Oxidative changes in some vegetable oils during heating at frying temperature

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The oxidative changes in refined sunflower, grape seed, soybean, corn and olive oils caused by frying temperature were studied. The oxidative degradation of the oils was evaluated by monitoring their respective peroxide value (PV), oxidation stability (IP), content of conjugated dienes as absorbance at 232 nm (A_{232nm}), content of conjugated trienes as absorbance at 270 nm (A_{270nm}), changes in fatty acid composition (C18:2/C16:0), and content of total polar components (TPC). Results showed that olive oil has better stability against thermal oxidation when compared to polyunsaturated oils. On the other hand, corn and soybean oils (among unsaturated oils) are most resistant to oxidation at frying temperature. The best correlation was observed between the rate of decrease in C18:2/C16:0 ratio and the content of total polar components.

Key words: frying temperature; sunflower oil; grape seed oil; soybean oil; corn oil; olive oil

INTRODUCTION

In recent years the contribution of frying oils to total energy intake has markedly increased in the industrialized countries. This is mainly due to the rising consumption of deep-fried products, which are very popular because of their desirable flavour, colour, and crispy texture. Recently, much concern has been expressed on the biological effects of oxidized lipids, and there is increasing evidence that they may be detrimental to health [1, 2]. The chemistry of oxidation at high temperatures is very complex since both thermal and oxidative reactions are involved [3]. During the deep fat frying a number of chemical reactions takes place – hydrolysis, oxidation, thermal decomposition and polymerization. The chemical mechanism of thermal oxidation is principally the same as the autoxidation mechanism, but the thermal oxidation rate is faster than the autoxidation rate [4]. Oxidative stability is very important factor in oil quality especially for these used for frying because of the high temperature applied. Frying oil must have high oxidative stability during use. From a nutritional point of view, it should be taken into account that oils with high amounts of saturated fatty acids and fats containing *trans* fatty acids are less desirable for good health [5]. More over, highly saturated fatty acid composition of some industrial frying oils may represent a problem in case it is necessary to keep the product in the liquid state [6].

Vegetable oils like soybean, sunflower, corn etc. are often judged as very unstable for continuous frying due to their content of polyunsaturated fatty acids. On the other hand, the presence of natural substances such as tocopherols, oryzanol, sterol fraction, squalene etc., enhances their stability at higher temperatures [7].

Since many factors affect the rate of deterioration of fats used for deep-fat frying, no single procedure will be reliable under all conditions [8]. With prolonged heating time the accumulation of deterioration products leads to organoleptic failures and a decrease of the nutritive value. Deep-fat frying decreases the unsaturated fatty acids and increases polar material. Many methods have been used for determination of fat deterioration during frying. They include methods for assessment of peroxide value, iodine value dienes, fatty acids, polar components etc. For the quality control of frying fats or oils the determination of total polar parts is an approved standard method.

The aim of the present study was to investigate the high temperature performance of some vegetable oils as a function of heating duration at simulated frying temperature of 180°C. The oxidative degradation of the oils was evaluated by monitoring peroxide value (PV), oxidation stability (IP), content of conjugated dienes as

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absorbance at 232 nm (A_{232nm}), content of conjugated trienes as absorbance at 270 nm (A_{270nm}), changes in fatty acid composition (C16:0/C18:2), and content of total polar components (TPC).

MATERIALS AND METHODS

Samples. Commercially available samples of refined sunflower oil ("Papas olio", Yambol, Bulgaria) refined grape seed oil (Olitalia, Forli, Italy), refined soybean oil ((Olitalia, Forli, Italy), refined corn oil (Olin Yag Sanagyi, Edirne, Turkey) and refined olive (pomace) oil (Cotoliva, Dos Hermanas, Spain) were purchased from the local markets, Sofia, Bulgaria.

Simulated deep frying. Oil samples (5g) were placed into glass vessels with an internal diameter of 12 mm and heated continuously at $180 \pm 5°C$ in an oven. At certain time intervals, samples from the oils were taken away and stored at -18°C until the parameters characterizing oxidation process were determined.

Ga*s chromatography of fatty acid methyl esters.* Fatty acid methyl esters (FAME) were prepared by acid-catalysed transesterification of the oil samples using 1% sulfuric acid in methanol [9]. If needed, the FAME were purified on silica gel G TLC plates developed with hexane-acetone (100:8, v/v) mobile phase. GC of the FAME was performed on a Shimadzu GC-17A gas chromatograph (Shimadzu Corp., Kyoto, Japan) equipped with a 30 m x 0.25 mm x 0.25 µm INNOWAX capillary column (Agilent Technologies, USA). The temperature gradient started from 165°C increased to 230°C with 4°C/min and held at this temperature for 15 min; injection volume was 1 µl. Injector and detector temperatures were 260°C and 280°C respectively. Nitrogen was the carrier gas at flow rate 0.8 ml/min. The analyses were performed in triplicate.

Determination of peroxide value (PV). The peroxide value was determined by modified iodometric method [10].

Measuring the content of conjugated dienes (CD) and trienes (CT). Content of conjugated dienes as absorbance at 232 nm (A_{232nm}) and content of conjugated trienes as absorbance at 270 nm (A_{270nm}), were determined by dissolving weighed-out samples in isooctane (0.1%) and reading the sample absorbance at 232 nm (A_{232nm}) and 270 nm (A_{270nm}), using a Cecil Series 8000 UV/VIS double-beam scanning spectrophotometer (Cecil Instruments Ltd., Cambridge, UK). The

A_{232nm} (1%) and A_{270nm} (1%) were calculated from the absorbance reading.

Determination of the oxidative stability. Oxidation at 100°C ($\pm 0.2°C$) was carried out by blowing air through the samples (2 g) in the dark at a rate of 50 ml/min. The process was followed by withdrawing samples at measured time intervals and estimating the degree of oxidation by determination of PV. Kinetic curves of PV accumulation were plotted. All of them represent a mean result of three independent experiments.

Determination of the amount of unchanged triacylglycerols (TAG) and total polar components (TPC). The amount of unchanged triacylglycerols (TAG) and polar components (PC) was determined after their separation by preparative thin-layer chromatography [11]. The developing system used was hexane – acetone (100:10). Upon registration of the triacylglycerol zone, the layers containing triacylglicerols and those corresponding to the polar components were scrapped off, transferred to glass columns and eluted with chloroform and methanol (2:1). The solvents were evaporated and test-tubes were weighed until constant weight was reached.

Statistical analysis. The coefficient of variation for the PV determination was 7-8% irrespective of the measured value. The reported values for the IP were a mean result from three independent experiments. The coefficient of variation ranged from 6-13% and was inversely related to the induction period. Linear relationships between parameters investigated were obtained using the Linear fit tool of Origin 6.1 software (OriginLab Corporation, One Roundhouse Plaza, Northampton MA, USA).

RESULTS AND DISCUSSION

The characteristics of the oils used in these experiments are given in Table 1. During heating each oil sample was analyzed periodically for PV, oxidation stability (IP determined at 100°C), absorption at 232 nm, absorption at 270 nm, fatty acid composition (18:2/16:0 ratio) and the content of total polar components (TPC).

Peroxide value (PV)

Whereas storage of oil leads to increases in peroxide value (PV), the use of oils for frying does not lead to substantial increases in PV because peroxides decompose spontaneously above 150°C [12, 13]. The changes in PV during heating of the oils investigated are presented in Fig. 1. It is shown that PVs are not representative for changes occurring with oil samples during heating at 180°C.

Table 1. Initial characteristics of the refined vegetable oils used in the experiments

Vegetable oil	PV (meq kg-1)	IP (h)	A232 (1%)	A268 (1%)	TPC (%)	Fatty acid composition					
						C16:0	C18:0	C20:0	C18:1	C18:2	C18:3
Sunflower	8.8	6.7	3.65	3.27	5	7.4	4.1	0.2	25.6	62.7	0.0
Grape	5.7	10.2	3.95	3.21	9	6.9	3.4	0.2	22.1	66.8	0.5
Soybean	4.0	11.5	5.07	4.29	5	9.8	3.4	0.6	25.1	55.6	5.6
Corn	6.9	12.0	3.35	1.51	7	10.4	1.8	1.0	28.1	58.5	1.0
Olive (pomace)	8.9	30.0	3.62	1.25	6	11.5	3.2	0.4	75.3	9.0	0.6
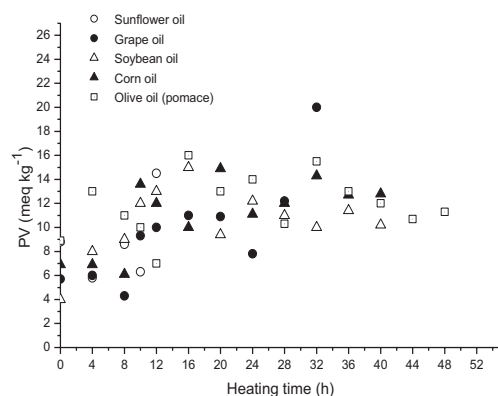
Fig. 1. Changes in the peroxide values (PV) of the oils during heating at 180°C.

Fig. 2. Kinetic curves of peroxides accumulation during heating of corn oil after: 0 – 0 h; 1 - 10 h; 2 – 20 h; 3 – 24 h; 4 – 32 h; 5 – 36 h.

Oxidation stability

The oxidation stability (or induction period, IP) is defined as the time during which the oil's natural resistance to oxidation, due to the presence of naturally occurring antioxidants, inhibits oxidation [13]. Vegetable oils contain a range of components such as tocopherols, phenolics, sterols, etc. which are beneficial to oil stability during heating. Fig.2 illustrates, by way of example, the kinetic curves of peroxides accumulation during heating of corn oil. After processing all the kinetic curves obtained, the lengths of the IP were determined. It was established that the IPs decrease gradually with increasing thermal treatment in all oils investigated (Fig. 3). From the values of the regression line slopes, the rates of the decrease of oxidation stability (RDOS) are determined (Table 2). As shown from the results the values of RDOS decreased in the following order: olive oil ≈ sunflower oil > grape seed oil > soybean oil ≈ corn oil. Obviously, the oils rich in γ-tocopherol, in this paper soybean and corn oils [14] showed higher oxidation stabilities during treating at high temperature.
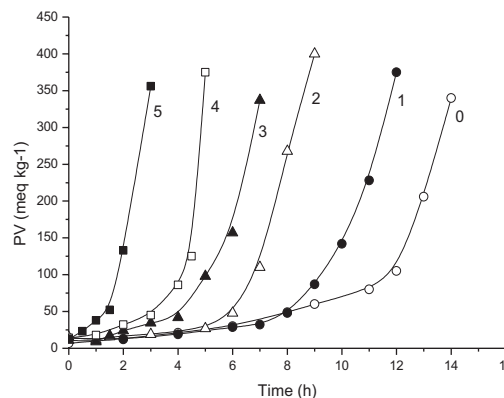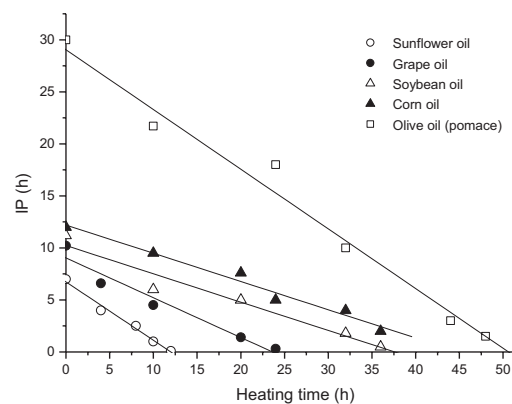

Fig. 3. Dependence of the induction periods (IP) on the heating times (h) of the oils.

Content of conjugated dienes (A_{232nm})

Thermal oxidation of unsaturated fatty acids is accompanied by considerable isomerization of double bonds leading to products containing *trans* double bonds and conjugated double bond systems [13].

From the Fig. 4A it is seen that UV absorbance at 232 nm tends to increase initially and then

plateau off during later stage of heating fat deterioration. This has been related to the establishment of equilibrium between the rate of formation of CD and the rate of formation of polymers formed by a Diels Alder reaction [4]. From the values of the regression line slopes the rates of CD accumulation (RCDA) during the first step of heating were determined (Fig.4B, Table 2). The results showed that the RCDA decreased in the following order: sunflower > grape seed > soybean > corn >olive oil. These data indicated that with respect to CD accumulation olive oil is most stable and among polyunsaturated oils - corn and soybean oils.

Table 2. Regression coefficients and coefficients of determination (r^2) from the linear regression of PV and CD

| Vegetable oil	Rate of the decrease of IP	Rate of CD accumulation	Rate of the decrease C18:2 / C16:0 ratio
Sunflower	$Y = 6.7 - 0.561x$ $r^2 = 0.986$	$Y = 2.6 + 1.64x$ $r^2 = 0.982$	$Y = 8.6 - 0.101x$ $r^2 = 0.682$
Grape	$Y = 9.0 - 0.382x$ $r^2 = 0.954$	$Y = 3.7 + 1.07x$ $r^2 = 0.998$	$Y = 9.8 - 0.092x$ $r^2 = 0.956$
Soybean	$Y = 10.2 - 0.272x$ $r^2 = 0.953$	$Y = 5.3 + 0.82x$ $r^2 = 0.992$	$Y = 5.6 - 0.032x$ $r^2 = 0.870$
Corn	$Y = 12.2 - 0.271x$ $r^2 = 0.976$	$Y = 3.1 + 0.73x$ $r^2 = 0.998$	$Y = 5.6 - 0.020x$ $r^2 = 0.910$
Olive (pomace)	$Y = 29.5 - 0.586x$ $r^2 = 0.981$	$Y = 3.2 + 0.34x$ $r^2 = 0.960$	$Y = 0.8 - 0.007x$ $r^2 = 0.996$
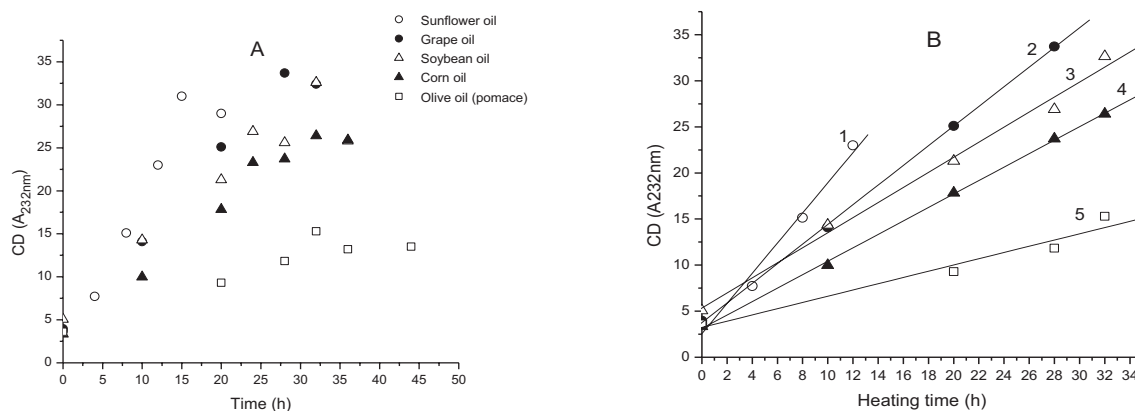
Fig. 4. Dependence of the content of conjugated dienes (A_{232nm}) on the heating times (h) of the oils: 1 – sunflower oil; 2 – grape seed oil; 3 – soybean oil; 4 – corn oil; 5 – olive (pomace) oil.
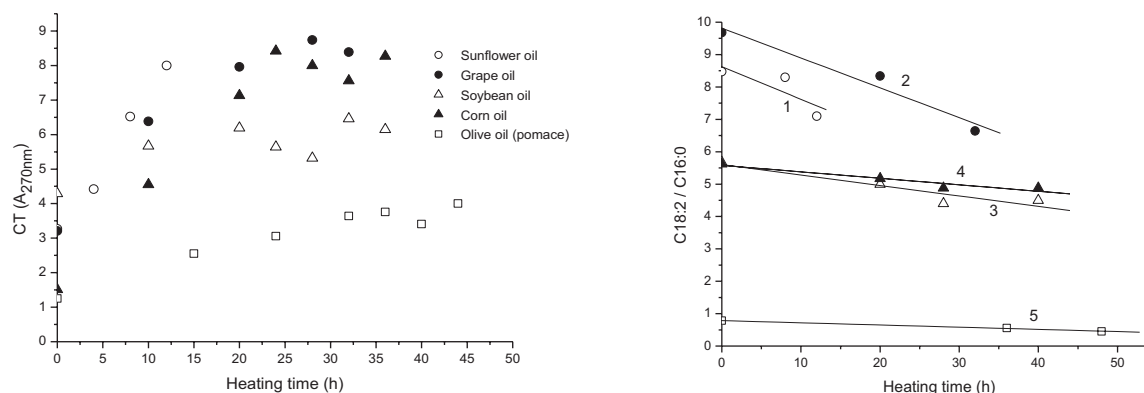

Fig. 5. Dependence of the content of conjugated trienes (A_{270nm}) on the heating times (h) of the oils.

Fig. 6. Dependence of the changes in C18:2/C16:0 ratio on the heating times (h) of the oils: 1 – sunflower oil; 2 – grape seed oil; 3 – soybean oil; 4 – corn oil; 5 – olive (pomace) oil.

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Content of conjugated trienes (A_{270nm})

Conjugated trienes absorbing at 270 nm are produced by linolenate oxidation products or by dehydration of hydroxylinoleate [13]. The results presented on Fig.5 show, that there was a trend of increasing triene content with the increase in heating time. This process is less pronounced in olive oil. In soybean oil conjugated trienes decompose more rapidly than in other oils.

Change in C18:2 C16:0 ratio

Monitoring of fatty acid changes in oils during deep fat frying is an effective method to assess thermal oxidative changes in the oils [15]. Linoleic acid content is frequently used as an indicator of the degree of oil degradation, since the polyunsaturated linoleyl chain is highly susceptible to oxidation. [16] found that changes in C18:2/C16:0 ratio was an effective parameter for assessing oxidation of oils. From Fig. 6, it can be seen that the C18:2/C16:0 ratio declined as time of heating is increased. From the values of the regression line slopes the rates of decrease in C18:2/C16:0 ratio (RD 18:2/16:0) were determined (Table 2). The results showed that this parameter decreased in the same order as RCDA: sunflower > grape seed > soybean > corn >olive oil.

Total polar components (TPC)

The content of total polar components (TPC) in used deep frying fats is until today an important criterion for assessing the decrease of fat quality [17]. TPC are considered to be nonvolatile compounds having a higher polarity than triacylgly-
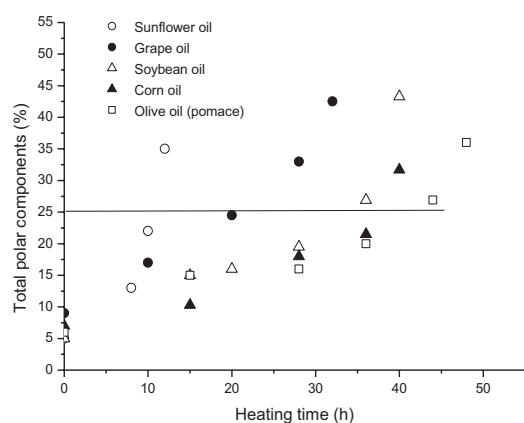

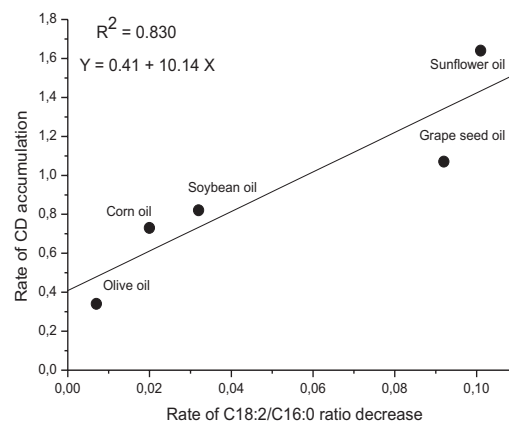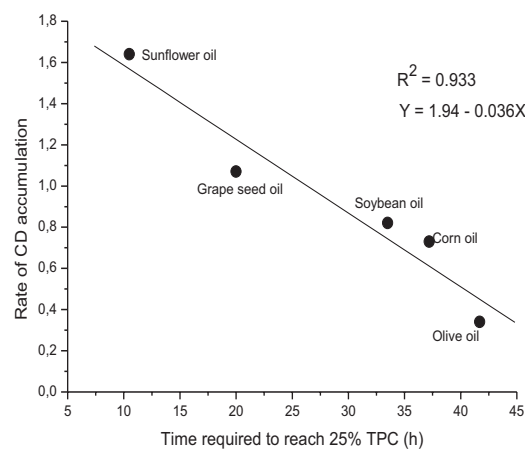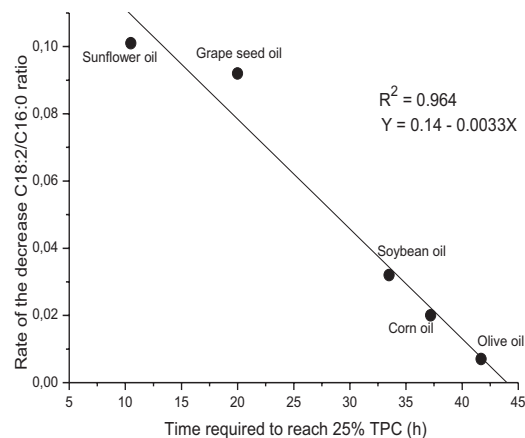**Fig. 7.** Changes in total polar components (TPC) on the heating times (h) of the oils.

Fig. 8. Correlation between some parameters characterizing changes in the vegetable oils during heating at 180°C.

cerols, resulting from thermal, hydrolytic and oxidative alteration [18]. In several European

countries the maximum value for TPC is between 24 and 27% for commercial frying oils [19-21]. Research has shown that the fraction of polar components isolated from oxidized oils is the most toxic to laboratory animals [22]. In all oils, examined in this study, TPC content increased throughout the heating period. The results are presented on Fig. 7. Assuming that the limit of acceptance for the TPC is 25%, the time required to reach this limit differed for the oils examined and were: olive oil (41.7 h) > corn oil > (37.2 h) > soybean oil (33.5 h) > grape seed oil (20.0 h) > sunflower oil (10.5 h).

Some correlations between monitored parameters are presented on Fig. 8. The best one was observed between the rates of decrease in C18:2 / C16:0 ratio and total polar components.

CONCLUSIONS

The results revealed that olive oil has better stability against thermal oxidation when compared to polyunsaturated oils, which is due to fatty acid composition. On the other hand, corn and soybean oils (among unsaturated oils) are most resistant to oxidation at frying temperature.

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ОКИСЛИТЕЛНИ ПРОМЕНИ В РАСТИТЕЛНИ МАСЛА, НАГРЯВАНИ ПРИ ТЕМПЕРАТУРА НА ПЪРЖЕНЕ

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(Резюме)

Изследвани са окислителните промени в рафинирани слънчогледово, гроздово, соево, царевично и маслиново масла при 180°С (условия на пържене). Определени са следните параметри: пероксидно число (ПОЧ), окислителна стабилност (ИП), съдържание на спрегнати диени като абсорбция при 232 нм ($A_{232нм}$), съдържание на спрегнати триени като абсорбция при 270 нм ($A_{270нм}$), промени в мастнокиселинния състав (съотношение С18:2/С16:0) и съдържание на тотални полярни компоненти (ТПК). Резултатите показаха, че маслиновото масло е с най-висока стабилност при термично третиране. Сред полиненаситените растителни масла с най-висока стабилност се характеризират царевичното и соевото масла. Най-добра корелация е регистрирана между скоростта на намаление на съотношението С18:2/С16:0 и тоталните полярни компоненти.