



Evaluation of Chemical and Physical Changes in Different Commercial Oils during Heating

De Alzaa F, Guillaume C* and Ravetti L

Modern Olives Laboratory Services, Australia

*Corresponding Author: Guillaume C, Modern Olives Laboratory Services, Australia.

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Abstract

When cooking oils are exposed to heat, oil degradation occurs, and by-products are produced (free fatty acids, secondary products of oxidation, polar compounds). Some by-products of oil degradation have adverse effects on health. The smoke point of an oil is believed to be correlated with the safety and stability under heat, although technical evidence to support this is limited. The aim of this study was to assess the correlation between an oil's smoke point and other chemical characteristics associated with stability/safety when heating. Analysis was undertaken in an ISO17025 accredited laboratory. Extra virgin olive oil (EVOO) and other common cooking oils were heated up to 240°C and exposed to 180°C for 6 hours, with samples assessed at various times, testing smoke point, oxidative stability, free fatty acids, polar compounds, fatty acid profiles and UV coefficients. EVOO yielded low levels of polar compounds and oxidative by-products, in contrast to the high levels of by-products generated for oils such as canola oil. EVOO's fatty acid profile and natural antioxidant content allowed the oil to remain stable when heated (unlike oils with high levels of poly-unsaturated fats (PUFAs) which degraded more readily). This study reveals that, under the conditions used in the study, smoke point does not predict oil performance when heated. Oxidative stability and UV coefficients are better predictors when combined with total level of PUFAs. Of all the oils tested, EVOO was shown to be the oil that produced the lowest level of polar compounds after being heated closely followed by coconut oil.

Keywords: Extra Virgin Olive Oil (EVOO); Poly-Unsaturated Fats (PUFAs); Heating

Introduction

Frying oil at high temperatures (approximately 180°C (356°F) or over) is a very common processing method used to prepare foods of vegetable and animal origin [1]. The numerous factors influencing the stability and performance of frying oil can be categorized into external and internal factors depending on whether they are operation-dependent (relatively independent of the inherent quality of the frying oil) such as frying temperature, accessibility to oxygen, and duration of frying; or oil-dependent (arising from the inherent composition of the frying oil) [2]. Edible oils are composed of triacylglycerols (> 96%) and endogenous minor components. It is generally agreed that the inherent composition of edible oils exerts considerable influence on their frying stability [3-5].

At elevated temperatures, oils will change significantly due to the many chemical and physical reactions which occur, such as oxidation, hydrolysis, cyclization, isomerization and polymerization [6-8]. When frying, oil also decomposes into a variety of volatile

compounds and monomeric and polymeric products, which are capable of influencing not only the sensory and health quality, but also the shelf life of the fried product [9,10]. Some of these compounds are, in fact, responsible for the pleasant flavor, taste and the typical crispness and golden color when food is fried under appropriate conditions. However, free radicals, trans-fatty acids, conjugated linoleic acids and some oxidized volatile products (acrolein and other α , β -unsaturated aldehydes) commonly formed during edible oil degradation, are known to be responsible for the off-flavor, reducing the shelf-life of edible oils and may further cause health problems [10-12].

Physical changes in oils that occur during heating and frying include increased viscosity, darkening in color, and increased foaming as frying time continues. At the same time, the smoke point of the oil decreases. The frying operator may not notice these effects until the oil has been used for prolonged periods of time. Specific methods exist to measure degradation processes and products quantitatively: free fatty acids, carbonyl compounds, and high molecular weight products will increase with increased frying time and can be measured chemically or by chromatography [10].

The principal aim of this work was to study different parameters to predict the stability of different edible oils when heated.

Materials and Methods

Heating procedures

Ten of the most commonly used cooking oils in Australia were selected from the supermarket (high quality extra virgin olive oil (EVOO), virgin olive oil (VOO), olive oil (OO), canola oil (CO), rice bran oil (RO), grapeseed oil (GO), coconut oil (CoO), high oleic peanut oil (PO), sunflower oil (SO) and avocado oil (AO). Each oil was subjected to two different heating trials.

The first trial consisted of gradually heating a sample of 250 mL of each oil in a pan fryer from 25°C to 240°C, collecting samples as the oils reached 150°C (302°F), 180°C (356°F), 210°C (410°F) and 240°C (464°F). The overall time to reach the highest temperature was approximately 20 minutes.

In the second trial, a sample of 3 L of each oil was heated in a deep fryer at 180°C (356°F), which is the highest recommended temperature for deep frying, for 6 hours collecting samples at 30, 60, 180 and 360 minutes.

All heated samples were cooled at room temperature ($25 \pm 1^\circ\text{C}$, $77 \pm 1^\circ\text{F}$) and then stored until chemical analysis.

Analytical determinations

Measurement of specific absorbance coefficient (K_{232} and K_{270})

Coefficients of specific extinction at 232 and 270 nm (K_{232} and K_{270}) were determined according to official method and recommended practices (Ch 5-91 reapproved 2009) of the American Oil Chemist Society (AOCS) [13]. A sample of each oil was weighed (0.04g) into a 10 mL volumetric flask, diluted and homogenised in isooctane. A rectangular quartz cuvette (optical light path of 1 cm) was filled with the resulting solution, and the extinction values were measured using Genesys 10 UV-VIS spectrophotometer.

Free Fatty Acids

Free fatty acids (FFAs) were determined following AOCS official method Ca 5a-40 [13]. A sample of each oil was weighed (10 g) into a 250 mL Erlenmeyer flask and diluted with ethyl ether: ethanol (50:50 v/v neutralized with NaOH), 10 drops of phenolphthalein were added, and it was titrated with standardised sodium hydroxide.

Fatty Acid Profile

The fatty acid profile (FAP) of the oils was determined according to IOC/T.20/N33 [14] method by gas chromatography FID detection, previous preparation of the fatty acid methyl esters derivatives.

Polar Compounds

Total polar compounds were determined in oil samples by HPLC following the standard method DGF-C-III 3d (02) [15]. HPLC analysis was performed using an Agilent 1100 system equipped with an autosampler, isopump, temperature-controlled column compartment at 35°C (95°F) and a refractive index detector at 35°C. The columns used were 2 x Phenomenex Phenogel 100A, 300 x 7.6 mm, 5 μm , connected in series. The injection volume was 20 μL and a flow rate of 0.7 mL/min was used. The mobile phase was tetrahydrofuran.

Oil Stability Index

Oxidative stability was measured according to AOCS Cd12b-92 (reapproved 2009) as the induction time in a Rancimat® at 110°C and air flow of 20 L/h [13].

Smoke Point

The smoke point of each oil was carried out using YD-1 Full automatic Oil Smoke Point instrument based on AOCS Official Method Cc 9a-48 [13]. A test portion of each oil was filled into a cup, and heated until a continuous bluish smoke appeared. Each measurement was made by duplicate.

Statistical analyses

Analyses of variance (ANOVA) and graphics were performed using SigmaPlot software, version 14.0. Significance defined at $p < 0.05$ was analysed using GraphPad software.

Results and Discussion

General

The initial characterization of the oils was based on absorption at 232 nm and 270 nm, smoke point, fatty acids, FFAs, oxidative stability and polar compounds. Data is summarized in table 1, where the differences between oils could be related to the method of extraction, their level of refining and the amount of saturated or unsaturated fatty acids determined by genetics. In terms of fatty acid composition, grapeseed oil showed the highest value of linoleic acid content (68.4%) followed by sunflower (50.4%), rice bran (32.4%) and canola (18.2%) oils. Coconut oil showed the lowest value of oleic acid (7.9%) followed by grapeseed oil (19.6%). High oleic acid peanut oil, which has been softly refined, presented similar chemical and physical characteristics to the different olive oil grades. The influence on fatty acid composition of oils on stability has been variously reported [16-18]. In general, oils that are more unsaturated oxidize more readily than less unsaturated [19]. This observation correlates with the relative rate of the fatty acid alkyl radical formation [20].

Initial characteristics of unheated oil samples											
	EVOO	VOO	OO	GO	AO	CO	SO	RO	CO	PO	
Smoke Point (°C)	206.67 ± 2.520	175.33 ± 0.577	208.00 ± 1.530	268.00 ± 1.000	196.67 ± 0.577	191.00 ± 3.610	254.67 ± 1.530	237.00 ± 1.730	255.67 ± 0.577	226.33 ± 2.080	
Oxidative stability (h at 110°C)	32.70 ± 2.020	30.00 ± 0.100	15.98 ± 0.289	6.5667 ± 0.493	10.17 ± 0.208	50.27 ± 5.460	6.10 ± 0.100	16.17 ± 0.29	10.83 ± 0.153	35.37 ± 1.170	
FFA (%)	0.17 ± 0.006	1.24 ± 0.060	0.27 ± 0.006	0.06 ± 0.010	0.38 ± 0.000	0.13 ± 0.000	0.08 ± 0.006	0.23 ± 0.017	0.07 ± 0.010	0.12 ± 0.006	
Polar Compounds (%)	5.54 ± 0.015	5.76 ± 0.015	6.44 ± 0.015	9.63 ± 0.015	5.42 ± 0.015	5.76 ± 0.015	6.32 ± 0.015	7.89 ± 0.015	5.64 ± 0.015	5.54 ± 0.015	
K ₂₃₂ (nm)	1.67 ± 0.026	1.75 ± 0.027	1.89 ± 0.030	4.06 ± 0.153	2.34 ± 0.040	1.37 ± 0.106	2.54 ± 0.106	4.41 ± 0.005	2.80 ± 0.081	1.11 ± 0.106	
K ₂₇₀ (nm)	0.09 ± 0.002	0.14 ± 0.001	0.46 ± 0.003	3.0877 ± 0.003	0.18 ± 0.007	0.17 ± 0.002	2.68 ± 0.002	3.42 ± 0.002	0.65 ± 0.003	0.20 ± 0.007	
Fatty acid concn (%)	Palmitic	12.27 ± 0.002	12.66 ± 0.002	10.67 ± 0.003	6.93 ± 0.000	14.56 ± 0.001	10.28 ± 0.002	5.78 ± 0.002	19.38 ± 0.002	4.41 ± 0.002	6.44 ± 0.006
	Palmitoleic	1.26 ± 0.002	1.08 ± 0.002	0.92 ± 0.001	0.18 ± 0.181	6.53 ± 0.002	0.03 ± 0.001	0.11 ± 0.002	0.24 ± 0.003	0.29 ± 0.002	0.22 ± 0.005
	Stearic	3.76 ± 0.002	2.27 ± 0.002	3.84 ± 0.001	3.94 ± 0.002	0.44 ± 0.002	3.09 ± 0.002	3.22 ± 0.002	2.17 ± 0.001	2.05 ± 0.002	2.17 ± 0.004
	Oleic	74.58 ± 0.002	72.96 ± 0.002	75.48 ± 0.001	19.57 ± 0.002	66.45 ± 0.001	7.87 ± 7.866	38.51 ± 0.001	41.80 ± 0.002	65.09 ± 0.002	75.49 ± 0.001
	Linoleic	6.51 ± 0.002	9.10 ± 0.002	7.39 ± 0.002	68.38 ± 0.002	10.81 ± 0.002	1.86 ± 0.001	50.39 ± 0.002	32.42 ± 0.003	18.16 ± 0.002	7.01 ± 0.001
	Linolenic	0.70 ± 0.002	0.67 ± 0.002	0.63 ± 0.001	0.35 ± 0.000	0.67 ± 0.001	0.03 ± 0.001	0.43 ± 0.001	1.27 ± 0.002	7.64 ± 0.002	0.14 ± 0.002
	C18:1 T	0.02 ± 0.002	0.02 ± 0.002	0.06 ± 0.002	0.08 ± 0.002	0.04 ± 0.001	0.07 ± 0.002	0.04 ± 0.003	0.11 ± 0.001	0.04 ± 0.002	0.04 ± 0.002
	C18:2 + C18:3 T	0.02 ± 0.002	0.02 ± 0.002	0.09 ± 0.002	1.04 ± 0.002	0.11 ± 0.006	0.07 ± 0.002	0.23 ± 0.001	0.62 ± 0.002	0.41 ± 0.002	0.43 ± 0.001

Table 1: Initial characteristics of unheated oil samples.

Each determination is the mean of three determinations ± standard deviation (SD).

Deterioration products

The major decomposition products of frying oil are non-volatile polar compounds and triacylglycerol dimers and polymers. The amounts of cyclic compounds are relatively low compared to the non-volatile polar compounds, dimers, and polymers. Dimers and polymers are large molecules and some (not all) of those polar components (in particular certain aldehydes, alkyl benzenes and other aromatic hydrocarbons) are known to have a detrimental effect on human health (as they have been consistently associated with various forms of cancer and neurodegenerative diseases such as Alzheimer’s and Parkinson’s Disease) [21,22].

The link between possible unhealthy compounds and effects on health often depends on the dose of the suspected compound. With respect to polar compounds, many legislations around the world have identified that a limit of polar compounds in frying oil of no more than 24 - 27% is typically considered safe [23]. This level will ensure that the level of polar compounds found in the resultant fried food are safe for human consumption. However, if fried foods are stored for a period of time before they are consumed, the level of polar materials must be much less than the 24% endpoint, with recommendations of < 10% polar materials [10].

The determination of the Extinction Coefficient (conventionally indicated by K) in ultraviolet at 232 and 270 nm provides a measurement of primary and secondary phases of oil oxidation, respectively. These methods are based on the ability of conjugated dienes and trienes to absorb UV radiation in specified wave length ranges. Many secondary products of oxidation such as alcohols, ketones, aldehydes, acids can have a detrimental effect on health and/or recombine to produce polar compounds. The fatty acid composition of frying oils has a major effect on the volatile compounds detected in the oil and on the flavour of the fried food. Although frying oils are complex mixtures of triacylglycerols, a wide variety of fatty acids, and many minor constituents, degradation compounds are primarily from the fatty acids [10]. Changes in fatty acid composition are shown in table 2. Although the behaviour was slightly different for each oil and for the type of heating, in general, palmitic (C16:0), stearic (C18:0) and oleic (C18:1) relative’s percentages increased, whereas linoleic (C18:2) and linolenic (C18:3) levels reduced during heating. In GO, oleic acid content increased by 26.83%, linoleic acid decreased by 9.81% and linolenic acid content decreased 66.48% after 360 minutes of heating at 180°C. The changes seen in GO were in general higher when compared with other oils tested, such as EVOO where oleic increased by 0.34%, linoleic acid decreased 11.15% and linolenic acid content did by 22.6%.

Fatty Acid (%)	Heating conditions	EVOO	VOO	OO	AO	GO
Palmitic C16:0	Initial	12.270 ± 0.002	12.658 ± 0.002	10.669 ± 0.003a	14.562 ± 0.001	6.929 ± 0.000
	240°C	12.360 ± 0.002	12.825 ± 0.002	10.855 ± 0.002a	15.325 ± 0.002	7.089 ± 0.002
	360 min	12.702 ± 0.002	12.985 ± 0.002	12.191 ± 0.809	15.911 ± 0.002	7.486 ± 0.002
Palmitoleic C16:1	Initial	1.260 ± 0.002	1.076 ± 0.002a	0.921 ± 0.001a	6.528 ± 0.002	0.181 ± 0.181
	240°C	1.254 ± 0.002	1.076 ± 0.002a	0.948 ± 0.002a	6.328 ± 0.002	0.176 ± 0.002
	360 min	1.265 ± 0.002	1.081 ± 0.002	1.089 ± 0.023	6.782 ± 0.002	0.169 ± 0.002
Stearic C18:0	Initial	3.760 ± 0.002	2.269 ± 0.002	3.837 ± 0.001a	0.444 ± 0.002	3.939 ± 0.002
	240°C	3.793 ± 0.002	2.297 ± 0.002	3.883 ± 0.002a	0.479 ± 0.002	4.016 ± 0.002
	360 min	3.909 ± 0.002	2.347 ± 0.002	2.815 ± 0.947a	0.484 ± 0.002	3.881 ± 0.002
Oleic C18:1	Initial	74.583 ± 0.002	72.963 ± 0.002	75.482 ± 0.001a	66.445 ± 0.001	19.574 ± 0.002
	240°C	74.647 ± 0.002	73.129 ± 0.002	75.818 ± 0.002a	66.823 ± 0.002	20.118 ± 0.002
	360 min	74.837 ± 0.002	73.290 ± 0.002	73.764 ± 1.390a	66.350 ± 0.002	24.826 ± 0.002
Linoleic C18:2	Initial	6.511 ± 0.002	9.101 ± 0.002	7.387 ± 0.002	10.809 ± 0.002	68.381 ± 0.002
	240°C	6.359 ± 0.002	8.779 ± 0.002	6.793 ± 0.002	9.863 ± 0.002	67.400 ± 0.002
	360 min	5.785 ± 0.002	8.395 ± 0.002	6.563 ± 0.053	9.373 ± 0.002	61.672 ± 0.002
Linolenic C18:3	Initial	0.698 ± 0.002	0.667 ± 0.002	0.628 ± 0.001ab	0.666 ± 0.001	0.350 ± 0.000
	240°C	0.665 ± 0.002	0.627 ± 0.002	0.595 ± 0.002 a	0.654 ± 0.002	0.335 ± 0.002
	360 min	0.540 ± 0.002	0.588 ± 0.002	0.648 ± 0.033b	0.572 ± 0.002	0.583 ± 0.002
	Heating conditions	SO	RO	PO	CO	CoO
Palmitic C16:0	Initial	5.776 ± 0.002	19.381 ± 0.002	6.444 ± 0.006	4.411 ± 0.002a	10.277 ± 0.002
	240°C	5.630 ± 0.002	19.664 ± 0.002	6.638 ± 0.002	4.680 ± 0.002a	10.066 ± 0.002
	360 min	5.907 ± 0.002	20.025 ± 0.002	6.729 ± 0.002	4.571 ± 0.002	11.765 ± 1.550
Palmitoleic C16:1	Initial	0.112 ± 0.002 a	0.244 ± 0.003	0.224 ± 0.005a	0.295 ± 0.002a	0.030 ± 0.001
	240°C	0.112 ± 0.002 a	0.254 ± 0.002a	0.229 ± 0.002a	0.303 ± 0.002	0.033 ± 0.002
	360 min	0.127 ± 0.002	0.255 ± 0.002 a	0.225 ± 0.002a	0.293 ± 0.002a	0.730 ± 0.599
Stearic C18:0	Initial	3.220 ± 0.002	2.170 ± 0.001	2.174 ± 0.004	2.050 ± 0.002	3.086 ± 0.002
	240°C	3.209 ± 0.002	2.203 ± 0.002	2.205 ± 0.002	2.177 ± 0.002	3.219 ± 0.002
	360 min	3.343 ± 0.002	2.214 ± 0.002	2.257 ± 0.002	2.118 ± 0.002	2.582 ± 0.543
Oleic C18:1	Initial	38.510 ± 0.001	41.802 ± 0.002	75.490 ± 0.001	65.085 ± 0.002	7.866 ± 7.866
	240°C	39.278 ± 0.002	42.186 ± 0.002	75.820 ± 0.002	67.144 ± 0.002	7.251 ± 0.002
	360 min	39.429 ± 0.002	42.506 ± 0.002	76.113 ± 0.002	65.723 ± 0.002	6.834 ± 0.002
Linoleic C18:2	Initial	50.387 ± 0.002	32.418 ± 0.003	7.012 ± 0.001	18.159 ± 0.002	1.861 ± 0.001
	240°C	49.804 ± 0.002	31.644 ± 0.002	6.604 ± 0.002	16.847 ± 0.002	1.458 ± 0.002
	360 min	49.075 ± 0.002	31.001 ± 0.002	6.604 ± 0.002	17.653 ± 0.002	0.993 ± 0.001
Linolenic C18:3	Initial	0.432 ± 0.001	1.270 ± 0.002	0.136 ± 0.002	7.641 ± 0.002	0.029 ± 0.001
	240°C	0.300 ± 0.002	1.199 ± 0.002	0.127 ± 0.002	6.279 ± 0.002	0.010 ± 0.002
	360min	0.388 ± 0.002	1.155 ± 0.002	0.124 ± 0.002	7.158 ± 0.002	0.071 ± 0.009

Table 2: Changes in the content of Palmitic, Palmitoleic, Stearic, Oleic, Linoleic and Linolenic Acids in Edible Oils when heated in a deep fryer for 360 minutes, and in a pan fryer at 240°C.

Each determination is the mean of three determinations ± standard deviation (SD).

Same letter within a column per acid shows insignificant difference (p < 0.5).

Trans fats levels of initial conditions, after reaching 240°C and after 6 hours of heating at 180°C are shown in figure 1. There is a remarkable difference between initial trans-fat content in refined oils and non-refined oils. Grapeseed showed the highest amount of initial trans-fat content while EVOO and VOO showed the lowest. These results are consistent with the oil production method, as refined oils are bleached and heated during the industrial process, and virgin oils such as EVOO, VOO and avocado (only produced with mechanical processes) maintain a naturally lower level of trans fats.

For most of the oils, the production of trans fat were more pronounced by temperature than prolonged time of heat exposure (Figure 1). The natural oils, such as EVOO, VOO and AO were more affected to elevated temperature, while refined oils were more affected by time of heat exposure at 180°C, except for CO that also was affected by temperature. GO and CO have shown the greatest increment of trans fat after the heat treatments.

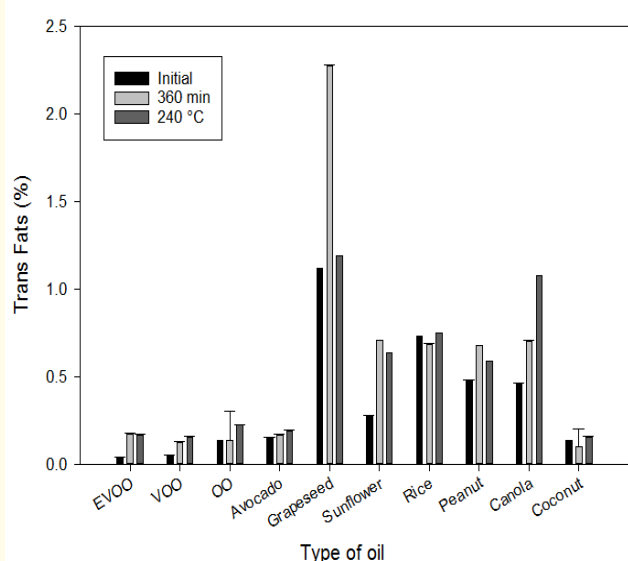


Figure 1: Trans fats levels before and after heating trials.

Effect of time

Figure 2 shows the evolution of polar compounds for oils tested from 0 to 6 hours of heating at 180°C. For all oils tested, the formation of polar compounds tended to increase with time. Higher values, after 6 hours of heating, were obtained in refined seed oils: So (21.75%), grapeseed oil (20.24%), canola oil (17.32%) and rice bran oil (15.66%). The lowest values were obtained in EVOO (10.5%) and coconut oil (9.68%).

An oils stability against oxidation depends not only on the degree of unsaturation, but also on the antioxidant content present in the unsaponifiable fraction [25]. Figure 3 shows oil’s oxidative stability decrement during time of heating at 180°C. PO, OO, SO and AO showed the lowest values after 6 hours of heating. Coconut oil demonstrated high stability at the end of the induction time.

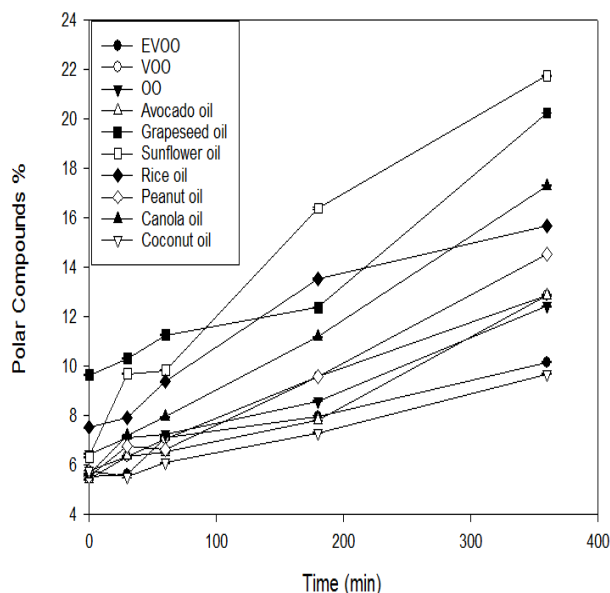


Figure 2: Evolution of Polar compounds while heating oils to 180°C.

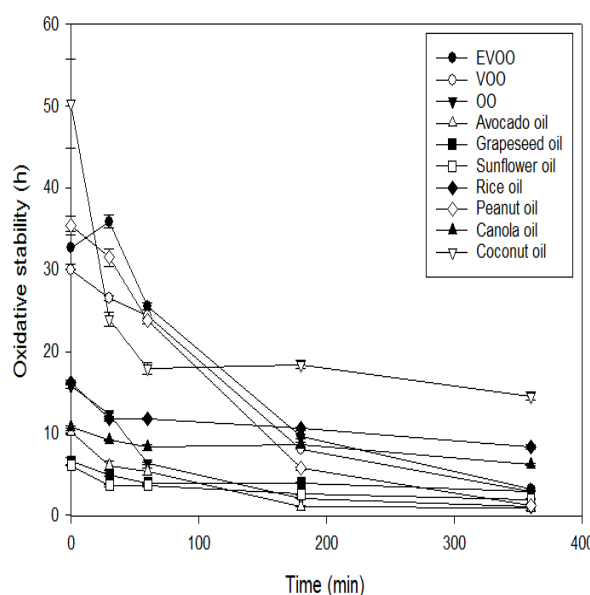


Figure 3: Oxidative stability while heating oils to 180°C.

Figures 4 and 5 show the evolution in K_{232} and K_{270} . As expected, both K_{232} and K_{270} indexes increased during the heating experiment. This increase indicates the formation of conjugated dienes or peroxides and trienes or unsaturated aldehydes and ketones over time. The initial and final values of K_{232} and K_{270} for grapeseed, sunflower and rice bran oil were higher than the rest of the oils tested.

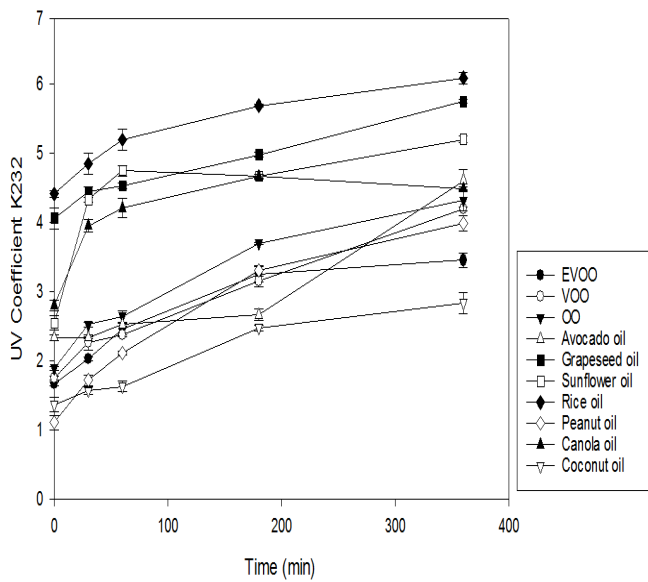


Figure 4: UV coefficient K232 while heating oils to 180°C.

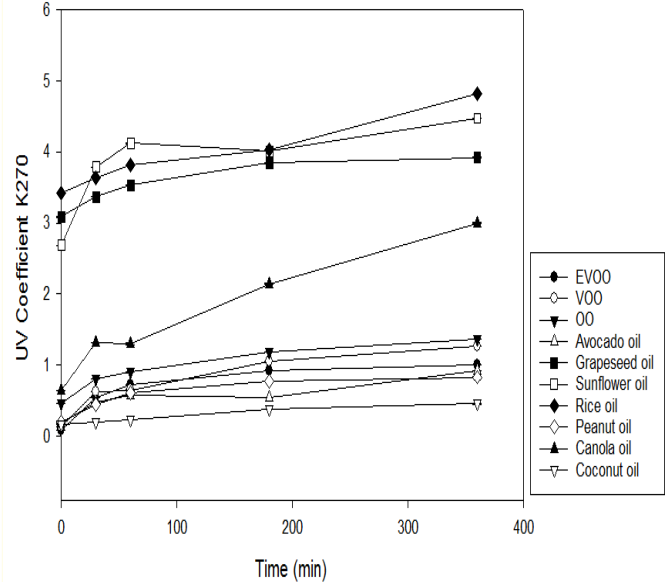


Figure 5: UV coefficient K270 while heating oils to 180°C.

The level of the FFA is a measure of the degree of hydrolysis in the oil. In this study FFA levels slowly increased during the thermal treatment over time. After 30 minutes of heating (Table 3), a slight increase was observed. Despite the temperature of the treatment

(180°C) being lower than some oil’s smoke points, most of the oils, after 360 minutes of deep heating experienced a significant rise of the level of FFA from the initial measure.

Changes in FFA % during heating at different times at 180°C										
Heating time (min)	EVOO	VOO	OO	GO	AO	CoO	SO	RO	CO	PO
0	0.17 ± 0.01a	1.24 ± 0.06a	0.27 ± 0.01	0.06 ± 0.01	0.38 ± 0.00	0.13 ± 0.00	0.08 ± 0.01a	0.23 ± 0.02	0.07 ± 0.01a	0.12 ± 0.01
30	0.17 ± 0.01ab	1.30 ± 0.03a	0.28 ± 0.00	0.11 ± 0.01a	0.45 ± 0.01a	0.18 ± 0.00	0.08 ± 0.00a	0.36 ± 0.00abc	0.08 ± 0.00ab	0.15 ± 0.01a
60	0.18 ± 0.01b	1.28 ± 0.02a	0.28 ± 0.00	0.10 ± 0.00a	0.45 ± 0.01a	0.19 ± 0.00	0.08 ± 0.00	0.34 ± 0.01bc	0.08 ± 0.00ab	0.15 ± 0.01a
180	0.19 ± 0.01	1.28 ± 0.02a	0.30 ± 0.00	0.11 ± 0.00a	0.45 ± 0.01a	0.24 ± 0.00	0.09 ± 0.00	0.38 ± 0.00b	0.09 ± 0.00b	0.16 ± 0.00
360	0.23 ± 0.01	1.31 ± 0.02a	0.32 ± 0.01	0.13 ± 0.00	0.45 ± 0.01a	0.36 ± 0.01	0.11 ± 0.01	0.35 ± 0.01c	0.11 ± 0.00	0.21 ± 0.00
Changes in FFA % during heating at different temperatures										
Heating tempereure (°C)	EVOO	VOO	OO	GO	AO	CoO	SO	RO	CO	PO
25	0.17 ± 0.01a	1.24 ± 0.06a	0.27 ± 0.00	0.06 ± 0.01a	0.38 ± 0.00	0.13 ± 0.00	0.08 ± 0.01a	0.23 ± 0.02	0.07 ± 0.01a	0.12 ± 0.00a
150	0.18 ± 0.00b	1.24 ± 0.02a	0.27 ± 0.00a	0.05 ± 0.00a	0.40 ± 0.01a	0.16 ± 0.00a	0.05 ± 0.01b	0.30 ± 0.00ab	0.06 ± 0.00b	0.13 ± 0.00ab
180	0.17 ± 0.00ac	1.28 ± 0.01a	0.28 ± 0.00ab	0.07 ± 0.01ab	0.41 ± 0.01ab	0.15 ± 0.00b	0.04 ± 0.01b	0.31 ± 0.00ac	0.06 ± 0.00ab	0.14 ± 0.00bc
210	0.17 ± 0.00c	1.24 ± 0.02a	0.28 ± 0.00b	0.08 ± 0.01bc	0.42 ± 0.01b	0.14 ± 0.00	0.05 ± 0.00bc	0.33 ± 0.00bc	0.10 ± 0.00	0.14 ± 0.01bc
240	0.17 ± 0.01bc	1.24 ± 0.06a	0.28 ± 0.00ab	0.09 ± 0.01c	0.45 ± 0.01	0.15 ± 0.00ab	0.06 ± 0.01ac	0.34 ± 0.00c	0.13 ± 0.00	0.15 ± 0.00c

Table 3: Changes in FFA %.

Each determination is the mean of three determinations ± standard deviation (SD).

Same letter within a column shows insignificant difference (p < 0.5).

Effect of temperature

Temperature is the most important factor to be considered in evaluating the oxidative stability of fats, especially unsaturated fats, because the mechanism of oxidation changes with temperature, and different hydroperoxides of linoleate, acting as precursors of volatile flavours, decompose at different temperatures. Furthermore, as the rate of oxidation is exponentially related to the temperature, the shelf life of a food lipid decreases logarithmically with increasing temperature [26]. An increment in frying temperature increases thermal oxidation and oligomerization reactions, not only of the fatty acids or triacylglycerol molecules, but also of the unsaponifiable minor components. Thus, antioxidant minor components in oil are either thermally inactivated during frying or have their levels severely reduced [27-30]. Canola oil demonstrated a rapid increase in polar compounds from 150°C to 240°C (Figure 6), with its highest value of polar compounds (27,5%) above the limits permitted for human consumption, followed by grapeseed (19,3%) and rice bran (13,0%) oils.

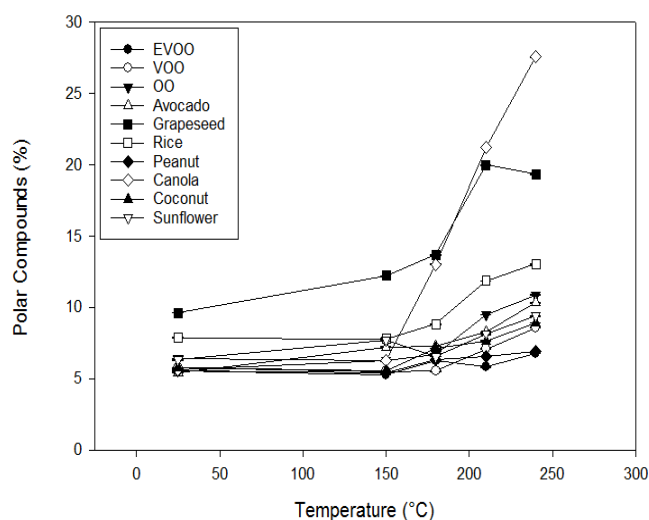


Figure 6: Evolution of Polar Compounds when heating oils at different temperatures.

The various reactions threatening oxidative stability of an oil require some energy to proceed. For instance, 50 Kcal/mol of energy is required to break the carbon-hydrogen bond on the carbon 11 of linoleic acid, and to initiate free radical formation [31]. The oxygen-oxygen bond of alkyl hydroperoxide requires 44 Kcal/mol to be broken [32]. This energy requirement is clearly fulfilled at the temperature employed during frying. Apart from accelerating the initiation step of oxidative degradation, elevated temperature enhances thermal degradation of alkyl hydroperoxides, the primary oxidation product. Consequently, oxidative degradation proceeds more rapidly during high temperatures than at room temperature [33]. The activation energy of lipid oxidation is higher in the presence of antioxidants, because antioxidants lower the rates of oxidation by increasing the overall energy of activation [26]. EVOO showed remarkable stability when heated at high temperatures, as determined by the Rancimat method (Figure 7). EVOO not only has

a more stable composition of fatty acids under such conditions, but also contains polyphenols which act by reacting rapidly with lipid radicals and are thereby consumed [34,35]. Peanut oil, with high oleic acid content showed a similar behaviour than EVOO. Avocado showed lower induction time values than EVOO. Seed oils, such as canola, grapeseed, sunflower and rice bran oils showed lower oxidation stability. These results are related to seed oils' fatty acid composition with higher PUFAs content, such as linoleic and linolenic acid and lower levels of natural antioxidants.

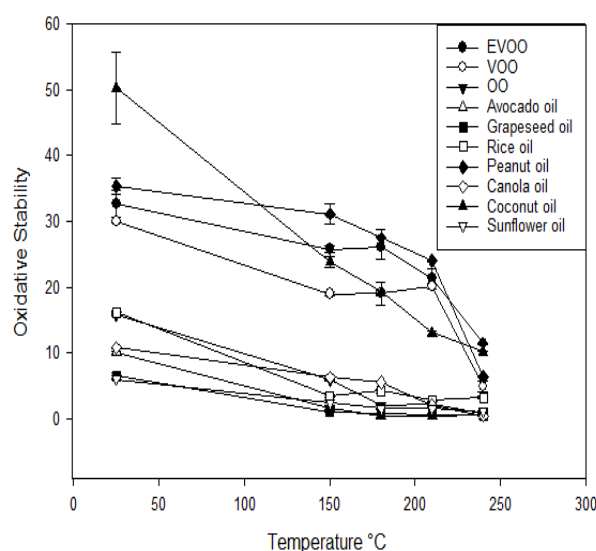


Figure 7: Oxidative stability when heating at different temperatures.

The effect of temperature on isomerisation reactions has also been reported. Moreno, *et al.* [36] utilized FTIR spectroscopy to monitor the formation of trans isomers while heating olive oil, sunflower oil, corn oil, and lard over a wide temperature range of 80 - 300°C. Their results showed that the amount of trans isomers consistently increased as a function of temperature irrespective of the type of oil.

Figures 8 and 9 show the evolution of K_{232} and K_{270} while increasing temperature. Both indexes (K_{232} and K_{270}) while increasing temperature have shown an increase during the heating experiment. As previously mentioned, a rise in these parameters indicates the formation of conjugated dienes, trienes or unsaturated aldehydes, and ketones over time. Seed oils showed higher values than the other oils tested when heated.

Despite the increasing temperature of treatment, FFA percentage did not change significantly for most of edible oil tested (Table 3). In some cases, the temperature reached was higher than the oil's smoke point. This was certainly the case for oils that had a low smoke point, such as VOO, avocado and coconut oil. As this experiment proceeded quickly and without repeated use of the oil, it is likely that the time of exposure at the selected temperatures was not sufficient to produce the expected hydrolytic breakdown. However, CO presented an increased in the levels of FFA after reaching 240°C.

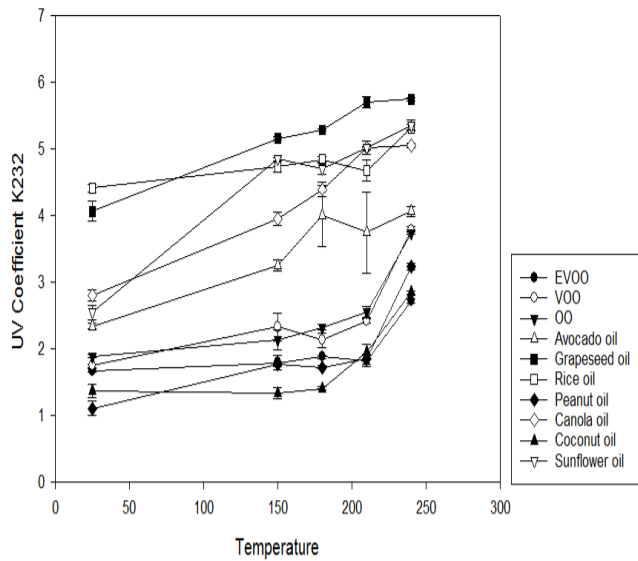


Figure 8: Evolution of K232 when heating oils at different temperatures

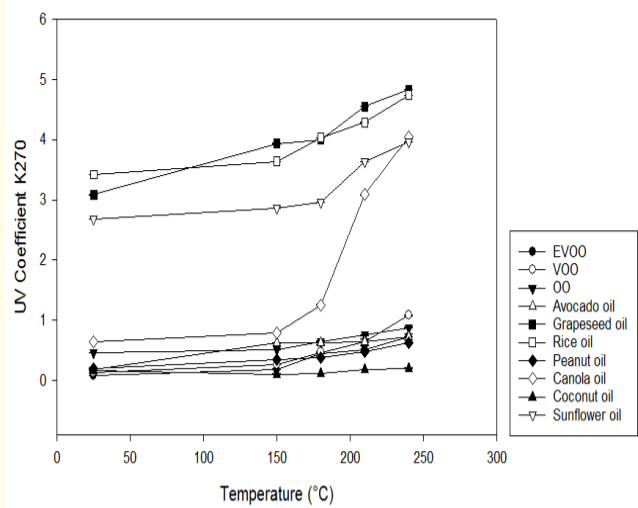


Figure 9: Evolution of K270 when heating oils at different temperatures

Impact of heating trials on smoke point

Smoke point is the temperature at which an oil begins to smoke continuously and can be seen as bluish smoke [13]. This smoke is an indication of chemical breakdown of the fat to glycerol and FFAs. The glycerol is then further broken down to acrolein (2-propenal), which is one of the main components of the bluish smoke. This point is greatly dependent on the content of FFA and to a lesser degree on partial glycerides. The influence of degree of unsaturation is minimal but chain length has an important effect; oils containing short chain fatty acids (e.g. lauric acid) have lower smoke point than oils with predominantly longer chain fatty acids [37]. All the oils yielded a reduction in their smoke point values after both

thermal treatments, and this is consistent with the increase in FFA percentage (Table 3). However, as shown in table 4, for most of the oils, the change in their smoke point was bigger after 360 minutes of heating at 180°C than after reaching 240°C in a short period of time. This is also consistent with changes in FFA % for each oil. In some oils, such as CO, PO and CoO their smoke point decreased more after heating at 240°C, and their respective FFA % presented similar behaviour. It seems that natural oils, such as OO grades and AO are particularly resistant to high temperatures. Despite EVOO’s smoke point being more susceptible to the time of exposure than temperature, it did not suffer abrupt changes and its final smoke point at the end of both treatments was on average 191.6°C, while VOO and AO after 30 minutes of heating suffered big changes in their smoke points.

Changes in Oil’s smoke Point during heating at different times at 180										
Heating time (min)	EVOO	VOO	OO	GO	AO	CoO	SO	RO	CO	PO
0	206.7 ± 2.5	175.3 ± 0.6	208.3 ± 1.5	268.0 ± 1.0	196.7 ± 0.6	191.0 ± 3.6	254.7 ± 1.5	237.0 ± 1.7	255.7 ± 0.6	226.3 ± 2.1
30	193.9 ± 0.5	137.5 ± 0.9a	189.1 ± 0.1a	222.0 ± 0.5a	151.0 ± 0.5	197.8 ± 1.1	219.0 ± 1.0ab	217.7 ± 0.8a	244.1 ± 0.1	215.7 ± 0.3a
60	189.5 ± 0.1a	137.3 ± 0.5a	189.5 ± 0.5a	222.2 ± 0.0a	149.5 ± 1.0ab	181.0 ± 1.0a	220.0 ± 0.0a	215.2 ± 1.0a	240.5 ± 0.0	214.5 ± 1.0a
180	189.8 ± 0.8a	136 ± 0.0a	189.5 ± 0.0a	222.5 ± 0.0a	148.6 ± 0.3b	178.0 ± 0.0a	217.2 ± 0.3b	195.8 ± 0.4b	232.1 ± 0.9	214.1 ± 0.3a
360	184.7 ± 1.6	133.5 ± 1.0	188.6 ± 0.8a	221.7 ± 0.8a	148.5 ± 0.9b	172.0 ± 1.0	215.0 ± 1.0b	195.5 ± 0.0b	223.6 ± 1.0	215.0 ± 1.0a
Changes in Oil’s smoke Point during heating at different temperatures										
Heating temperature (°C)	EVOO	VOO	OO	GO	AO	CoO	SO	RO	CO	PO
25	206.7 ± 2.5a	175.3 ± 0.6	208.3 ± 1.5	268.0 ± 1.0	196.7 ± 0.6	191.0 ± 3.6	254.7 ± 1.5	237.0 ± 1.7	255.7 ± 0.6	226.3 ± 2.1
150	207.0 ± 1.0a	163.0 ± 1.0	187.0 ± 1.0a	252.0 ± 1.0	187.0 ± 1.0	150.0 ± 1.0a	235.0 ± 1.0a	221.0 ± 1.0a	229.0 ± 1.0a	218.0 ± 1.0
180	205.5 ± 0.0a	168.3 ± 0.3a	187.0 ± 1.0ab	226.0 ± 1.0	176.0 ± 1.0	150.0 ± 1.0a	234.0 ± 1.0a	220.0 ± 1.0a	228.0 ± 1.0a	208.0 ± 1.0
210	207.5 ± 1.0a	168.5 ± 1.0a	190.0 ± 1.0b	226.0 ± 1.0c	164.0 ± 1.0a	156.0 ± 1.0b	228.0 ± 1.0b	212.0 ± 1.0b	228.0 ± 1.0a	204.0 ± 1.0
240	198.5 ± 0.9	168.5 ± 1.0a	178.0 ± 1.0	226.0 ± 1.0	165.0 ± 1.0a	156.0 ± 1.0b	230.0 ± 1.0b	211.0 ± 1.0b	215.0 ± 1.0	197.0 ± 1.0

Table 4: Changes in Oil’s Smoke Point (°C).

Each determination is the mean of three determinations ± standard deviation (SD).

Same letter within a column shows insignificant difference (p < 0.5).

Table 5 ranks oils based on their average level of final polar compounds at the end of both trials. EVOO ranked first, followed by coconut oil. Analysing the correlation between this score and oil chemical analysis, it would appear as if an oil's smoke point is not a relevant parameter to explain the oil's behaviour when heated, as it showed a positive correlation with the increase in polar compounds. This shows that the higher the smoke point, the more polar

compounds that are produced. PUFAs, K_{232} and K_{270} showed a positive correlation with polar compounds. K_{232} and K_{270} initial values were higher for refined seed oils such as grapeseed and rice bran oil. Oxidative stability was negatively correlated with final content of polar compounds, demonstrating that a non-stable oil, in terms of thermal degradation, will produce more polar compounds when heated.

Oil type	Final Polar Compounds (%)	Smoke Point (°C)	Oxidative Stability (h)	Free Fatty Acids (%)	PUFAs (%)	K232 (nm)	K270 (nm)
Extra Virgin Olive Oil	8.47 ± 1.841	206.67 ± 2.520	32.70 ± 2.020	0.17 ± 0.006	7.21 ± 0.003	1.67 ± 0.026	0.09 ± 0.002
Virgin Olive Oil	10.71 ± 2.337	175.33 ± 0.577	30.00 ± 0.100	1.24 ± 0.060	9.77 ± 0.003	1.75 ± 0.027	0.14 ± 0.001
Olive Oil	11.65 ± 0.836	208.00 ± 1.530	15.98 ± 0.289	0.27 ± 0.006	8.02 ± 0.002	1.89 ± 0.030	0.46 ± 0.003
Grapeseed Oil	19.79 ± 0.502	268.00 ± 1.000	6.56 ± 0.490	0.06 ± 0.010	68.73 ± 0.000	4.06 ± 0.153	3.09 ± 0.003
Avocado Oil	11.60 ± 1.401	196.67 ± 0.577	10.17 ± 0.208	0.38 ± 0.000	11.48 ± 0.003	2.34 ± 0.040	0.18 ± 0.007
Coconut Oil	9.30 ± 0.415	191.00 ± 3.610	50.27 ± 5.460	0.13 ± 0.000	1.89 ± 0.002	1.37 ± 0.106	0.17 ± 0.002
Sunflower Oil	15.57 ± 6.770	254.67 ± 1.530	6.10 ± 0.100	0.08 ± 0.006	50.82 ± 0.002	2.54 ± 0.106	2.68 ± 0.002
Rice Bran Oil	14.35 ± 1.433	237.00 ± 1.730	16.17 ± 0.29	0.23 ± 0.017	33.69 ± 0.002	4.41 ± 0.052	3.42 ± 0.002
Peanut Oil	10.71 ± 4.159	226.33 ± 2.080	35.37 ± 1.170	0.12 ± 0.006	7.15 ± 0.001	1.11 ± 0.106	0.20 ± 0.007
Canola Oil	22.43 ± 5.609	255.67 ± 0.577	10.83 ± 0.153	0.07 ± 0.010	25.80 ± 0.003	2.80 ± 0.081	0.65 ± 0.003
Correlation	100%	83%	-65%	-34%	74%	80%	54%

Table 5: Correlation Between Final Polar Compounds After Heating and Initial Oil Parameters.

Conclusion

From this study, it can be concluded that, under different heating conditions, the generation of polar compounds with temperature and time was more pronounced for refined seed oils with higher initial values of smoke point, PUFAs, K_{232} and K_{270} . It is important to note that the experiments were carried out without food being cooked. While cooking, the water and steam which comes from the food being cooked aids the process of hydrolysis. The absence of food in these trials may have allowed for a greater impact of oil oxidation when compared with other deterioration reactions.

Reasonable predictors of how an oil will perform when heated have been oxidative stability, secondary products of oxidation, and total level of PUFAs. EVOO has demonstrated to be the most stable oil when heated, followed closely by coconut oil and other virgin oils such as avocado and high oleic acid seed oils.

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