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Comparison of the Frying Performance of High Oleic Oils Subjected to Discontinuous and Prolonged Thermal Treatment

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Abstract Frying is a popular practice because of its unique sensory characteristics and low cost. The high temperature reached with this cooking method alters molecules present in the oil. The deterioration of the oil depends primarily on its chemical composition. The aim of this study was to evaluate the thermal stability of high oleic sunflower oil (HOSO), sunflower oil (SO) and mixed oil (MIX) during deep frying of French fries. Octanoic acid and unsaturated fatty acid (UFA)/saturated fatty acid (SFA) ratio showed a good correlation with total polar compounds (TPC) for all frying samples analyzed. HOSO and MIX were characterized by reduced levels of thermal degradation, while SO resulted in the highest values of oxidation products (highest TPC values). SO was also the oil more retained by the food matrix, whereas MIX was the least absorbed. HOSO and MIX, having a high oleic acid content (77.58 and 59.92 %, respectively) and a low linoleic acid content (13.42 and 25.70 %, respectively), showed the best characteristics for the frying process.

Keywords Deep frying · High oleic sunflower oil · Sunflower oil · Total polar compounds · Hydroperoxides · Volatile organic compounds · Oleic acid · Linoleic acid

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Introduction

Frying is a popular method of cooking food. Frying oils transfer heat to cook foods and produce the characteristic flavor of fried food. During this treatment, undesirable reactions occur, forming numerous volatile and non-volatile compounds (fatty acids, aldehydes, and polar compounds) [1]. Many factors affect the deterioration of a frying oil, such as the presence of unsaturated fatty acids, the oil temperature, oxygen absorption, the presence of metals, and the type of food [2]. The amounts and chemical structures of the compounds that are formed depend on the type of oil and food, the frying conditions, and the oxygen availability [3]. High temperature, oxygen and water cause alterations that affect oil quality [4]. These reactions lead to the polymerization and homolytic β-scission of hydroperoxides. Oxidation is a significant problem because it results in the development of rancid flavors and in the formation of substances that can be harmful for human health. Hydroperoxides are the primary oxidation products [5], and in fact they decompose to form dimers and volatile compounds during heat treatment [6].

The amount of total polar compounds (TPC) is the parameter used to evaluate the degree of oil degradation. Its limit has been established by legislation to be 25/100 g oil. Oils suitable for frying need to have a low polyunsaturated acid content [7].

The aim of this study was to evaluate and compare the effects of discontinuous and prolonged thermal treatment (typical of restaurants and fast food restaurants) on three oils with different monounsaturated/saturated fatty acid (MUFA/SFA) ratios, and to propose new markers to establish the degree of alteration of frying oils because the official method (determination of TPC) has several disadvantages [8].

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Materials and Methods

Materials and Frying Protocol

Sunflower oil (SO), mixed oil (MIX) composed of rapeseed oil (60 %), sunflower oil (38 %), and grape seed oil (2 %), high oleic sunflower oil (HOSO) and frozen French fries were obtained from Italian markets. The frying process was carried out according to the procedure described in [9].

Analytical Methods

Thermo-oxidized oils, frying oils and fat extracted from the French fries [9] were subjected to the following determinations: free fatty acids (FFA), peroxide value (PV), fatty acids (FA), TPC, and volatile organic compounds (VOCs), as described by Romano, Giordano, Vitiello, Le Grottaglie and Spagna Musso [9]; water activity was measured using Aqualab, Series 4 (Steroglass), that is able to measure this with high precision (±0.003 Aw) in less than 5 min.

All determinations and experiments were performed in triplicate and the presented results are the average values of three determinations. Data were subjected to analysis of variance (ANOVA) (XLSTAT 2006; ADDINSOFT, Paris, France). Differences at $P \leq 0.05$ were considered significant.

Results and Discussion

Yield Extraction

Oil absorption is related to the quality of the oil. During heat treatment, the polarity [10] and the amount of oil on the food surface increase [11]. As shown in Fig. 1, in all three oils, there was an increase in the amount of oil absorbed during heat treatment. The extraction yield of fat from the potatoes showed that more oil was retained by the food matrix after frying in SO, whereas MIX oil was the least absorbed. In fact, at the end of the thermal treatment, the absorption of SO was 192 % higher than that of the samples at time 0, but the absorption was only 128 % higher for the MIX samples. The HOSO sample had an intermediate value of 151 %.

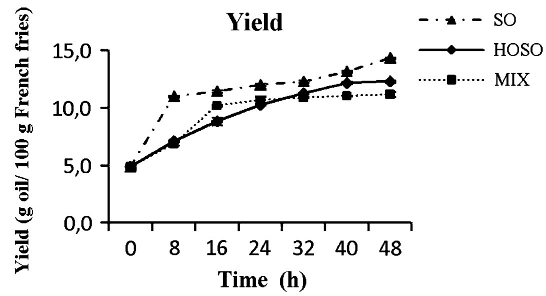

Fig. 1 Extraction yield from French fries during frying

Free Acidity, Peroxide Value and Total Polar Compounds

FFA

The FFA level is a measure of the degree of hydrolysis in the oil [12, 13].

The FFA values for the three oils analyzed are shown in Table 1. The FFA content increased during the heat treatment for each sample. Generally, for all three oils, the fried samples showed higher FFA levels than did the thermo-oxidized oils, because the food releases water in the bath oil. The FFA levels found in frying HOSO and frying MIX showed good correlations with the TPC ($R^2 = 0.92$ and 0.86, respectively).

PV

The PV values are reported in Table 2. Fresh SO showed the highest PV value (3.14 meq O_2/kg of oil) in comparison to the other fresh experimental oils. At the end of the thermal treatment, the thermo-oxidized HOSO exhibited the highest PV value (9.16 meq O_2/kg oil), indicating that the hydroperoxides accumulated in the food matrix and were then transformed more slowly into secondary oxidation compounds. This result

Table 1 FFA trends in HOSO, SO and MIX at different treatment times

Time (h)	FFA (% oleic acid)								
	HOSO			SO			MIX		
	T	F	FF	T	F	FF	T	F	FF
0	$0.28^b \pm 0.02$	$0.28^b \pm 0.00$	$0.32^c \pm 0.05$	$0.55^c \pm 0.01$	$0.55^b \pm 0.00$	$0.32^d \pm 0.02$	$0.24^c \pm 0.01$	$0.24^b \pm 0.09$	$0.32^d \pm 0.02$
16	$0.49^b \pm 0.09$	$0.47^b \pm 0.11$	$0.58^b \pm 0.07$	$0.56^c \pm 0.02$	$0.69^b \pm 0.00$	$0.86^c \pm 0.01$	$0.52^b \pm 0.03$	$0.61^a \pm 0.10$	$0.82^c \pm 0.04$
32	$0.83^a \pm 0.07$	$0.99^a \pm 0.14$	$1.03^a \pm 0.15$	$0.7^b \pm 0.06$	$1.02^a \pm 0.09$	$1.15^b \pm 0.02$	$0.76^a \pm 0.02$	$0.74^a \pm 0.07$	$1.03^b \pm 0.05$
48	$1.06^a \pm 0.08$	$1.08^a \pm 0.11$	$1.16^a \pm 0.11$	$0.84^a \pm 0.02$	$1.11^a \pm 0.00$	$1.44^a \pm 0.01$	$0.77^a \pm 0.09$	$0.78^a \pm 0.10$	$1.3^a \pm 0.04$

FFA free fatty acid, *HOSO* high oleic sunflower oil, *SO* sunflower oil, *MIX* mixed oil, *T* thermo-oxidized oil, *F* frying oil, *FF* French fry fat

Different superscript letters in the same column correspond to statistically significant differences ($P \leq 0.05$) for the same oil between treatment times

Table 2 PV trend in HOSO, SO and MIX at different treatment times

PV (mEq O_2/Kg oil)									
Time (h)	HOSO			SO			MIX		
	T	F	FF	T	F	FF	T	F	FF
0	$2.20^{e} \pm 0.09$	$2.20^{g} \pm 0.03$	$5.30^{f} \pm 0.11$	$3.14^{f} \pm 0.02$	$3.14^{a} \pm 0.04$	$5.30^{e} \pm 0.01$	$0.64^{d} \pm 0.05$	$0.64^{f} \pm 0.03$	$5.30^{f} \pm 0.04$
8	$2.45^{e} \pm 0.04$	$3.00^{f} \pm 0.04$	$13.17^{e} \pm 0.13$	$5.03^{e} \pm 0.01$	$2.38^{b} \pm 0.03$	$21.32^{d} \pm 0.02$	$0.59^{d} \pm 0.07$	$5.23^{d} \pm 0.03$	$5.44^{f} \pm 0.01$
16	$4.85^{d} \pm 0.11$	$3.50^{e} \pm 0.02$	$13.23^{e} \pm 0.10$	$5.34^{c} \pm 0.03$	$2.26^{c} \pm 0.00$	$22.16^{b} \pm 0.03$	$1.40^{b} \pm 0.08$	$5.71^{c} \pm 0.06$	$32.50^{a} \pm 0.03$
24	$5.50^{c} \pm 0.10$	$4.84^{d} \pm 0.11$	$18.96^{c} \pm 0.09$	$6.23^{b} \pm 0.02$	$1.41^{e} \pm 0.01$	$22.60^{a} \pm 0.01$	$0.95^{c} \pm 0.04$	$7.76^{a} \pm 0.09$	$26.60^{c} \pm 0.03$
32	$8.41^{a,b} \pm 0.12$	$5.50^{c} \pm 0.10$	$22.00^{b} \pm 0.07$	$6.29^{b} \pm 0.04$	$0.95^{f} \pm 0.02$	$22.60^{a} \pm 0.02$	$1.94^{a} \pm 0.03$	$7.92^{a} \pm 0.06$	$31.60^{b} \pm 0.05$
40	$8.50^{b} \pm 0.07$	$6.94^{b} \pm 0.04$	$15.50^{d} \pm 0.04$	$5.15^{d} \pm 0.02$	$0.95^{f} \pm 0.05$	$22.60^{a} \pm 0.01$	$1.96^{a} \pm 0.02$	$6.31^{b} \pm 0.08$	$15.50^{e} \pm 0.05$
48	$9.16^{a} \pm 0.09$	$7.98^{a} \pm 0.03$	$32.00^{a} \pm 0.03$	$6.74^{a} \pm 0.01$	$1.70^{d} \pm 0.00$	$21.73^{c} \pm 0.00$	$2.00^{a} \pm 0.01$	$5.00^{e} \pm 0.03$	$18.90^{d} \pm 0.04$

PV peroxide value, *HOSO* high oleic sunflower oil, *SO* sunflower oil, *MIX* mixed oil, *T* thermo-oxidized oil, *F* frying oil, *FF* French fry fat

Different superscript letters in the same column correspond to statistically significant differences ($P \leq 0.05$) for the same oil between treatment times

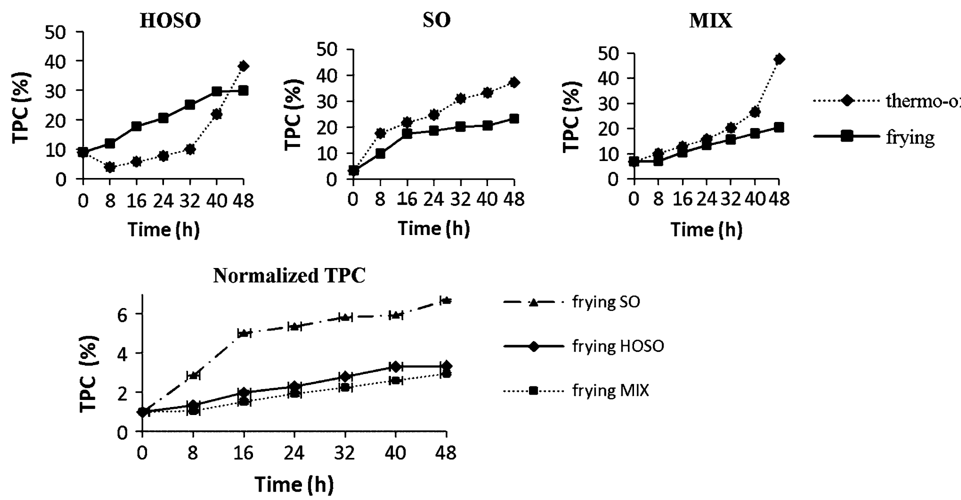

Fig. 2 TPC trends in HOSO, SO and MIX samples (thermo-oxidized and frying) at different treatment times and normalized TPC values for frying oils

correlates with the fact that TPC value slowly increased, especially during the first 32 h of treatment (Fig. 2). The PV value for the MIX samples showed a variable trend during the heat treatment. The degradation rate of the thermo-oxidized oils is faster than that of the frying oils because water plays a protective role [14], preventing the contact between oxygen and the oil [8, 15]. The legal limit (20 meq O_2/kg of oil) was exceeded only for the HOSO and SO extracted from the French fries after 40 h of treatment and before 8 h of treatment, respectively. The MIX extracted from the French fries did not exceed the legal limit.

TPC

Because hydroperoxides are unstable products, the measurement of the polar materials is considered the most important test for assessing the degradation level of an oil. Many researchers, including Fritch [16], have reported that the analysis of the percentage of polar compounds is the main indicator of oil degradation. The maximum level of TPC in many countries is 25 %. As shown in Fig. 2, the TPC of all samples increased as the heat treatment progressed.

Frying HOSO exceeded the maximum limit (25 %) at 32 h of treatment, whereas the thermo-oxidized oil exceeded this limit after 40 h of treatment, reaching a value of 38.3 at 48 h. The thermo-oxidized SO nearly reached the legal limit after only 24 h of treatment, although the fresh oil had a lower TPC value than did HOSO. Among the three tested frying oils, SO showed the highest increase in TPC value, while MIX showed the lowest increase. In fact, a principal component analysis (PCA) of the normalized FFA and TPC values (Fig. 3) showed that, for the SO samples, the TPC increased during the heat treatment due to the rapid transformation of SO free fatty acids into secondary compounds; however, for the HOSO and MIX samples, an accumulation of free fatty acids was observed.

Fatty acid composition

Tables 3, 4, and 5 show the FA composition of the frying and thermo-oxidized oils at different times for HOSO, SO and MIX, respectively.

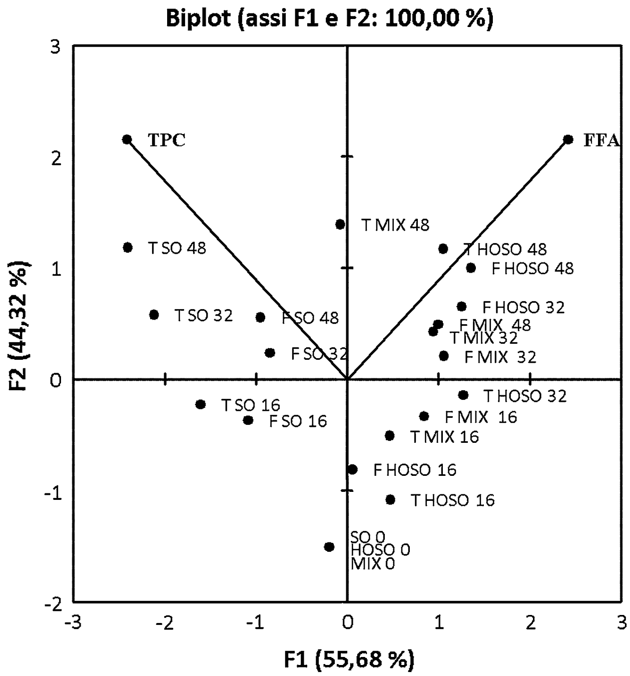

Fig. 3 PCA of FFA and TPC for thermo-oxidized (*T*) and frying (*F*) HOSO, SO and MIX samples at different treatment times

The main FAs detected in the three fresh oils were the following: 3.61 % palmitic acid (C16:0), 77.58 % oleic acid (C18:1), 2.9 % stearic acid (C18:0), 13.42 % linoleic acid (C18:2) and 0.34 % linolenic acid (C18:3) for HOSO; 5.53 % palmitic acid, 3.10 % stearic acid, 31.62 % oleic acid and 58.49 % linoleic acid for SO; 5 % palmitic acid, 2.41 % stearic acid, 59.92 % oleic acid, 25.70 % linoleic acid and 4.43 % linolenic acid for MIX.

Short-chain fatty acids, such as octanoic acid, can be good indicators of the degree of oxidative deterioration of frying oils due to their stability [17]. C8:0 was absent in fresh oil. During the frying process, the amount of C8:0 reached a value of 0.24 % in HOSO, 0.22 % in SO, and 0.18 % in MIX. Octanoic acid showed a good correlation with the TPC, with R^2 values of 0.91, 0.95 and 0.94 for frying HOSO, SO and MIX, respectively, while this fatty acid did not show a good correlation with the TPC for any thermo-oxidized sample.

In fresh oils, small amounts of Trans fatty acids (TFA) were found (0.03 % in HOSO, 0.32 % in SO and 0.02 % in MIX). In particular, C18:1 n9 trans showed a significant ($P < 0.05$) increase during both the frying process and the thermo-oxidation process for all samples except frying SO

Table 3 Fatty acid composition (%) of HOSO (thermo-oxidized and frying oil) at different treatment times

High oleic sunflower oil							
Thermo-oxidized oil							
FAME (%)	0	8	16	24	32	40	48
C8:0	–	$0.07^{c} \pm 0.02$	$0.11^{b,c} \pm 0.00$	$0.06^{c} \pm 0.03$	$0.26^{a,b} \pm 0.03$	$0.35^{a} \pm 0.11$	$0.34^{a} \pm 0.00$
C14:0	0.06 ± 0.02	0.04 ± 0.00	0.04 ± 0.00	0.07 ± 0.01	0.06 ± 0.03	0.10 ± 0.07	0.06 ± 0.01
C15:0	–	0.05 ± 0.05	0.02 ± 0.00	0.01 ± 0.01	0.01 ± 0.01	–	0.02 ± 0.01
C16:0	$3.61^{d} \pm 0.04$	$3.76^{d} \pm 0.01$	$3.92^{b,c,d} \pm 0.01$	$3.76^{c,d} \pm 0.01$	$4.28^{a,b,c} \pm 0.15$	$4.48^{a} \pm 0.34$	$4.45^{a,b} \pm 0.00$
C16:1	0.11 ± 0.01	0.09 ± 0.02	0.10 ± 0.01	0.10 ± 0.01	0.09 ± 0.01	0.16 ± 0.09	0.11 ± 0.01
C17:0	0.04 ± 0.01	0.10 ± 0.10	0.04 ± 0.00	0.04 ± 0.01	0.05 ± 0.02	0.09 ± 0.05	0.05 ± 0.00
C17:1	0.04 ± 0.00	0.07 ± 0.05	0.06 ± 0.02	0.05 ± 0.00	0.03 ± 0.00	0.02 ± 0.02	0.06 ± 0.01
C18:0	$2.90^{b} \pm 0.04$	$2.94^{b} \pm 0.11$	$3.18^{a,b} \pm 0.00$	$2.98^{b} \pm 0.08$	$3.21^{a,b} \pm 0.26$	$3.34^{a,b} \pm 0.25$	$3.59^{a} \pm 0.02$
C18:1t	$0.03^{b} \pm 0.04$	$0.22^{b} \pm 0.00$	$0.30^{b} \pm 0.13$	$0.28^{b} \pm 0.02$	$0.95^{a} \pm 0.22$	$1.21^{a} \pm 0.29$	$1.33^{a} \pm 0.05$
C18:1c	$77.58^{a,b} \pm 0.11$	$77.95^{a,b} \pm 0.34$	$78.29^{a} \pm 0.03$	$78.31^{a} \pm 0.39$	$77.87^{a,b} \pm 0.36$	$77.29^{a,b} \pm 0.34$	$76.88^{b} \pm 0.10$
C18:2t	–	$0.01^{a} \pm 0.02$	$0.03^{a} \pm 0.01$	$0.00^{a} \pm 0.00$	$0.25^{a} \pm 0.33$	$0.23^{a} \pm 0.33$	$0.03^{a} \pm 0.01$
C18:2c	$13.42^{a} \pm 0.02$	$11.59^{b} \pm 0.19$	$9.91^{c} \pm 0.02$	$10.01^{c} \pm 0.49$	$7.32^{d} \pm 0.16$	$6.26^{e} \pm 0.09$	$5.96^{e} \pm 0.09$
C20:0	0.25 ± 0.02	0.42 ± 0.24	0.28 ± 0.00	0.27 ± 0.01	0.25 ± 0.07	0.27 ± 0.07	0.32 ± 0.01
C18:3n3	$0.34^{a} \pm 0.01$	$0.30^{a} \pm 0.08$	$0.34^{a} \pm 0.01$	$0.35^{a} \pm 0.05$	$0.20^{a} \pm 0.05$	$0.23^{a} \pm 0.06$	$0.22^{a} \pm 0.00$
C21:0	–	–	–	–	–	–	–
C22:0	0.72 ± 0.01	0.71 ± 0.02	0.83 ± 0.00	0.68 ± 0.10	0.77 ± 0.13	0.80 ± 0.11	0.89 ± 0.01
C20:3n6	–	–	–	–	–	–	–
C20:4n6	0.01 ± 0.00	–	0.01 ± 0.00	–	0.02 ± 0.00	0.01 ± 0.02	0.02 ± 0.00
C23:0	0.03 ± 0.01	0.03 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.07 ± 0.03	0.05 ± 0.00
C24:0	0.30 ± 0.01	0.30 ± 0.01	0.36 ± 0.01	0.30 ± 0.05	0.35 ± 0.05	0.36 ± 0.10	0.41 ± 0.01
C24:1	0.05 ± 0.01	–	0.01 ± 0.02	0.11 ± 0.11	–	–	–
C22:6n3	0.02 ± 0.00	0.05 ± 0.01	0.06 ± 0.00	0.10 ± 0.01	0.09 ± 0.01	0.07 ± 0.01	0.07 ± 0.01
SFA	$7.91^{c} \pm 0.02$	$8.41^{b,c} \pm 0.07$	$8.83^{b} \pm 0.00$	$8.20^{b,c} \pm 0.05$	$9.29^{a} \pm 0.11$	$9.86^{a} \pm 0.11$	$10.19^{a} \pm 0.02$
MUFA	$77.82^{a} \pm 0.04$	$78.33^{a} \pm 0.08$	$78.75^{a} \pm 0.04$	$78.86^{a} \pm 0.11$	$78.94^{a} \pm 0.12$	$78.68^{a} \pm 0.15$	$78.38^{a} \pm 0.04$
PUFA	$13.79^{a} \pm 0.01$	$11.95^{b} \pm 0.06$	$10.36^{c} \pm 0.01$	$10.46^{c} \pm 0.11$	$7.89^{d} \pm 0.11$	$6.80^{e} \pm 0.10$	$6.29^{e} \pm 0.02$

Table 3 continued

High oleic sunflower oil

Thermo-oxidized oil

FAME (%)	0	8	16	24	32	40	48
∑TRANS	0.03^{c} ± 0.02	0.24^{b,c} ± 0.01	0.33^{b} ± 0.07	0.28^{b,c} ± 0.01	1.20^{a} ± 0.28	1.44^{a} ± 0.31	1.36^{a} ± 0.03
UFA	91.61^{a} ± 0.02	90.28^{b} ± 0.07	89.11^{c} ± 0.03	89.32^{c} ± 0.11	86.83^{d} ± 0.12	85.47^{e} ± 0.13	84.67^{e} ± 0.03
C18:1c/C18:2c	5.78^{e}	6.73^{d}	7.90^{c}	7.82^{c}	10.63^{b}	12.35^{a}	12.91^{a}
C18:2n6c/C16:0	3.71^{a}	3.08^{b}	2.52^{c}	2.66^{c}	1.71^{d}	1.39^{d,e}	1.33^{e}
MUFA/SFA	9.84^{a}	9.31^{a,b}	8.92^{b}	9.62^{a,b}	8.50^{c}	7.98^{c}	7.69^{c}
PUFA/SFA	1.74^{a}	1.42^{b}	1.17^{c}	1.28^{c}	0.85^{d}	0.69^{d,e}	0.62^{e}
UFA/SFA	11.58^{a}	10.73^{a,b}	10.09^{b}	10.89^{b}	9.34^{c}	8.67^{c}	8.31^{c}

Frying oil

FAME (%)	8	16	24	32	40	48
C8:0	0.04^{c} ± 0.00	0.07^{c} ± 0.00	0.16^{b} ± 0.01	0.21^{a,b} ± 0.01	0.19^{a,b} ± 0.01	0.24^{a} ± 0.04
C14:0	0.06 ± 0.00	0.02 ± 0.03	0.05 ± 0.01	0.08 ± 0.01	0.06 ± 0.00	0.10 ± 0.08
C15:0	–	0.02 ± 0.00	–	–	0.01 ± 0.01	0.04 ± 0.02
C16:0	3.74^{b} ± 0.01	3.84^{a,b} ± 0.03	3.89^{a,b} ± 0.22	4.04^{a,b} ± 0.01	4.10^{a,b} ± 0.05	4.22$^{a.}$ ± 0.03
C16:1	0.10 ± 0.00	0.11 ± 0.00	0.06 ± 0.01	0.11 ± 0.01	0.13 ± 0.03	0.11 ± 0.01
C17:0	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.01	0.05 ± 0.02	0.05 ± 0.01	0.03 ± 0.00
C17:1	0.06 ± 0.01	0.09 ± 0.06	0.04 ± 0.02	0.03 ± 0.01	0.04 ± 0.01	0.04 ± 0.02
C18:0	3.07^{b} ± 0.00	3.13^{b} ± 0.02	2.86^{b} ± 0.00	3.13^{a,b} ± 0.08	3.31^{a,b} ± 0.01	3.27^{a} ± 0.06
C18:1t	0.11^{b} ± 0.00	0.25^{b} ± 0.00	0.27^{b} ± 0.09	0.58^{a,b} ± 0.01	0.61^{a,b} ± 0.16	0.83^{a} ± 0.26
C18:1c	77.14^{a} ± 0.05	76.83^{a} ± 0.11	76.34^{a,b} ± 0.14	75.93^{a,b} ± 0.55	75.09^{b} ± 0.70	74.66^{b} ± 0.51
C18:2t	–	0.02^{a} ± 0.03	–	–	0.07^{a} ± 0.08	0.03^{a} ± 0.02
C18:2c	12.71^{a} ± 0.00	12.02^{b} ± 0.09	12.14^{b} ± 0.05	11.61^{c} ± 0.03	11.17^{d} ± 0.09	11.26^{d} ± 0.09
C20:0	0.31 ± 0.00	0.27 ± 0.01	0.50 ± 0.07	0.34 ± 0.12	0.27 ± 0.01	0.27 ± 0.01
C18:3n3	0.31^{a} ± 0.00	0.33^{a} ± 0.04	0.20^{a} ± 0.01	0.27^{a} ± 0.07	0.25^{a} ± 0.01	0.29^{a} ± 0.04
C21:0	–	0.03 ± 0.00	–	–	0.03^{a} ± 0.01	0.03^{a} ± 0.00
C22:0	0.80 ± 0.02	0.78 ± 0.02	0.65 ± 0.06	0.73 ± 0.00	0.81 ± 0.02	0.86 ± 0.03
C20:3n6	0.03 ± 0.03	–	–	–	–	–
C20:4n6	–	–	–	0.02 ± 0.01	–	–
C23:0	0.03 ± 0.00	0.04 ± 0.00	0.03 ± 0.01	0.04 ± 0.02	0.02 ± 0.01	0.01 ± 0.00
C24:0	0.34 ± 0.01	0.33 ± 0.01	0.26 ± 0.02	0.33 ± 0.02	0.36 ± 0.00	0.36 ± 0.02
C24:1	0.07 ± 0.00	0.05 ± 0.02	–	–	–	–
C22:6n3	0.05 ± 0.00	0.08 ± 0.02	0.05 ± 0.03	0.10 ± 0.05	0.05 ± 0.02	0.03 ± 0.02
SFA	8.43^{c} ± 0.00	8.58^{b,c} ± 0.02	8.46^{b,c} ± 0.04	8.96^{a,b} ± 0.05	9.20^{a} ± 0.02	9.42^{a} ± 0.04
MUFA	77.48^{a} ± 0.07	77.33^{a} ± 0.18	76.72^{a,b} ± 0.26	76.64^{a,b} ± 0.57	75.87^{b} ± 0.90	75.64^{b} ± 0.80
PUFA	13.10^{b}a ± 0.04	12.45^{b} ± 0.18	12.39^{b,c} ± 0.09	12.00^{c,d} ± 0.16	11.54^{e} ± 0.20	11.61^{d,e} ± 0.16
∑TRANS	0.11^{b} ± 0.00	0.27^{a,b} ± 0.03	0.27^{a,b} ± 0.09	0.58^{a,b} ± 0.01	0.68^{a,b} ± 0.24	0.86^{a} ± 0.29
UFA	90.57^{a} ± 0.05	89.78^{a} ± 0.18	89.11^{a} ± 0.18	88.64^{a} ± 0.37	87.40^{a} ± 0.55	87.25^{a} ± 0.48
C18:1c/C18:2c	6.07^{d}	6.39^{b,c}	6.29^{c,d}	6.54^{a,b}	6.72^{a}	6.63^{a}
C18:2n6c/C16:0	3.39^{b}	3.13^{b,c}	3.12^{b,c}	2.87^{c,d}	2.72^{d}	2.66^{d}
MUFA/SFA	9.19^{a}	9.01^{b}	9.07^{b}	8.55^{c}	8.25^{c,d}	8.03^{d}
PUFA/SFA	1.55^{a}	1.45^{a,b}	1.46^{a,b}	1.34^{a,b}	1.25^{a,b}	1.23^{b}
UFA/SFA	10.73^{a}	10.46^{a,b}	10.53^{a,b}	9.89^{b,c}	9.50^{c}	9.26^{c}

Different superscript letters for the same treatment (thermo-oxidation or frying) correspond to statistically significant differences ($P \leq 0.05$) in the same line

– Under detection limit (<0.01 %)

and MIX. The TFAs showed a good correlation with the TPC in frying HOSO.

Linoleic acid (C18:2 n6 *cis*-9, *cis*-12) is often used as a marker of thermal degradation because it is easily oxidized. The amount of this fatty acid significantly ($P < 0.05$) decreased during the heat treatment for all samples except frying SO. In all samples, the thermal treatment reduced the amount of unsaturated fatty acids (UFAs) and increased the amount of saturated fatty acids (SFAs). In fact, the UFA/SFA ratio was a good indicator of oil degradation for all of the frying oils analyzed. This ratio, which decreased during the heat treatment, was highly correlated with the

Table 4 Fatty acid composition (%) of SO (thermo-oxidized and frying oil) at different treatment times

Sunflower oil

Thermo-oxidized oil

FAME (%)	0	8	16	24	32	40	48
C8:0	–	–	–	–	–	–	–
C11:0	–	0.07 ± 0.13	–	–	–	0.04 ± 0.06	–
C14:0	0.10 ± 0.36	0.16 ± 0.06	0.20 ± 0.00	0.15 ± 0.07	0.27 ± 0.12	0.23 ± 0.06	0.20 ± 0.00
C15:0	–	0.10 ± 0.00	0.10 ± 0.00	0.05 ± 0.07	0.14 ± 0.06	0.10 ± 0.00	0.10 ± 0.00
C16:0	5.53 ± 0.78	5.87 ± 0.22	6.75 ± 0.74	6.43 ± 0.18	8.59 ± 3.00	7.78 ± 0.71	7.15 ± 0.09
C16:1	0.10 ± 0.06	0.10 ± 0.00	0.14 ± 0.06	0.10 ± 0.00	0.24 ± 0.06	0.21 ± 0.00	0.17 ± 0.06
C17:0	–	0.07 ± 0.06	0.11 ± 0.00	0.05 ± 0.08	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00
C17:1	0.05 ± 0.06	–	0.04 ± 0.06	–	–	0.07 ± 0.06	–
C18:0	3.10^{a} ± 0.50	3.22^{ab} ± 0.11	3.37^{ab} ± 0.09	3.62^{b} ± 0.06	3.58^{b} ± 0.23	3.78^{b} ± 0.10	3.94^{b} ± 0.09
C18:1 n9t	–	0.04^{a} ± 0.07	0.04^{a} ± 0.07	0.06^{a} ± 0.08	0.27^{ab} ± 0.07	0.27^{ab} ± 0.07	0.31^{b} ± 0.07
C18:1 n9c	31.62^{a} ± 3.02	32.29^{ab} ± 0.18	33.04^{ab} ± 0.29	34.20^{ab} ± 0.36	33.98^{b} ± 1.36	35.18^{b} ± 0.35	36.08^{b} ± 0.15
C18:2 n6t	0.32 ± 0.06	0.36 ± 0.06	0.11 ± 0.00	0.11 ± 0.00	0.26 ± 0.17	0.29 ± 0.13	0.29 ± 0.13
C18:2 n6c	58.49^{a} ± 4.49	56.98^{ab} ± 0.52	54.90^{bc} ± 0.41	53.98^{c} ± 0.18	51.17^{d} ± 1.88	50.61^{d} ± 0.35	50.32^{d} ± 0.42
C18:3 n3	–	–	0.10 ± 0.00	0.21 ± 0.00	0.14 ± 0.06	0.10 ± 0.10	0.21 ± 0.00
C20:0	0.12 ± 0.07	0.12 ± 0.00	0.12 ± 0.00	0.06 ± 0.08	0.04 ± 0.07	0.08 ± 0.14	–
C20:1	–	–	–	–	–	0.06 ± 0.11	–
C20:2	0.10 ± 0.06	0.10 ± 0.00	0.17 ± 0.06	0.10 ± 0.15	0.21 ± 0.00	0.14 ± 0.12	0.21 ± 0.00
C20:4 n6	0.47 ± 0.23	0.47 ± 0.00	0.51 ± 0.06	0.62 ± 0.07	0.73 ± 0.21	0.67 ± 0.00	0.64 ± 0.05
C24:0	–	0.04 ± 0.06	0.11 ± 0.00	0.11 ± 0.00	0.07 ± 0.06	0.11 ± 0.00	0.11 ± 0.00
C24:1 n9	–	–	0.08 ± 0.00	0.04 ± 0.06	0.06 ± 0.05	0.06 ± 0.05	0.08 ± 0.00
C22:6 n3	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.15 ± 0.06	0.11 ± 0.00	0.07 ± 0.06
C20:3n6	–	–	–	–	–	–	–
C20:3n3	–	–	–	–	–	–	–
C23:0	–	–	–	–	–	–	–
SFA	8.84^{c} ± 0.06	9.66^{bc} ± 0.49	10.76^{abc} ± 0.67	10.47^{abc} ± 0.26	12.80^{a} ± 2.85	12.23^{a} ± 0.46	11.61^{ab} ± 0.17
MUFA	31.77^{f} ± 0.13	32.31^{ef} ± 0.09	33.34^{de} ± 0.10	34.40^{cd} ± 0.20	34.55^{bc} ± 0.10	35.85^{ab} ± 0.08	36.64^{a} ± 0.15
PUFA	59.49^{a} ± 0.21	58.02^{a} ± 0.18	55.90^{b} ± 0.30	55.13^{b} ± 0.28	52.65^{c} ± 0.25	51.92^{c} ± 0.12	51.74^{c} ± 0.10
UFA	91.26^{a} ± 0.06	90.45^{ab} ± 0.49	89.24^{ab} ± 0.73	89.53^{ab} ± 0.41	87.20^{b} ± 2.85	87.77^{b} ± 0.34	88.39^{b} ± 0.17
ΣTRANS	0.32^{a} ± 0.00	0.40^{a} ± 0.13	0.15^{a} ± 0.07	0.17^{a} ± 0.08	0.53^{a} ± 0.24	0.56^{a} ± 0.19	0.60^{a} ± 0.06
18:2/16:0	10.57^{a}	9.70^{ab}	8.13^{bc}	8.39^{bc}	5.95^{c}	6.50^{c}	7.04^{c}
18:1/18:2	0.54^{g}	0.56^{f}	0.60^{e}	0.63^{d}	0.66^{c}	0.69^{b}	0.71^{a}
MUFA/SFA	3.59^{a}	3.34^{ab}	3.10^{ab}	3.28^{ab}	2.70^{b}	2.93^{b}	3.15^{ab}
PUFA/SFA	6.73^{a}	6.01^{ab}	5.19^{bc}	5.26^{bc}	4.11^{cd}	4.24^{d}	4.46^{cd}
UFA/SFA	10.32^{a}	9.36^{ab}	8.29^{bc}	8.55^{bc}	6.81^{c}	7.17^{c}	7.61^{c}

Frying oil

FAME (%)	8	16	24	32	40	48
C8:0	0.09^{a} ± 0.10	0.13^{ab} ± 0.09	0.14^{ab} ± 0.01	0.19^{ab} ± 0.10	0.20^{b} ± 0.10	0.22^{b} ± 0.10
C11:0	–	–	0.01 ± 0.00	–	0.02 ± 0.00	–
C14:0	0.08 ± 0.01	0.08 ± 0.01	0.10 ± 0.01	0.08 ± 0.01	0.12 ± 0.10	0.12 ± 0.09
C15:0	0.02 ± 0.00	–	0.02 ± 0.01	–	0.02 ± 0.01	–
C16:0	6.20^{b} ± 0.37	$7.31^{a,b}$ ± 0.40	$7.13^{a,b}$ ± 0.53	7.59^{a} ± 0.48	7.81^{a} ± 1.05	8.47^{a} ± 0.97
C16:1	0.13 ± 0.01	0.13 ± 0.02	0.14 ± 0.06	0.10 ± 0.05	0.14 ± 0.063	0.11 ± 0.07
C17:0	0.04 ± 0.02	0.03 ± 0.01	0.04 ± 0.02	0.04 ± 0.03	0.04 ± 0.01	0.03 ± 0.02
C17:1	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.02	0.01 ± 0.03	0.01 ± 0.00	–
C18:0	3.47 ± 0.05	3.60 ± 0.04	3.66 ± 0.42	3.06 ± 0.36	3.81 ± 0.37	3.84 ± 0.45
C18:1 n9t	0.08 ± 0.054	0.08 ± 0.06	0.14 ± 0.10	0.08 ± 0.09	0.17 ± 0.10	0.22 ± 0.10
C18:1 n9c	32.68 ± 0.95	31.20 ± 1.63	33.58 ± 0.23	33.65 ± 0.22	34.18 ± 0.10	32.61 ± 0.09
C18:2 n6t	0.02^{b} ± 0.01	0.03^{b} ± 0.02	0.04^{b} ± 0.03	0.02^{b} ± 0.02	0.04^{b} ± 0.00	–
C18:2 n6c	56.82 ± 1.05	56.90 ± 0.95	54.77 ± 0.90	54.91 ± 1.27	53.22 ± 0.60	54.12 ± 0.54
C18:3 n3	0.03 ± 0.02	0.06 ± 0.01	0.04 ± 0.00	–	0.05 ± 0.00	–
C20:0	0.01^{b} ± 0.00	0.29^{c} ± 0.01	–	0.22^{ac} ± 0.07	–	0.25^{c} ± 0.18

Table 4 continued

Frying oil						
FAME (%)	8	16	24	32	40	48
C20:1	0.02 ± 0.01	0.11 ± 0.00	0.09 ± 0.01	0.05 ± 0.00	0.09 ± 0.01	–
C20:2	–	–	–	–	–	–
C20:4 n6	–	–	–	–	–	–
C24:0	–	–	–	–	–	–
C24:1 n9	0.03 ± 0.02	–	0.02 ± 0.00	–	0.03 ± 0.01	–
C22:6 n3	–	–	–	–	–	–
C20:3n6	–	–	0.01 ± 0.00	–	0.01 ± 0..01	–
C20:3n3	0.04 ± 0.01	–	0.04 ± 0.02	–	0.05 ± 0.02	–
C23:0	0.23 ± 0.01	–	–	–	–	–
SFA	10.13^{bc} ± 0.12	11.45^{abc} ± 0.15	11.11^{abc} ± 0.16	11.18^{abc} ± 0.20	12.01^{ab} ± 0.28	12.94^{a} ± 0.31
MUFA	32.96^{ab} ± 0.30	31.55^{b} ± 0.23	33.99^{ab} ± 0.25	33.89^{ab} ± 0.21	34.62^{a} ± 0.27	32.94^{ab} ± 0.30
PUFA	56.91^{b} ± 0.25	57.00^{b} ± 0.16	54.91^{bc} ± 0.10	54.93^{bc} ± 0.15	53.37^{c} ± 0.18	54.12^{c} ± 0.21
UFA	89.87^{a} ± 0.21	88.55^{a} ± 0.19	88.89^{a} ± 0.20	88.82^{a} ± 0.15	87.99^{a} ± 0.19	87.06^{a} ± 0.25
ΣTRANS	0.10^{a} ± 0.06	0.12^{a} ± 0.10	0.19^{a} ± 0.04	0.10^{a} ± 0.08	0.21^{a} ± 0.12	0.22^{a} ± 0.13
18:2/16:0	9.16^{b}	7.78^{c}	7.68^{cd}	7.23^{cd}	6.81^{cd}	6.38^{d}
18:1/18:2	0.57^{c}	0.54^{d}	0.61^{b}	0.61^{b}	0.64^{b}	0.60^{a}
MUFA/SFA	3.25^{ab}	2.75^{c}	3.06^{abc}	3.03^{abc}	2.88^{bc}	2.55^{c}
PUFA/SFA	5.62^{ab}	4.98^{bc}	4.94^{bc}	4.91^{bc}	4.44^{c}	4.18^{c}
UFA/SFA	8.87^{ab}	7.73^{bc}	8.00^{bc}	7.94^{bc}	7.33^{c}	6.73^{c}

Different superscript letters for the same treatment (thermo-oxidation or frying) correspond to statistically significant differences ($P \leq 0.05$) in the same line

– Under detection limit (<0.01 %)

Table 5 Fatty acid composition (%) of MIX (thermo-oxidized and frying oil) at different treatment times

MIX oil							
Thermo-oxidized oil							
FAME (%)	0	8	16	24	32	40	48
C8:0	–	0.03^{a} ± 0.01	0.05^{ab} ± 0.00	0.07^{b} ± 0.01	0.11^{c} ± 0.01	0.14^{d} ± 0.01	0.18^{e} ± 0.00
C14:0	0.05 ± 0.01	0.04 ± 0.01	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.06 ± 0.01
C15:0	0.02 ± 0.00	0.02 ± 0.01	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.01	0.02 ± 0.00
C16:0	4.99^{a} ± 0.04	4.99^{a} ± 0.06	4.99^{a} ± 0.05	5.17^{ab} ± 0.02	5.38^{bc} ± 0.09	5.44^{c} ± 0.02	5.60^{c} ± 0.08
C16:1	0.17 ± 0.00	0.16 ± 0.02	0.16 ± 0.00	0.17 ± 0.00	0.17 ± 0.02	0.18 ± 0.01	0.19 ± 0.00
C17:0	0.05 ± 0.00	0.05 ± 0.00	0.06 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.01	0.05 ± 0.01
C17:1	0.05 ± 0.00	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.06 ± 0.00
C18:0	2.41^{a} ± 0.01	2.43^{ab} ± 0.02	2.51^{bc} ± 0.02	2.54^{c} ± 0.00	2.56^{c} ± 0.05	2.69^{d} ± 0.01	2.74^{d} ± 0.02
C18: 1 n9t	0.02^{a} ± 0.01	0.09^{a} ± 0.01	0.29^{b} ± 0.08	0.24^{b} ± 0.00	0.28^{b} ± 0.03	0.44^{c} ± 0.01	0.53^{c} ± 0.02
C18:1 n9c	59.92^{a} ± 0.09	60.34^{ab} ± 0.04	60.77^{ab} ± 0.10	61.67^{bc} ± 0.03	62.28^{cd} ± 0.48	63.01^{cd} ± 0.13	63.54^{d} ± 0.74
C18:2 n6t	–	0.01^{a} ± 0.01	0.03^{ab} ± 0.02	0.02^{ab} ± 0.00	0.03^{ab} ± 0.01	0.07^{bc} ± 0.01	0.08^{c} ± 0.02
C18:2 n6c	25.70^{a} ± 0.01	25.12^{b} ± 0.04	24.63^{c} ± 0.03	23.86^{d} ± 0.00	22.90^{e} ± 0.06	22.06^{f} ± 0.01	21.07^{g} ± 0.15
C20:0	0.43 ± 0.02	0.47 ± 0.03	0.47 ± 0.01	0.46 ± 0.00	0.50 ± 0.04	0.51 ± 0.04	0.50 ± 0.01
C18:3 n6	0.16^{a} ± 0.00	0.22^{ab} ± 0.00	0.27^{bc} ± 0.00	0.32^{cd} ± 0.00	0.35^{de} ± 0.03	0.42^{e} ± 0.02	0.40^{e} ± 0.02
C20:1	0.74 ± 0.04	0.91 ± 0.05	0.80 ± 0.02	0.83 ± 0.00	0.81 ± 0.06	0.88 ± 0.01	0.87 ± 0.02
C18:3 n3	4.43^{a} ± 0.00	4.04^{ab} ± 0.03	3.74^{abc} ± 0.01	3.35^{bc} ± 0.02	3.04^{bc} ± 0.04	2.67^{c} ± 0.00	2.82^{c} ± 0.80
C21:0	–	–	0.02^{a} ± 0.01	0.01^{a} ± 0.00	0.06^{a} ± 0.01	0.08^{b} ± 0.04	0.04^{a} ± 0.03
C20:2	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.01	0.05 ± 0.00	0.04 ± 0.00	0.04 ± 0.01	0.04 ± 0.00
C22:0	0.42 ± 0.04	0.49 ± 0.01	0.53 ± 0.01	0.51 ± 0.01	0.49 ± 0.06	0.56 ± 0.02	0.56 ± 0.03
C20:3 n6	0.01 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.03 ± 0.01
C22:1 n9	0.18 ± 0.00	0.20 ± 0.01	0.21 ± 0.01	0.21 ± 0.01	0.20 ± 0.02	0.22 ± 0.01	0.22 ± 0.00
C23:0	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.01	0.03 ± 0.00
C22:2	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
C24:0	0.11^{a} ± 0.02	0.16^{ab} ± 0.00	0.17^{ab} ± 0.00	0.16^{ab} ± 0.00	0.15^{ab} ± 0.02	0.19^{b} ± 0.01	0.18^{b} ± 0.03
C24:1	0.05^{a} ± 0.01	0.07^{ab} ± 0.01	0.08^{ab} ± 0.01	0.08^{ab} ± 0.01	0.07^{ab} ± 0.01	0.08^{ab} ± 0.00	0.10^{b} ± 0.01

Table 5 continued

MIX oil

Thermo-oxidized oil

FAME (%)	0	8	16	24	32	40	48
C22:6 n3	0.01 ± 0.02	0.03 ± 0.01	0.03 ± 0.01	0.05 ± 0.00	0.34 ± 0.40	0.07 ± 0.00	0.09 ± 0.01
SFA	8.49^{g} ± 0.04	8.70^{f} ± 0.05	8.87e ± 0.05	9.06d ± 0.01	9.39c ± 0.01	9.77^{b} ± 0.07	9.96^{a} ± 0.00
MUFA	61.14^{f} ± 0.05	61.81^{ef} ± 0.06	62.35^{de} ± 0.01	63.24^{cd} ± 0.04	63.87bc ± 0.33	64.86^{ab} ± 0.11	65.49^{a} ± 0.69
PUFA	30.36^{a} ± 0.00	29.50^{ab} ± 0.00	28.78^{bc} ± 0.06	27.69^{cd} ± 0.03	26.74d ± 0.34	25.38^{e} ± 0.04	24.55^{e} ± 0.69
UFA	91.51^{a} ± 0.04	91.30^{b} ± 0.05	91.13c ± 0.05	90.94d ± 0.01	90.61e ± 0.01	90.23^{f} ± 0.07	90.04^{g} ± 0.00
ΣTRANS	0.02^{d} ± 0.00	0.10^{cd} ± 0.03	0.32b ± 0.11	0.26bc ± 0.08	0.31b ± 0.13	0.51^{a} ± 0.16	0.61^{a} ± 0.09
18:2/C16:0	5.15^{a}	5.04^{ab}	4.94b	4.61c	4.26^{d}	4.05^{e}	3.77f
18:1/18:2	2,33^{g}	2,40^{f}	2,46^{e}	2,58^{d}	2,71^{c}	2,85^{b}	3,01^{o}
MUFA/SFA	7.20^{a}	7.10^{ab}	7.03^{ab}	6.98^{bc}	6.80^{cd}	6.64^{de}	6.57^{e}
PUFA/SFA	3.57^{a}	3.39^{b}	3.24^{c}	3.06^{d}	2.85^{e}	2.60^{f}	2.46^{f}
UFA/SFA	10.77^{a}	10.50^{b}	10.27^{c}	10.03^{d}	9.65^{e}	9.24^{f}	9.04^{f}

Frying oil

FAME (%)	8	16	24	32	40	48
C8:0	0.05^{ab} ± 0.01	0.07^{b} ± 0.01	0.09^{bc} ± 0.00	0.14^{cd} ± 0.03	0.17^{d} ± 0.01	0.18^{d} ± 0.01
C14:0	0.04^{a} ± 0.01	0.05^{ab} ± 0.00	0.05^{ab} ± 0.00	0.05^{ab} ± 0.01	0.06^{b} ± 0.00	0.06^{b} ± 0.00
C15:0	0.04 ± 0.02	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.01	0.02 ± 0.00
C16:0	5.06^{ab} ± 0.04	5.18^{ab} ± 0.06	5.31^{bc} ± 0.03	5.50^{cd} ± 0.17	5.58^{cd} ± 0.04	5.65^{d} ± 0.05
C16:1	0.19 ± 0.02	0.18 ± 0.01	0.17 ± 0.00	0.18 ± 0.01	0.18 ± 0.00	0.18 ± 0.00
C17:0	0.05 ± 0.01	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.06 ± 0.00
C17:1	–	–	–	0.04 ± 0.01	0.05 ± 0.00	0.05 ± 0.00
C18:0	2.36^{a} ± 0.20	2.53^{abc} ± 0.00	2.57^{abc} ± 0.01	2.61^{abc} ± 0.02	2.68^{bc} ± 0.02	2.77^{c} ± 0.01
C18: 1 n9t	0.07^{a} ± 0.01	0.12^{a} ± 0.01	0.18^{a} ± 0.01	0.22^{a} ± 0.01	0.24^{a} ± 0.02	0.15^{a} ± 0.19
C18:1 n9c	59.60^{b} ± 0.68	60.43^{ab} ± 0.08	60.50^{ab} ± 0.05	60.68^{ab} ± 0.07	60.67^{ab} ± 0.12	60.99^{a} ± 0.15
C18:2 n6t	0.05^{a} ± 0.02	0.02^{a} ± 0.01	0.03^{a} ± 0.02	0.02^{a} ± 0.00	0.03^{a} ± 0.00	0.05^{a} ± 0.01
C18:2 n6c	25.51^{ab} ± 0.15	25.23^{bc} ± 0.02	25.14^{c} ± 0.02	25.15^{c} ± 0.08	25.05^{cd} ± 0.05	24.69^{d} ± 0.16
C20:0	0.58 ± 0.17	0.44 ± 0.01	0.45 ± 0.00	0.41 ± 0.04	0.41 ± 0.00	0.43 ± 0.01
C18:3 n6	0.44 ± 0.30	0.28 ± 0.01	0.31 ± 0.01	0.28 ± 0.00	0.30 ± 0.00	0.32 ± 0.01
C20:1	0.84 ± 0.07	0.77 ± 0.03	0.74 ± 0.03	0.71 ± 0.06	0.70 ± 0.01	0.72 ± 0.03
C18:3 n3	4.25^{a} ± 0.32	3.65^{b} ± 0.00	3.41^{bc} ± 0.01	3.05^{cd} ± 0.00	2.85^{d} ± 0.00	2.64^{d} ± 0.05
C21:0	0.02 ± 0.02	0.05 ± 0.01	0.05 ± 0.01	0.01 ± 0.01	0.03 ± 0.02	0.03 ± 0.03
C20:2	0.04 ± 0.01	0.03 ± 0.01	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.03 ± 0.00
C22:0	0.42 ± 0.08	0.45 ± 0.06	0.45 ± 0.02	0.41 ± 0.06	0.43 ± 0.01	0.46 ± 0.03
C20:3 n6	0.01 ± 0.01	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.03 ± 0.00
C22:1 n9	0.17 ± 0.04	0.18 ± 0.02	0.18 ± 0.01	0.16 ± 0.01	0.16 ± 0.00	0.17 ± 0.01
C23:0	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00
C22:2	0.01 ± 0.01	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00
C24:0	0.13 ± 0.02	0.13 ± 0.03	0.13 ± 0.02	0.12 ± 0.02	0.12 ± 0.01	0.14 ± 0.01
C24:1	0.06 ± 0.01	0.07 ± 0.01	0.06 ± 0.00	0.05 ± 0.01	0.06 ± 0.00	0.07 ± 0.01
C22:6 n3	0.02^{ab} ± 0.00	0.03^{ab} ± 0.01	0.04^{abc} ± 0.01	0.05^{bc} ± 0.00	0.06^{bc} ± 0.01	0.07^{c} ± 0.01
SFA	8.75^{e} ± 0.10	8.99^{de} ± 0.05	9.16^{cd} ± 0.01	9.33^{bc} ± 0.07	9.57^{b} ± 0.08	9.83^{a} ± 0.03
MUFA	60.92^{c} ± 0.65	61.74^{abc} ± 0.03	61.83^{abc} ± 0.03	62.04^{ab} ± 0.15	62.05^{ab} ± 0.11	62.33^{a} ± 0.08
PUFA	30.33^{a} ± 0.75	29.27^{ab} ± 0.01	29.01^{b} ± 0.02	28.63^{bc} ± 0.08	28.38^{bc} ± 0.03	27.83^{c} ± 0.11
UFA	91.25^{b} ± 0.10	91.01^{bc} ± 0.05	90.84^{cd} ± 0.01	90.67^{de} ± 0.07	90.43^{e} ± 0.08	90.17^{f} ± 0.03
ΣTRANS	0.12^{a} ± 0.03	0.14^{a} ± 0.02	0.21^{a} ± 0.05	0.24^{a} ± 0.06	0.27^{a} ± 0.04	0.20^{a} ± 0.07
18:2/C16:0	5.04^{ab}	4.87^{bc}	4.74^{cd}	4.57^{de}	4.49^{e}	4.37^{e}
18:1/18:2	2,33^{c}	2,39^{bc}	2,40^{ab}	2,41^{ab}	2,42^{ab}	2,47
MUFA/SFA	6.96^{b}	6.87^{bc}	6.75^{cd}	6.65^{de}	6.49^{ef}	6.34^{f}
PUFA/SFA	3.47^{o}	3.26^{b}	3.16^{bc}	3.07^{bc}	2.97^{cd}	2.83^{d}
UFA/SFA	10.42^{b}	10.13^{bc}	9.91^{cd}	9.72^{de}	9.45^{ef}	9.17^{f}

Different superscript letters for the same treatment (thermo-oxidation or frying) correspond to statistically significant differences ($P \leq 0.05$) in the same line

– Under detection limit (<0.01 %)

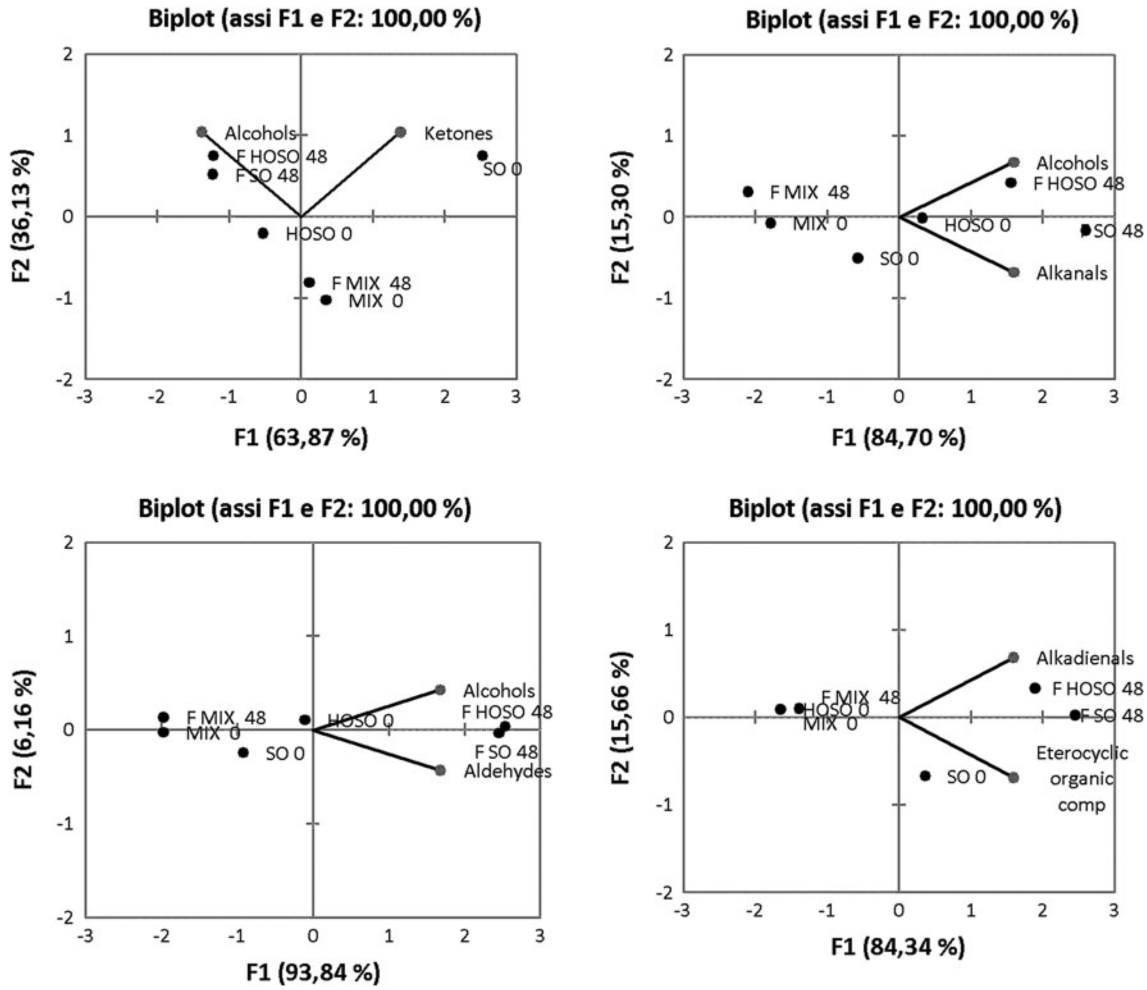

Fig. 4 PCA of different groups of VOCs for frying (F) HOSO, SO and MIX at 0 and 48 h of treatment. **Aldehydes* $\sum$ alkanals, alkenals, and alkadienals

TPC (R^2 of 0.96, 0.94 and 0.97 for frying HOSO, SO and MIX, respectively). The C18:2 n6/C16:0 ratio can also be considered to be an oil degradation indicator. This ratio showed a good linear correlation with the TPC for frying HOSO ($R^2 = 0.967$) and frying MIX ($R^2 = 0.984$). The C18:1 / C18:2 ratio showed a linear increase in all samples, but only thermo-oxidized SO, thermo-oxidized MIX and frying MIX showed a good correlation with the TPC, with R^2 values of 0.91, 0.89 and 0.92, respectively.

Volatile Organic Compounds

The dynamic headspace method has the advantage of using a lower temperature than that used in the static headspace method and permits the enhancement of trace components in complex mixtures of a wide range of volatile compounds. This purge and trap method is applicable to oil samples without manipulation, and it has the great advantage of avoiding extractions that can create many artifacts that may confound the analyses of rancid foods.

VOCs identified included the products of the β-scission of oleic and linoleic acids. At time zero, alkanals, alkenes, and monoterpenes represented the main classes of volatile compounds identified for the HOSO samples (28.74, 15.24 and 14.62 ppb, respectively); small amounts (<2 ppb) of alkanes, alcohols, alkenals and ketones were also observed. For fresh SO, the main classes of observed compounds were alkanes, alkanals and ketones (75.6, 30.58 and 11.21 ppb, respectively); small amounts of alkenals, heterocyclic aromatic hydrocarbons, alkadienals and alcohol were also detected (5.69, 3.68, 0.33 and 0.16 ppb, respectively). The lowest amount of VOCs was found in the fresh MIX. The main volatile compounds identified were alkanals (14.86 ppb), and traces of alkanes and alkenals were also found. During the heat treatment, an increase or decrease of the pattern of VOCs was observed.

High levels of octane (>100 ppb) from the decomposition of oleic acid hydroperoxides were found in HOSO, which contained the highest value of C18:1 (77.6 %). High levels of hexanal (>170 ppb), which was generated by linoleic acid decomposition, were found in the thermo-oxidized SO, which contained the highest value of C18:2 (58.5 %).

New classes of compounds were observed after 48 h of heat treatment, such as alkadienals and heterocyclic aromatic organic compounds in the HOSO and MIX samples and acid compounds in the SO samples. Small amounts of trans, *trans*-2,4-decadienal (3.82 ppb) and undecenal (6.38 ppb) were found in the HOSO frying samples. Different 2,4-decadienal isomers are the main compounds responsible for the frying flavor, although a high amount of these compounds can cause a rancid flavor [6]. Small amounts of 2,4-decadienal may be derived from oleic acid [13].

A VOC analysis showed that MIX contained the lowest amounts of volatile organic compounds. In fact, these samples can be easily separated from other fresh and frying oils by the principal component analysis plot (Fig. 4).

The VOCs presented a random evolution during thermal treatment; thus, it was not possible to correlate the results obtained with other markers of heat treatment, such as the TPC.

Water activity

HOSO and MIX showed an increased Aw value during deep fat frying, while the Aw value in the thermo-oxidized samples remained the same because there was no interchange of water (due to the absence of a food matrix). The thermo-oxidized SO samples showed an increase in the Aw value, while the fried samples did not show any interesting trend. This result may be because, in SO, the water exchanged during the deep fat frying is immediately used in oxidation reactions, creating an interesting increase in the TPC (Fig. 2). As shown in Fig. 5a, there is an increase in the water activity value during heat treatment for frying HOSO and frying MIX because water is slowly used in the production of the TPC (as already observed) and tends to accumulate, acting as an emulsifier in the frying oil. Therefore, the correlation between the Aw values of these three oils and the TPC was determined. A good correlation was found for the frying HOSO (Fig. 5b) and frying MIX samples (Fig. 5c) but not for the frying SO samples.

Conclusion

Among the indices tested under our experimental conditions, C8:0 and the UFA/SFA ratio can be used as markers of heat treatment because these parameters had a good correlation with the TPC value for frying HOSO, SO and MIX; the C18:2/C16:0 ratio and the Aw value only for frying HOSO and MIX; and the C18:1/C18:2 for thermo-oxidized SO, MIX and frying MIX and TFA for frying HOSO. However, volatile compounds, which have been proposed as indicators of the oxidation state of frying oils in other studies [9], showed a random distribution; thus, it was not possible to correlate the presence of these compounds with the TPC.

According to the obtained results, thermal degradation was faster in the thermo-oxidized samples than in the frying samples, and they confirmed that high oleic oils, which have a low polyunsaturated fatty acid content, may

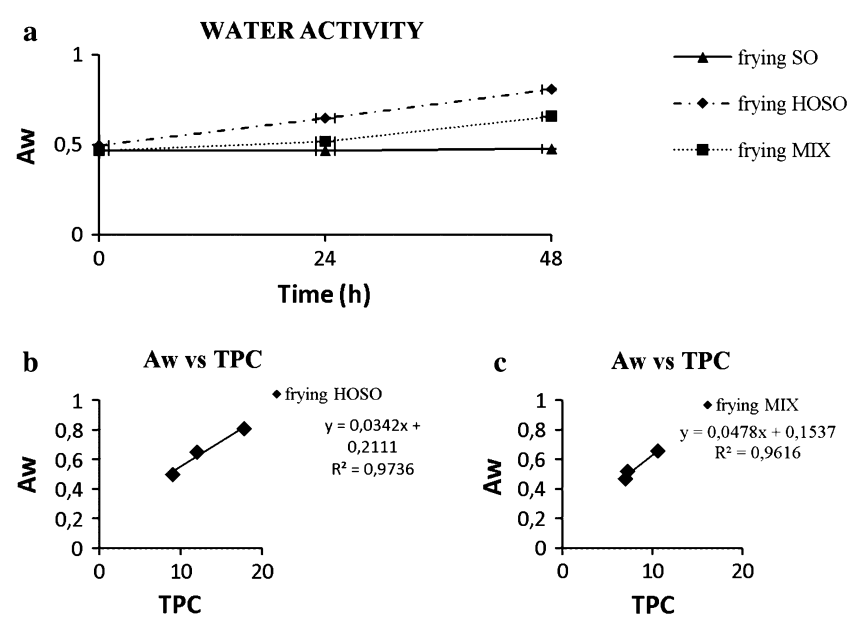

Fig. 5 **a** Water activity during the frying treatment of different oils, **b** correlation between Aw and TPC for HOSO, **c** correlation between Aw and TPC for MIX

be an alternative to conventional frying oils. Results obtained from our analytical determinations suggest that HOSO and MIX oils are more suitable for frying French fries than SO.

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