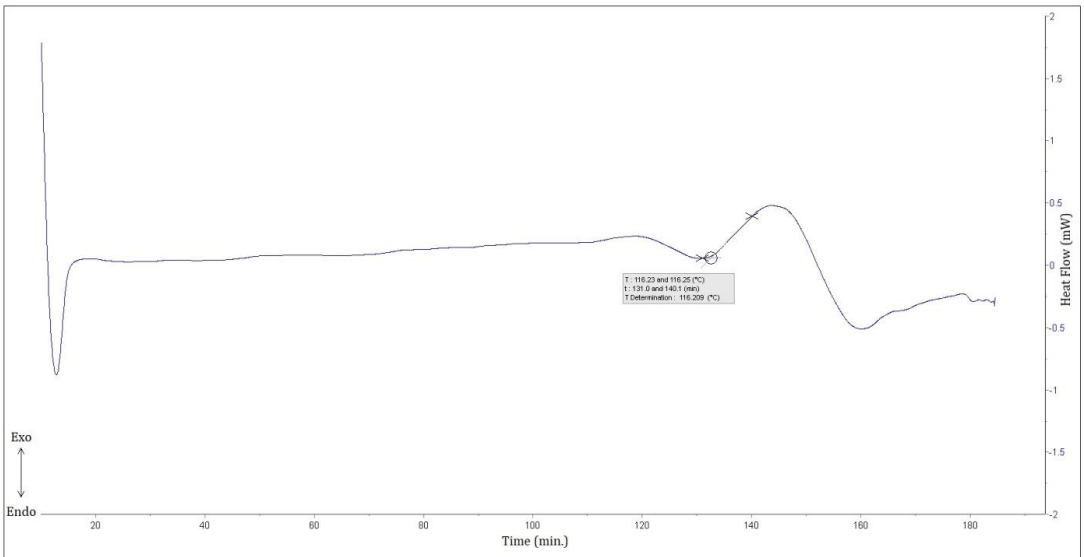

Fig.1 DSC Oxidation Curve of SO at Isothermal Temperature (110ºC)

Fig.1 represents DSC oxidation curve of SO at isothermal temperature (110ºC). The onset point is connected with initiation and formation of primary auto-oxidation products, and then further oxidation occurs with decomposition of oxidation products [39]. DSC curves for all oil samples have similar shapes but are shifted towards higher onset times depending on types of oils with oxidative stability values more than that of SO which is the oil with least onset time.

It is observed that DSC T_o at 110ºC appeared at 116.23ºC instead of 110ºC because of the exothermic reaction effect that raised the temperature of the DSC oven which was adjusted and held at 110ºC accurately with high sensitivity to resist any change in temperature along the experiment period at the start of experiment. Also, when observing the heat flow, the start was recorded at -5.30039 mW as an endothermic process at zero time and zero temperature, then the negative value of the heat flow was converted to positive value on gaining energy and start of oxidation process with an exothermic reaction resulted in raising the heat flow to 11.46425 mW which is the maximum heat flow acquired by the sunflower oil sample then the oxidation process increased gradually by time till it reached the onset time T_o = 131 min. which is the onset time with heat flow 0.055917 mW. It was reported that the oxidation process is a principally exothermic reaction which occurs in between the oil and oxygen. The Rancimat instrument at the same isothermal temperature (110ºC) gave significantly ($p < 0.05$) higher oxidative induction time than DSC technique. This variation may be due to the smaller sample size which was used in the DSC analysis as compared to Rancimat instrument [40].

The isothermal DSC oxidation measurements of oxidative induction time or onset time (T_o, DSC, 60 ml min^{-1}) at four different isothermal temperatures (110ºC, 120ºC, 130ºC, 140ºC) were shown **(Table 3)**, where the start of the exothermic reaction value measured as extrapolated onset time (T_o). The sample with a higher T_o at the same temperature is more stable than the one for which this parameter is lower. The DSC thermograms of EVOO, CO+BHA, CO, SO+BHA and SO exhibited similar flat profiles in the initial heating stage before a sudden increase to maximum heat flow temperatures. The T_0 values obtained by DSC curve extrapolation showed that EVOO had the highest induction period being 525.6, 234.9, 105.7, 44.3 min. at four different isothermal temperatures: 110ºC, 120ºC, 130ºC, 140ºC, respectively, indicating the superior resistance to oxidation, followed by CO+BHA (407.4, 202.8, 92.0, 39.0 min.), CO (245.4, 123.2, 60.0, 28.5 min.), SO+BHA (198.0, 90.1, 41.5, 23.2 min.), SO (131.0, 70.0, 37, 19.5 min.) at four different isothermal temperatures: 110ºC, 120ºC, 130ºC, 140ºC, respectively. For the analyzed oils, with increasing the isothermal temperature, a significant decrease was observed for T_0. Generally, with an increase in 10ºC from 110 to 140 ºC, the T_0 value was reduced approximately to half of its earlier value shown in **Table 3,** with an agreement with Q10 law for the association among the rate of chemical reaction and temperature [40, 41].

Relationship between Rancimat (IP) and DSC (T_0)

To compare the two instruments at similar analytical conditions, the working temperature was set at 110 °C for both, taking into account that temperature can play a crucial role in fat oxidation, therefore, affecting the determination of the IP values. It should also be pointed out that when using the Rancimat instrument the oil sample (5 grams) was exposed to a continuous flow of air at atmospheric pressure (20 L/h) compared to DSC having an air flow of 60 ml/min for very small oil sample (20 milligrams). The oxidative induction time (T_o) values were in the same order of Rancimat method but with considerably lower time or IP values. The T_o values obtained with DSC were compared to those achieved with Rancimat, as reported in **Table 3**. Analyzing the results obtained for both oil classes, we noted the apparent differences in induction time between the two methods. The reasons for these different values had to be related to the different analytical conditions used during oxidative stability analysis, in particular different sample weight (5 grams in Rancimat versus 20 milligrams in DSC). In fact, the purpose of this report was to verify the correlation degree of two different oxidative stability determination techniques, regardless of the analytical conditions used for each sample class. The difference between DSC and Rancimat due to the much lower sample size required for DSC against Rancimat could be interpreted by the fact that: the surface to volume ratio in DSC samples is so great that should be considered as an important parameter, since the accelerated oxidation reaction affects firstly the surfaces of the particles effectively than the inner content of the bulk sample [42]. The DSC and Rancimat instruments achieved the same significant results in spite of their different measurement approach. In particular, with the Rancimat instrument, where the accelerating oxidation factors are temperature and air flow, the IP values were assessed as the time needed for achieving an increase in the measured water conductivity due to the production of oxidation-related moieties. Conversely, with the DSC method, where the accelerating factors are temperature and air flow, the T_o values or the onset point and first maximum peak are connected with initiation and formation of primary auto-oxidation products, and the second maximum peak informs about further oxidation and decomposition of oxidation products [39], thus a sudden change in the lipid oxidation rate. Rancimat and DSC methods are based on generation of volatiles and thermal release, respectively, which are indicative of the onset of advanced oxidation (termination).

The relationship between Rancimat and DSC methods reveals that there exists a regular linear directly proportional relationship implies that increasing Rancimat IP values is followed by increasing DSC T_o values for oils. These findings may be useful in predicting the unknown Rancimat IP values from the known DSC T_o values and vice versa. The Pearson correlation coefficient is the measure of degree of linear relationship between the two variables. DSC T_o showed high correlation coefficient with Rancimat IP values, independent of vegetable oil source as shown in **Table 4.** The coefficients of correlation were also highly significant ($p < 0.01$) for each evaluation. In observation of the high association between DSC T_0 and Rancimat IP, linear regression equations were calculated (**Table 5**), where we can see the *p*-values to each regression equation. However, due to the different chemical compositions of the analyzed vegetable oils, different regression equations were elaborated to evaluate them individually. Constructing a model requires more than one regression equation [43].

The Pearson correlation coefficient showed excellent correlations between Rancimat IP at 110ºC with DSC T_o at different isothermal temperatures (110, 120, 130, 140 ºC) for different oils.

Considering DSC T_o at 110ºC, the correlation coefficient was 1.000 (perfect correlation) with Rancimat IP at 110ºC, whereas, the coefficients of correlation were 0.993, 0.988, 0.994 for the rest DSC T_o isothermal temperatures.

Table 5 shows the linear regression equation relationships between Rancimat IP at 110ºC and DSC T_o at different isothermal temperatures. The variation of regression equations is due to differences in vegetable oils compositions which make it difficult to assign a standard regression equation to evaluate the relationship between the two methods.

Table 6 shows the regression equations of logarithms of DSC *To* values versus DSC isothermal temperature of oils, where the result gave a linear relation ($p<0.0001$) for each oil. The coefficients of determination (R^2) were all above 0.891. With this observation, one can easily predict oxidative stability of a given oil when the temperature is a known variable [29].

Table 7 shows the relationship between logarithms of Rancimat IP ($\log_{10}$IP) and Rancimat isothermal temperatures (T) of oils, where it has appeared the linear relationship shown graphically in **Fig.2**.

Table 8 shows the relationship between logarithms of DSC T_o ($\log_{10}T_o$) and DSC isothermal temperatures (T) of oils, where it has appeared the linear relationship shown graphically in **Fig.3**.

From the **Figures (4-8)**, it is obvious that there are excellent correlations between Rancimat IP and DSC T_o at different isothermal temperatures (110, 120, 130, 140 ºC) for each oil. Linear relationships exist with excellent R^2 of values: 0.998, 0.999, 0.983, 0.995, 0.997 for the corresponding oils: EVOO, CO+BHA, CO, SO+BHA, SO, respectively.

Table 4. Pearson correlation coefficient matrix between DSC and Rancimat methods

		Rancimat IP 110ºC	**DSC T_0 110ºC**	**DSC T_0 120ºC**	**DSC T_0 130ºC**	**DSC T_0 140ºC**
Rancimat IP 110ºC	Pearson Correlation	-	1.000**	0.993**	0.988**	0.994**
	Sig. (2-tailed)		0.000	0.000	0.000	0.000
DSC T_0 110ºC	Pearson Correlation	1.000**	-	0.993**	0.988**	0.994**
	Sig. (2-tailed)	0.000		0.000	0.000	0.000
DSC T_0 120ºC	Pearson Correlation	0.993**	0.993**	-	0.998**	0.999**
	Sig. (2-tailed)	0.000	0.000		0.000	0.000
DSC T_0 130ºC	Pearson Correlation	0.988**	0.988**	0.998**	-	0.997**
	Sig. (2-tailed)	0.000	0.000	0.000		0.000
DSC T_0 140ºC	Pearson Correlation	0.994**	0.994**	0.999**	0.997**	-
	Sig. (2-tailed)	0.000	0.000	0.000	0.000	

** Correlation is significant at the 0.01 level (2-tailed)

Table 5. Regression and Relationships between Rancimat (IP) at 110ºC and DSC (T_o) at different isothermal temperatures[a]

Indicator (Y)	**Indicator (X)[a]**	**Regression Equation**	***p-value***
Rancimat IP 110ºC	DSC T_o 110ºC	$IP_{Rancimat\ 110^oC} = (5.551)\ T_{o\ DSC\ 110^oC} + (1.692)$	0.0001
	DSC T_o 120ºC	$IP_{Rancimat\ 110^oC} = (3.787)\ T_{o\ DSC\ 120^oC} - (30.404)$	0.0001
	DSC T_o 130ºC	$IP_{Rancimat\ 110^oC} = (8.846)\ T_{o\ DSC\ 130^oC} - (79.151)$	0.0001
	DSC T_o 140ºC	$IP_{Rancimat\ 110^oC} = (25.851)\ T_{o\ DSC\ 140^oC} - (283.142)$	0.0001

[a] Significance at 0.0001 level ($p<0.0001$)

Table 6. Regression and Relationships between logarithms of DSCT_o ($\log_{10}T_o$) and DSC isothermal temperature (T) of oils[a]

Oil	**Regression Equation**	**Coefficient of Determination (R^2)**
EVOO	$T= (438.306)\ \log_{10}T_o - 732.446$	0.891
CO+ BHA	$T= (352.318)\ \log_{10}T_o - 560.872$	0.901
CO	$T= (227.821)\ \log_{10}T_o - 325.027$	0.914
SO+ BHA	$T= (186.043)\ \log_{10}T_o - 248.284$	0.922
SO	$T= (133.052)\ \log_{10}T_o - 162.486$	0.931

[a] Significance at 0.0001 level ($p<0.0001$)

Table 7. Relationships between logarithms of Rancimat IP ($log_{10}IP$) and Rancimat isothermal temperatures (T) of oils[a]

Indicator (Y) log_{10} IP	EVOO	CO+BHA	CO	SO+BHA	SO
Rancimat 110°C	2.9513	2.8426	2.6232	2.534	2.3545
Rancimat 120°C	2.6373	2.5549	2.4014	2.2405	2.1045
Rancimat 130°C	2.2765	2.239	2.0546	1.9657	1.7782
Rancimat 140°C	2.0358	1.8987	1.7324	1.6532	1.5185

[a] Significance at 0.0001 level ($p<0.0001$)

Table 8. Relationships between logarithms of DSC T_o ($log_{10}T_o$) and DSC isothermal temperatures (T) of oils[a]

Indicator (Y) log_{10} T_o	EVOO	CO+BHA	CO	SO+BHA	SO
DSC 110°C	2.7207	2.6100	2.3899	2.2967	2.1173
DSC 120°C	2.3709	2.3071	2.0906	1.9547	1.8451
DSC 130°C	2.0241	1.9638	1.7782	1.6180	1.5682
DSC 140°C	1.6464	1.5911	1.4548	1.3655	1.2900

[a] Significance at 0.0001 level ($p<0.0001$)

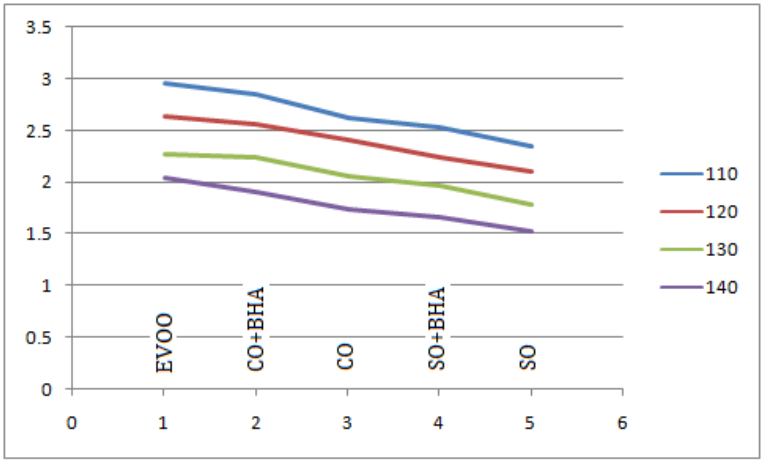

Fig. 2. Relationships between logarithms of Rancimat IP ($log_{10}IP$) and Rancimat isothermal temperatures (T) of oils

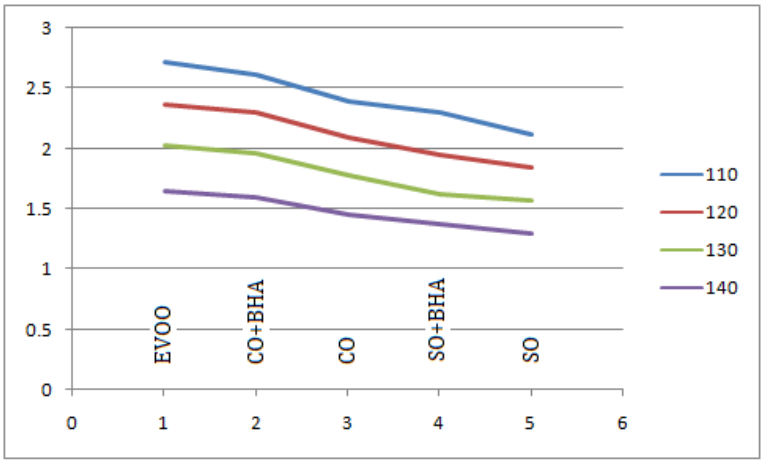

Fig. 3. Relationships between logarithms of DSC T_o ($log_{10}T_o$) and DSC isothermal temperatures (T) of oils

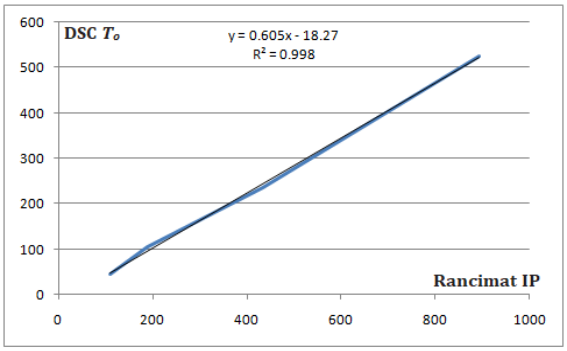

Fig. 4 Relationship between Rancimat IP and DSC T_o at different isothermal temperatures of EVOO

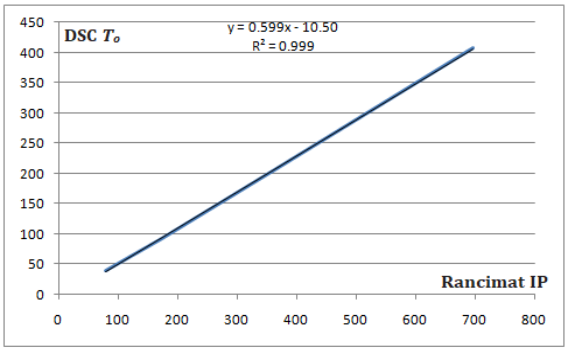

Fig. 5 Relationship between Rancimat IP and DSC T_o at different isothermal temperatures of CO+BHA

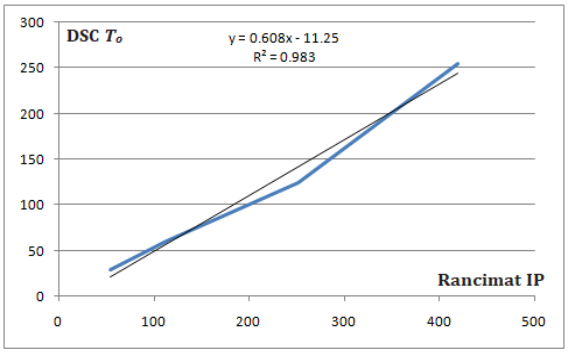

Fig. 6 Relationship between Rancimat IP and DSC T_o at different isothermal temperatures of CO

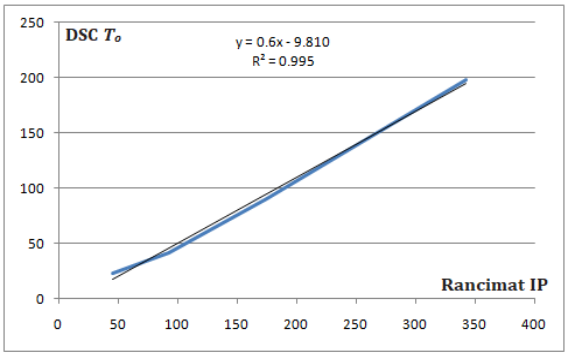

Fig. 7 Relationship between Rancimat IP and DSC T_o at different isothermal temperatures of SO+BHA

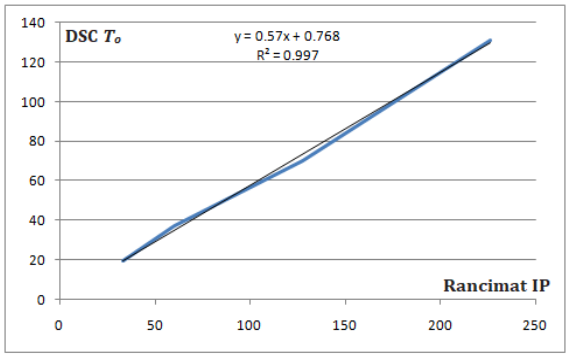

Fig. 8 Relationship between Rancimat IP and DSC T_o at different isothermal temperatures of SO

Conclusions

Differential scanning calorimetry (DSC) and a traditional Rancimat analytical instrument were applied to evaluate the oxidative stability of EVOO, CO and SO at isothermal temperatures (110, 120, 130, 140°C) with an air flow of 20 L/h in Rancimat and 60 ml/min in DSC. The results revealed that there was an excellent correlations ($p<0.0001$) found between DSC (T_0) values and Rancimat (IP) measurements where the Pearson correlation coefficient (>0.98) between the two methods with coefficient of determination (R^2 >0.89) for DSC independent of vegetable oil source, imply that DSC can be recommended as an alternative appropriate objective method for assessing the oxidative stability of vegetable oils as an accurate, reliable and fast method for the evaluation of the oxidative stability in oils and fats for its simplicity, absence of toxic chemicals, time-saving nature, and lack of hazardous chemicals leading to a decrease in pollution and lowering economical cost and could be used for routine analysis in the oils and fats industry.

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