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TECHNOLOGYRESEARCH ON QUALITY OF FOOD FRYING OILS USED IN COMMERCIAL
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ABSTRACT

The aim of this research is to evaluate the quality of oils used in the frying process in commercial restaurants. Oil samples were collected from deep fryers in two commercial restaurants in the area of Bosnia and Herzegovina. One of the restaurants used partially hydrogenated oil and the other sunflower oil. The analysis samples were collected during one 12-hour shift, in two-hour intervals. Physico - chemical parameters, changes in fatty acid composition during frying, and the presence of metals were analyzed.

The research results have shown that there is a statistically significant difference ($p < 0.05$) between all analyzed parameters, for both types of oils. During frying, the composition of fatty acids for both oils changes significantly. Total oxidation value for partially hydrogenated oil was increased from 2.165 to 55.983 mg/kg oil, and for sunflower oil from 15.332 to 153.888 mg/kg. During frying, there is an increase in the metal content ($p < 0.05$) in the tested oils.

KEYWORDS: sunflower oil, partially hydrogenated oil, food frying.

1. INTRODUCTION

Deep fried food has a long tradition, and nowadays frying is one of the most common food preparation procedures around the world. During the frying process, the food acquires a crispy structure, pleasant aroma and taste, which is probably one of the reasons for frequent consumption of food prepared by the deep frying process in deep fryers [1,2]. Consumers prefer to consume fried foods, regardless of being well informed that this type of food is not recommended for frequent consumption. Public health systems, in most world countries, make efforts to educate consumers well about the high probability of the harmful effects of fried food on human health.

Despite this fact, the consumption of fried food is constantly growing, especially due to the significant social, economic and technological changes taking place in society in general, which is why most of the population most often consumes food outside their homes. This has led to the accelerated development of ready-to-eat food technology, commercial restaurants, collective food systems, as well as the offer of fried food in direct sales, most often as ready meals. Consumption of food products obtained in frying processes is constantly growing due to the fact that fats and oils have a high heat capacity, which allows heat transfer at temperatures significantly higher than the boiling point of water [3]. This allows a very fast food preparation, compared to other food preparation methods. This fact makes edible oils and fats the most appreciative media for food preparation both in commercial restaurants and in the ready-to-eat food industry, the snack product industry, and in smaller fast food preparation facilities, the number of which is not negligible. Also, The conditions to which food are submitted during the frying process initiate physical and chemical changes that depend on the composition of the food, and affect the development of color, flavor, and taste, besides changing [4].



According to previous researches, it is known that oil is absorbed into food in the amount of 8 to 25 % during frying, depending on the type of food being fried and the conditions of the frying process [5]. In this way, frying oil becomes a basic ingredient in fried food. Despite, efforts to reduce the amount of oil absorbed in food frying processes, fried foods often contain over 30% absorbed frying oil [6].

The process of food frying in deep oil takes place at temperatures of 150–190° C, in the presence of atmospheric oxygen and moisture, where frying oils are subject to a large number of physico-chemical changes that usually occur at temperature of about 175°C or higher [7, 8, 9,10,11].

These changes usually involve the development of oil hydrolysis reaction, and oil oxidation (autooxidation, thermal oxidation and polymerization), with a large number of harmful compounds occurring in frying oils that cause oil decomposition [7, 8, 12, 13]. The types and quantities of the resulting decomposition products differ in accordance with the frying process conditions, and in addition to the hydrolysis and primary oxidation products, the products of secondary oxidation, usually aldehydes, are also formed.

Due to the harmful effects of frying products, this area has been in the center of interest of both the food industry and nutritionists, as well as public health worldwide for many years. In order to improve the health safety of fried foods, a large number of developed countries in the EU and the world have enacted special legislation on the quality of oils intended for food frying. Such legislation prescribes the maximum permitted values of the reaction products that occur during the food frying process, and which are most often harmful to human health. In addition, the legislation prescribes some parameters of the frying process, such as the maximum allowed frying temperature, the duration of frying, the obligation to change the oil in fryers, etc.

Due to the fact that Bosnia and Herzegovina has not yet adopted special legislation on the quality of oils used in frying processes, and legislation on limit values of frying parameters, nor on the maximum permissible concentrations of products resulting from chemical reactions during frying process, quality research of frying oils in commercial restaurants can certainly be considered a priority. Likewise, the conducted research could provide initial information, which would be used to develop guidelines for fried food producers, and which would contain specific instructions governing the oil quality and frying process management, because from the experience of other countries it is known that without regulations on limit values of frying products, and a precisely determined maximum frying temperature and defining the frequency of oil change in the fryer, it is not possible to ensure the health safety of fried food.

In this paper, some of the parameters of frying oil quality are examined, with the aim of obtaining information on the health safety of fried food consumed in commercial restaurants in Bosnia and Herzegovina. In addition, the obtained results can provide useful data for the adoption of special legislation on the frying oils quality, and the conditions for food frying in commercial restaurants in Bosnia and Herzegovina.

2. MATERIALS AND METHODS

Sampling

Frying oil samples, used in this research, were collected from two commercial restaurants, of medium capacity (80-100 seats). The restaurants are randomly selected in Bosnia and Herzegovina. One of the restaurants used partially hydrogenated vegetable oil for food frying processes, while the other restaurant used standard sunflower oil. Both restaurants used professional fryers for food frying, and during the frying process, different types of food were treated, primarily vegetables and meat. The treatment of food in the fryer lasted from a few seconds to a few minutes, since different types of food were fried. Oil samples were collected at intervals of every 2 hours, during one shift of 12 hours. The first oil sample was taken in the morning, during the first filling of the fryer (0 h of frying), before the start of the frying process, and later samples were taken after 2, 4, 6, 8, 10 and 12 hours of frying. Oil samples were taken in quantity of about 500 ml, directly from the fryer, into appropriate sampling vessels, closed and labeled, and stored in the refrigerator during the analysis. All physical and chemical analyzes were performed with three replicates, and a statistical analysis of the obtained results was performed.

Physico - chemical parameters of oils

Physico - chemical analyses, before and during the frying period were determined by Standard IUPAC methods as follows [15]:

The acid value is a measure of the oil hydrolysis degree, and is defined as the value of milligrams of KOH required to neutralize free fatty acids in 1g of oil. The oil sample was titrated with ethyl ether - ethanol mixture (1:1), previously neutralized with NaOH, with phenolphthaleine as indicator, according to the Standard IUPAC method (2.201). The acid value is expressed as the percentage of free fatty acids (oleic), % FFA.

The saponification value represents mg of KOH, required for complete saponification of free fatty acids in 1 g of oil. Saponification of the oil was performed using an alcoholic solution of KOH, in accordance with the Standard IUPAC method (2.202). The saponification value is expressed as mg KOH/g oil.

The iodine value expresses the oil unsaturation degree as mg J₂ which is added to the unsaturated fatty acids from 100 g of oil. Chloroform (trichloromethane, CHCl₃) was used for the oil sample dissolution, and it was treated with iodine monobromide, which is added to the double bonds of unsaturated fatty acids. After that, potassium iodide was added, and titration with sodium thiosulfate solution was performed. Along with the main test, a blind test was performed. The analysis procedure and results calculation was performed according to the Standard IUPAC method (2.205).

The refraction index of oil samples was determined by measuring the light bending index, refractometrically, according to the Standard IUPAC method (2.102), using ABBE- refractometer, model 2WAJ, measurement range n_D = 1.300 – 1.700.

Oxidative parameters of oils

The peroxide value (PV) represents the primary oxidation degree of fats and oils at which peroxides are formed, as the primary products of oil oxidation. The oil sample was treated with a mixture of glacial acetic acid and chloroform with the addition of potassium iodide. The released iodine was titrated with a standard solution of sodium thiosulfate, with vigorous shaking to release all the iodine from chloroform. A blind test was performed under the same conditions. The peroxide value is expressed in milliequivalents of active oxygen per kg of oil (meqO₂/kg oil). The analysis procedure and results calculation were performed in accordance with the Standard IUPAC method (2.501).

The determination of 2-thiobarbituric acid (TBA) was performed according to the Standard IUPAC method (2.531), and serves for the general assessment of the oxidation degree of fats and oils. Thiobarbituric acid, with oxidation products, in this case malondialdehyde, at an absorbance of 530 nm gives a characteristic pink color, which is extracted in organic solvents and shows the presence of secondary oxidation products. Preparation of TBA - reagent was performed according to the Standard IUPAC method (2.531), and was used in further analysis. To determine the oil TBA value, 50 - 200 mg of the oil sample was weighed and dissolved with a small amount of 1- butanol. Then top up the volumetric vessel to the mark. The prepared sample in the amount of 5 mL was transferred to a test tube, 5 mL of TBA reagent was added and shaken well. The sample was placed in a water-bath at 95 ° C for 120 minutes. There after, the sample was cooled under running water, approximately 10 minutes until it reached room temperature. Spectrophotometric measurements were performed using a UV Vis spectrophotometer (UV mini 1240 - Shimadzu) with a UV ray interval of 320 - 560 nm. The calculation was done according to the above method, the equation (i):

$$TBA = 50 \times (A - B) / m \quad (i)$$

Wher is A – absorbance of the tested solution, B – absorbance of the blind test, m - weighed sample amount in mg, 50- correction factor (if the volumetric flask is of 25 mL and cuvette is of 10 mm). The results are expressed as milliequivalent of TBA per kilogram of oil (meq/kg oil).

Determination of *para* - anisidine value (p - AnV) allows a clear insight into the amount of non - volatile carboxylic compounds representing secondary products of oil oxidation, with aldehydes being most commonly formed. These products are formed by the decomposition of unstable primary oxidation products, hydroperoxides.

The analysis was performed in accordance with the Official method (ISO 6885:2012). The reagent anisidine was prepared in a 50 mL volumetric flask by dissolving 0.125 g of p-anisidine (4-methoxyaniline) in a small amount of glacial acetic acid and then adding up to the mark with the same solvent, avoiding the action of strong light on the reagent. The sample was prepared by weighing a precisely determined amount of 0.05 - 2.00 mg of the test sample into a 25 mL volumetric vessel and dissolved with a small amount of isooctane. A non - reactive solution was prepared with 5 mg of test sample in 1 mL of glacial acetic acid, shaken well and left in place for 8 minutes. The reacting solution is prepared with exactly 5 mL of the previously prepared test sample to which 1 mL of anisidine reagent has been added, shaken well and allowed to stand in the dark place for 8 minutes. The blind test was prepared with 5 mL of isooctane and 1 mL of anisidine reagent, shaken well in a test tube and left for 8 minutes in a dark place. The absorbance was measured at 350 nm, and a UV VIS spectrophotometer - UVmini 1240 (Shimadzu) with a UV interval of 320 -560 nm was used for analysis. The calculation was done according to the above method, equation (ii):

$$p - AnV = \frac{100 \times Q \times V}{m} [1,2 \times (A_1 - A_2 - A_0)] \quad (ii)$$

Where is V – volume in which the sample was dissolved (25mL), m – mass of the sample in g, Q – sample amount, based on p- anisidine solution, mg/mL, A₀ – absorbance of unreacted tested solution, A₁ – absorbance of the reacting solution, A₂ – absorbance of the blind test, and 1,2 – correction factor. The results are expressed as milliequivalents of per kilogram of oil (meq/kg oil). The determination of the total oxidation value (Totox value) was determined according to the Official method (ISO 6885:2012). Peroxide value (PV) are used in the calculation, in combination with p – AnV it is used to determine the total oxidation value of oil or the Totox value. Totox value is calculated according to equation (iii):

$$Totox \text{ value} = 2 \times PV + AnV \quad (iii)$$

Determination of fatty acid content

Analysis of fatty acid content in oil samples was done according to the Standard method (IUPAC 2.301). For analysis, the standards are typically dissolved in hexane at a 0.01% - 0.1% (w/v) concentration. Weigh 100 mg sample in a 20 mL test tube with screw cap, and dissolve the sample in 10 mL hexane. Add 100 µL 2 N potassium hydroxide in methanol (11.2 g in 100 mL). Close the tube for 30 s, and centrifuge. Transfer the clear supernatant into a 2 mL autosampler vial. The fatty acid content was determined by GC/FID gas chromatography, using AGILENT-7890A device, with HP-INNOWAX column (0.25 mm x 30 m).

Determination of metal content

Metals content determination was performed in three replicates, according to Official method (ISO 11466:1996) for extraction of trace elements, using ICP OES Optima 2100 DV (Perkin Elmer). To determine the metal content in the oil samples, 3.0 g of the oil sample were weighed, with the 0,001 g accuracy, in a 250 mL reaction flask. The sample was moistened with 0.5 to 1.0 mL of water, and, with stirring, 21 mL of HCl was added, followed by 7 mL of nitric acid, dropwise to reduce foaming. 15.0 mL of nitric acid was added to the absorption flask, and the absorption flask and condenser were connected with the reaction flask and left at room temperature for 16 h for slow organic matter oxidation. After 16 hours, the reaction flask was heated, gradually raising the temperature to maintain refluxion for 2 h, ensuring that the condensation zone was lower than 1/3 of the condenser height, and then the mixture was cooled. Thereafter, the content of the absorbent flask was quantitatively transferred to the reaction flask, through the condenser, rinsing both the absorbent flask and the condenser with additional 10 mL of HNO₃. After boiling, the reaction flask was placed to stand, to allow the undissolved particles to pass into suspension. The clear part was then carefully decanted onto filter paper (No. 5.119), collecting the filtrate in a 100 mL volumetric flask. After passing the entire amount of initial filtrate through the filter paper, wash the undissolved particles on the filter paper with a minimum amount of HNO₃. All the obtained filtrates were combined, and the extract prepared in this way was ready for the determination of trace elements.

Statistical analysis

The results are presented as mean value and standard deviation, of three replicates, and are analyzed by various statistical analyzes, including T-test, standard deviation and analysis of variance (ANOVA), using SPSS software (version 22). Duncan's test was used to rank the samples, and to determine the statistical significance between the examined samples (P < 0.05).

3. RESULTS AND DISCUSSION

For commercial restaurants, the availability and price of frying oil represent the most important factors of economic sustainability, because food absorbs a significant amount of frying oil during frying. In addition, other factors are important for the choice of frying oil, such as oil expiration date, acceptable sensory and oil nutritional properties, and it is known that these properties largely depend on the physico-chemical oil properties and fatty acids composition [10,11,12]. The tested physico-chemical oil properties, in addition to assessing the oil quality, are often used as parameters of oil identification.

Consideration of oil quality parameters before the frying process

The results obtained in this research have shown that the oils, in the fresh state (0 hours of frying), had a free fatty acid (FFA) content of 0.54 % for HO and 0.35 % for SO, and that there is no statistically significant difference ($p < 0.05$) in the content of FFA in fresh oils (Table 1.). The obtained results show that the values of FFA for both tested oils are increased in relation to the value of free fatty acids (0.3 % FFA as oleic), prescribed by the Rulebook on edible vegetable oils, edible vegetable fats and mayonnaises (Official Gazette of Bosnia and Herzegovina, No.21/11).

Table 1. Physico-chemical properties of frying oils

Frying duration in hours (h)	Type of oil	Saponification Value	Free fatty acids Value	Iodine Value	Refractive Index
		(mgKOH/g oil)	% FFA	(mg I ₂ /100 g oil)	-
0	HO	194.55 ± 0.47 ^a	0.54 ± 0.00 ^a	78.85 ± 0.04 ^g	1.4703 ± 0.00 ^a
	SO	186.48 ± 0.08 ^b	0.35 ± 0.00 ^a	125.033 ± 0.03 ^g	1.4746 ± 0.00 ^a
2	HO	220.86 ± 0.75 ^{a,b}	0.69 ± 0.00 ^b	76.75 ± 0.04 ^f	1.4715 ± 0.00 ^b
	SO	210.87 ± 0.01 ^a	0.52 ± 0.00 ^c	122.19 ± 0.02 ^e	1.4753 ± 0.00 ^b
4	HO	231.63 ± 7.26 ^d	0.92 ± 0.00 ^c	74.92 ± 0.06 ^e	1.4720 ± 0.00 ^{c,d}
	SO	227.75 ± 0.03 ^g	0.51 ± 0.00 ^b	122.44 ± 0.04 ^f	1.4754 ± 0.00 ^b
6	HO	219.17 ± 0.85 ^a	1.23 ± 0.00 ^g	71.27 ± 0.02 ^d	1.4725 ± 0.00 ^e
	SO	223.24 ± 0.06 ^d	0.67 ± 0.00 ^d	120.16 ± 0.12 ^d	1.4762 ± 0.00 ^e
8	HO	229.27 ± 1.10 ^{c,d}	1.04 ± 0.00 ^d	61.30 ± 0.06 ^c	1.4716 ± 0.00 ^{b,c}
	SO	226.56 ± 0.02 ^f	0.76 ± 0.00 ^e	119.11 ± 0.03 ^c	1.4754 ± 0.00 ^b
10	HO	225.06 ± 0.19 ^{b,c}	1.08 ± 0.00 ^f	60.88 ± 0.53 ^b	1.4721 ± 0.00 ^{d,e}
	SO	222.26 ± 0.03 ^c	0.93 ± 0.00 ^f	116.47 ± 0.04 ^a	1.4762 ± 0.00 ^e
12	HO	221.43 ± 0.95 ^{a,b}	1.06 ± 0.00 ^e	54.22 ± 0.01 ^a	1.4722 ± 0.00 ^{d,e}
	SO	223.55 ± 0.02 ^e	0.93 ± 0.00 ^f	117.50 ± 0.02 ^b	1.4753 ± 0.00 ^b

Mean values (± standard deviation) abcdefg– (different superscript letters within the same column indicate significant difference ($p < 0,05$); HO- hydrogenated oil; SO - sunflower oil

The results of the iodine value for both tested oils are in accordance with the stated legislation, and the iodine value for HO is 78.85 mg I₂/100 g of oil, while for SO the iodine value is 125.033 mg I₂/100 g of oil (Table 1).

The results for the iodine value are in accordance with the fatty acid composition of the tested fresh oils, because the fatty acid composition of SO dominated by linolenic acid (C18:2) 60.923 %, while the composition of HO is dominated by oleic (C: 18:1) 43.850 % and palmitic fatty acid (C16: 0) 39.233 % (Figure 2.).

The obtained values of the refractive index of fresh oils are 1.4703 for HO, and 1.4746 for SO and they do not show a statistically significant difference ($p > 0.05$) between the tested oils (Table 1).

The results for the value of the saponification value are also in accordance with the stated legislation, and for HO the saponification value is 194.55 mg KOH/g of oil, and for SO the saponification value is 186.48 mg KOH/g of oil, and have shown a statistically significant difference between the tested oils (Table 1).

Oxidative parameters of fresh oils have shown a statistically significant difference in peroxide values between the two tested oils. For HO, the peroxide value is 0.473 meq O₂/kg of oil, while for fresh SO the peroxide value is 0.569 meq O₂/kg of oil, which is in accordance with the legislation in Bosnia and Herzegovina, because prescribed maximum permitted peroxide value is 7 meqO₂/kg of oil (Rulebook on edible vegetable oils, edible vegetable fats and mayonnaises/Official Gazette of Bosnia and Herzegovina, No.21/11).

Observing the parameters of secondary oil oxidation, it can be seen that the values of 2- thiobarbiturate acid (TBA) of the tested oils were 1.335 meq/kg for HO, and 2.915 meq/kg for SO. The obtained p-anisidine value was 1.219 meq/kg for HO, while for SO it was 14.763 meq/kg and showed statistically significant differences between the tested oils .

The total oxidation value of the tested oils (Totox value), obtained on the basis of the PV and p - AnV, was 2.165 meq/kg for (HO) and 14.763 meq/kg for SO (Table 3).

From the obtained values of oxidative parameters it is clear that SO shows a tendency to faster oxidation compared to HO, which is in accordance with the fatty acid composition of the tested oils (Table 2; Figure 3).

The development of oil oxidation reactions is greatly contributed to by the presence of metals in frying oils, whether they are present in traces after the oil hydrogenation process or have entered the frying oil from the food being fried. Metal content in fresh oils is also in accordance with the legislation for edible oils and fats (Rulebook on maximum permitted quantities for certain contaminants in food / Official Gazette of Bosnia and Herzegovina, No.68/2014). The copper content for HO is 0.09 mg/kg of oil, while for SO the copper content is 0.02 mg/kg of oil (Table 4). The iron content for HO is 0.04, while for SO it is 0.03 mg/kg. The nickel content is 0.06 mg/kg for HO, while for SO the nickel content is 0.02 mg/kg of oil .

Also, the obtained results for manganese and zinc for HO are 0.45 mg/kg for manganese, and 0.13 mg/kg of oil for zinc. For SO, the results of manganese and zinc content are 0.32 mg / kg of oil and 0.42 mg/kg of oil, respectively. Also, during the analysis of the metals presence in the oil samples, the presence of cadmium was not identified in any of the samples (Table 2).

Changes in physico-chemical parameters during the frying process

During the frying process, the FFA contents for HO are from 0.69 % FFA to 1.23 %, while the FFA values for SO ranged from 0.52 % to 0.93 %. Comparing the obtained results with the research of the authors Yilmaz and Aydeniz [10] where the FFA content is in the range of 0.856 - 4.083 % FFA, it is noticeable that the values obtained in this research are significantly lower, and there is a possibility of occasional addition of fresh oils during frying.

Also, the authors Freire *et al.* [16] found values for FFA in their study in the range of 0.19 % to 0.80 % and also explained with the possible addition of fresh oil to fryers, while the authors Sebastian *et al.* [2] obtained FFA values in the range of 0.080 % to 2.36 % during the frying process, and finally in the oil disposal 0.38 to 4.30 % FFA. Likewise, Flores *et al.* [11] found FFA content from 0.38 % to 1.48 %. In accordance with the increase in the value of FFA in this research, there is an increase in the saponification value for both tested oils (Table 1; Figure 1).

The iodine value, after 2 hours of frying, for hydrogenated oil is 76.75 mg I₂/100 g of oil, while for sunflower oil the iodine value after 2 hours of frying is 122.19 mg I₂/100 g of oil. During the further frying process, occurs a constant decrease in the iodine value for both tested oils (Table 1).

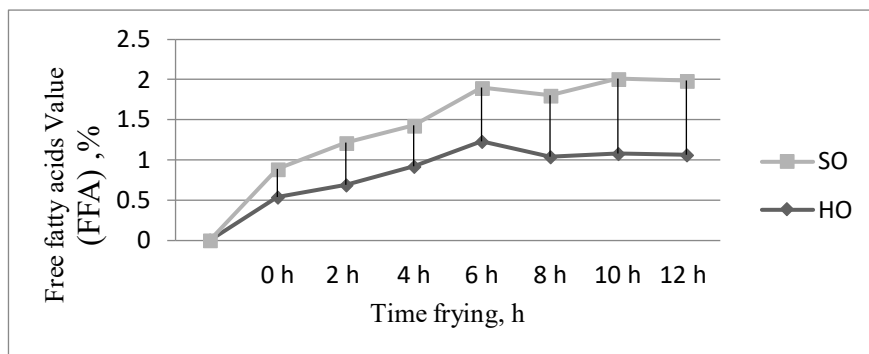


Figure 1. Free fatty acid value, % (HO - hydrogenated oil; SO- sunflower oil)

The appearance of a constant decrease in the iodine value, for both oils, during frying is in accordance with the changes in the fatty acids composition during the frying process. In correlation with the changes in the physico-chemical parameters of the oil during the frying process, changes in the refractive index value can be found, as an identification parameter of the oil (Table 1).

Changes in fatty acid composition

Observing the fatty acid composition of fresh oils, used in the research, it is shown that the fatty acid composition for SO is dominated by linoleic acid (C18:2) 60.923 %, followed by oleic acid (C18:1) 28.317 %, palmitic acid (C16:0) 6.633 % and stearic acid (C18:0) 3.327 % were significantly present, while other fatty acids were present to a lesser extent.

After 6 h of frying, the content (C18:2) decreases and it is 57.803 %, and after 12 h of frying the value (C18:2) is 55.203 %, which is correlated with the results of the authors [Abiona *et al.*, 2011; Alireza *et al.*, 2010;]. Also, these authors state that a significant decrease in the content (C18:2) in frying oil can be explained by the higher rate of oxidation at (C18:2), compared to oleic (C18:1) acid. Unlike linoleic (C18:2) acid, during the frying process in SO oil the content of oleic acid (C18:1) after 6 hours of frying increases (29.523 %), and after 12 hours of frying the content (C18:1) is 30.710 %, which is due to the lower rate of oleic acid oxidation (C18:1).

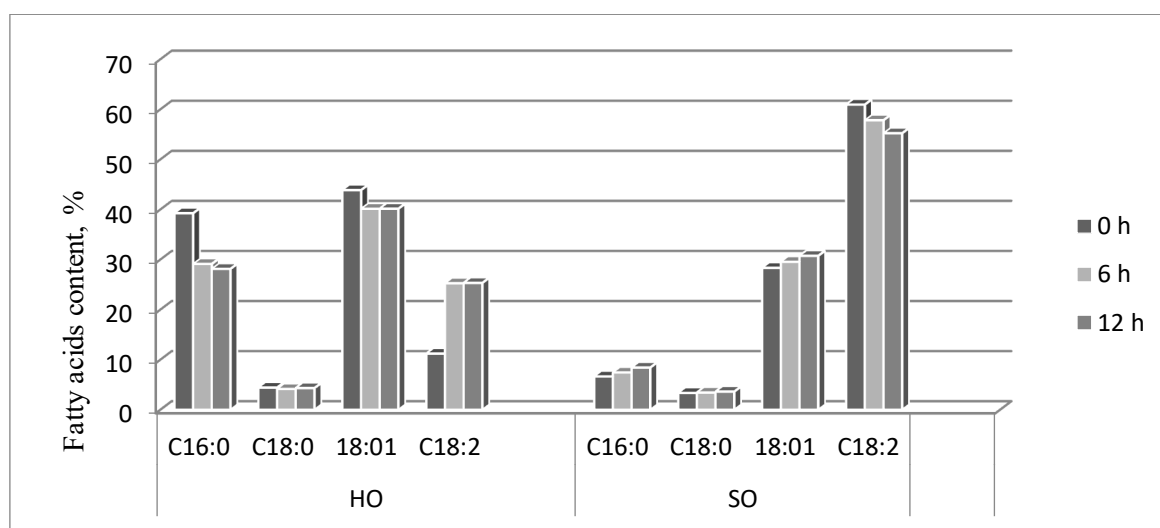


Figure 2. Changes in fatty acids composition of oils as affected by frying, (HO- hydrogenated oil; SO - sunflower oil)

The content of stearic acid (C18:0) in HO increases after 12 h of frying and is 4.403 % in fresh oil, 4.123 % (6 h of frying), and 4.300 % (12 h of frying), while for SO the stearic acid content (C18:0) is 3.327 %, 3.410 %, and 3.600 %, respectively. Also, the content of palmitic acid (C16:0) increases during the frying process, at the beginning it has a value of 6.633 %, after 6 hours of frying this value is 7.420 %, while for 12 hours of frying it is 8.400 % (Figure 2). The fatty acid composition for HO is dominated by oleic acid (C18:1) 43.850 %, and palmitic fatty acid (C16:0) 39.233 %, which confirms that it is also partially hydrogenated oil due to its high content (C18:1). During frying in HO, the content of oleic acid decreases, so after 6 hours of frying the content (C18:1) is 40,120 %, and after 12 hours of frying (C18:1) 40,133 %. According to the obtained results, there is no statistically significant difference in content (C18:1) for 6 hours and 12 hours of frying, which indicates better stability of oil with high content of oleic fatty acid, compared to oil dominated by linoleic (C18:2) acid (Figure 2).

After oleic acid (C18:1), in fresh HO the highest content has palmitic fatty acid (C16:0) 39.233 %, and this value is significantly reduced during the 6 hours frying process (29,100 %), while the content of palmitic acid does not change significantly in the period from 6 to 12 hours of frying (Figure 2).

The content of linoleic acid (C18:2) in fresh hydrogenated oil is 11.183 %, while the content (C18:2) after 6 hours of frying is significantly increased and is 25,240 %, and after 12 hours frying, the content (C18:2) is 25.310 %, and there is no statistically significant difference in content (C18:2) for 6 and 12 hours frying, and there is a possibility of adding fresh oil to the fryer (Figure 2). Based on the consideration of the dominant fatty acids composition in the oils used, it can be observed that HO after 6 hours and 12 hours of frying showed statistically significantly greater stability in terms of changes in fatty acid composition after 6 and 12 hours of frying, which is correlated with the obtained oxidation parameters of the analyzed oils.

Changes in oxidative parameters of oils

The considered results of frying oil oxidation parameters show that the value of peroxide during the frying process for HO is in the range of 0.473 to 1.463 meqO₂/kg, while for SO the peroxide value was in the range of 0.476 to 1,863 meq O₂/kg of oil (Figure 3). Although peroxides as primary oxidation products are the most commonly used parameter for assessing oil and fat oxidation, peroxides are very rapidly converted to secondary oxidation products and therefore cannot be considered the only parameter for assessing oil and fat oxidation in accordance with Flores *et al.* [11].

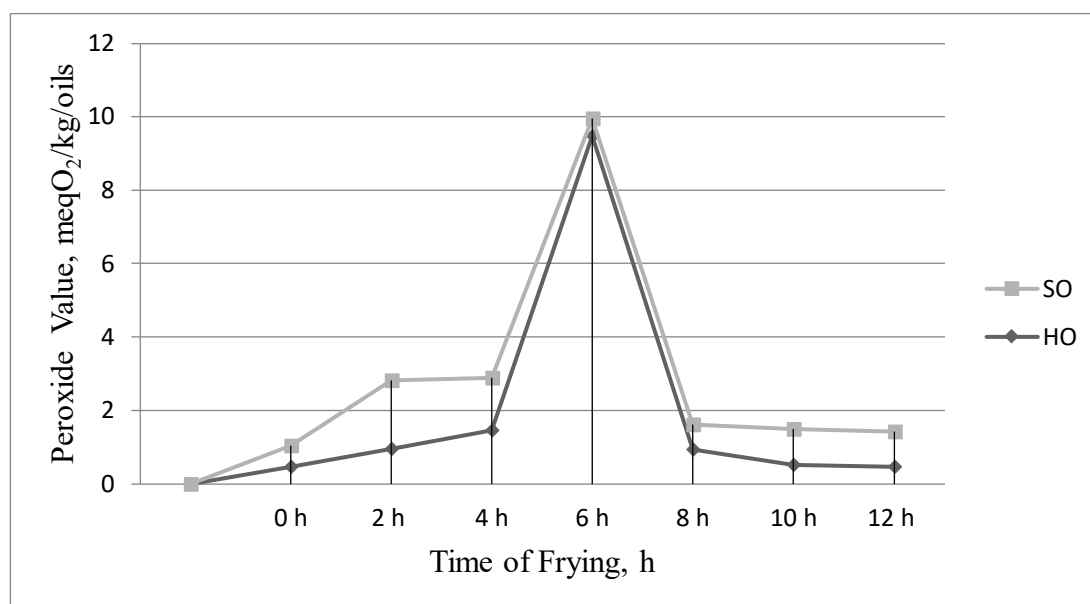


Figure 3. Peroxide Value, meq O₂/kg oils, (HO- hydrogenated oil; SO - sunflower oil)

According to statements made by A. Sebastian, et al [2], an increase in frying oil temperature can cause a decrease of peroxide value (PV) due to hydroperoxide decomposition. Comparing the results for the PV, the authors obtained different results, so during frying they obtained a peroxide value in the range of 3.3 meqO₂/kg to 48.1 meqO₂/kg, and M. Flores et al. [11] obtained a PV value in the range of 1.7 to 103.3 meqO₂/kg, while the authors Yilmaz & Aydeniz [10] in their study obtained PV in the range of 2.50 - 59.06 meqO₂/kg.

According to available research, it is noticeable that significantly different results were obtained for the peroxide value, which is conditioned by the frying process parameters and the type of fried food, but also by the fact that peroxides, as primary oxidation products, decompose rapidly at high temperatures. Therefore, the state of total oxidation of frying oil is determined by combining peroxide values and values of secondary oxidation products, p-anisidine value (p-AnV), Totox value and TBA value .

The p-anisidine value for fresh sunflower oil was 14.763 meq/kg of oil, and during the frying process it constantly increased to 151.995 meq/kg of oil, at 12 hours of frying. The total oxidation for fresh sunflower oil (Totox value) was 15,332 meq/kg of oil, while at the end of the frying process it was 153,888 meq/kg of oil (Figure 4).

The p - anisidine value for fresh hydrogenated oil was 1.219 meq/kg of oil, while after two hours of frying this value was 13.3 meq/kg of oil, and was constantly increased to 57.636 meq/kg of oil at 12 h of frying (Figure 4). The Totox value for fresh HO is 2.165 meq/kg of oil, while the Totox number at the end of frying (12 h), for hydrogenated oil is 55.983 meq/kg of oil (Figure 4).

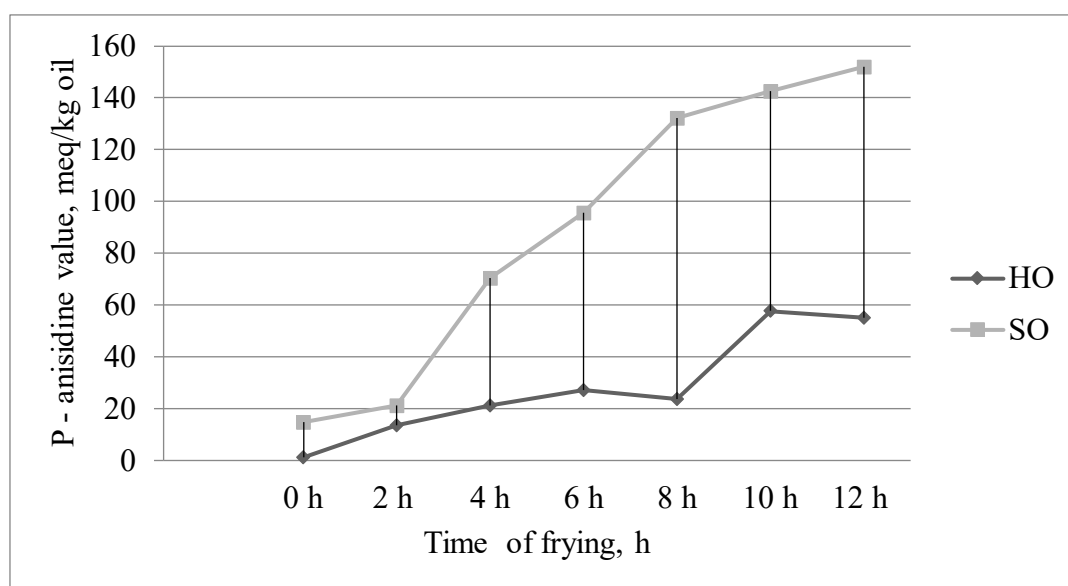


Figure 4. P-anisidine Value , meq/kg oil, (HO- hydrogenated oil; SO - sunflower oil)

Comparing the obtained results for p-anisidine value and Totox value, it is noticeable that a number of authors also obtained very high values of total oil oxidation during food frying. Thus, in the research of Esfarjani et al. [1] recorded a p-anisidine value (p-AnV) of 48.95 meq/kg of oil during frying, while a Totox value was 53.05 meq/kg of oil, during daily frying. Flores et. al [11] in the process of food frying obtained p-AnV in the range of 135 to 311.0 meq/kg of oil, while the Totox value was in the range of 103.6 to 366,1 meq/kg of oil.

Also, researcher Sebastian et al. [2], for oil during frying obtained p-AnV from 7.6 to 41.0 meq/kg of oil, while Tarmizi et al.[9] by testing p-AnV of frying oil, using vacuum frying, and obtaining p-AnV in the range of 40.0-100.0 meq/kg of oil. These data indicate the fact that the total values of oxidative parameters depend on several factors, primarily on the type of oil used for frying, frying temperature, frying time, etc.

In addition to the p-anisidine value and the Totox value, the value of thiobarbiturate acid (TBA) is also of great importance for the evaluation of frying oil, because it shows the content of aldehydes which are very stable products of secondary oxidation and very negatively affect the quality of frying oil, that is, of food that is fried. The results obtained for 2-thiobarbiturate acid values (TBA value) for hydrogenated oil (HO) increased from 1.335 meq/kg oil, at the beginning of frying, to 4.50 meq/kg of oil in 10 hours of frying. After 12 hours of frying, the TBA value decreases again to 3.875 meq/kg of oil, which indicates the possibility of adding fresh oil to the fryer. For sunflower oil, the results of the TBA value were 2.915 meq/kg of oil, for fresh oil, up to 6.526 meq/kg for oil after 12 hours of frying.

Changes in the metal content during the frying process

Given that fresh oils, before the frying process, had a content of tested metals that is in accordance with the legislation (Rulebook on maximum permitted amounts for certain contaminants in food/Official Gazette of Bosnia and Herzegovina, No. 68/2014), which was previously stated in this paper, it can be observed that the metal content after 2 h of frying increases for all tested metals, except for cadmium which is not identified in any way in the analyzed oils (Table 2).

Table 2. Metal content in different frying oils (mg/kg)

Frying duration in hours (h)	Type of oil	Metal content in frying oils (mg/kg)					
		Cadmium	Copper	Iron	Manganese	Nickel	Zinc
0	HO	N.D.	0.09 ± 0.01 ^a	0.04 ± 0.01 ^a	0.45 ± 0.01 ^a	0.06 ± 0.00 ^a	0.13 ± 0.00 ^c
	SO	N.D.	0.02 ± 0.01 ^b	0.03 ± 0.01 ^b	0.32 ± 0.01 ^b	0.02 ± 0.01 ^b	0.32 ± 0.01 ^b
2	HO	N.D.	1.31 ± 0.02 ^b	4.72 ± 0.03 ^d	1.53 ± 0.00 ^c	1.30 ± 0.01 ^c	6.22 ± 0.03 ^g
	SO	N.D.	1.74 ± 0.26 ^b	1.94 ± 0.22 ^b	1.54 ± 0.01 ^b	1.30 ± 0.01 ^b	1.73 ± 0.24 ^b
4	HO	N.D.	1.36 ± 0.01 ^c	4.42 ± 0.02 ^c	1.45 ± 0.01 ^a	1.23 ± 0.00 ^d	0.31 ± 0.01 ^d
	SO	N.D.	0.92 ± 0.46 ^{a,b}	0.92 ± 0.46 ^{a,b}	0.917 ± 0.46 ^{a,b}	0.92 ± 0.46 ^{a,b}	0.917 ± 0.46 ^{a,b}
6	HO	N.D.	1.35 ± 0.01 ^c	5.95 ± 0.01 ^f	1.45 ± 0.00 ^a	1.52 ± 0.01 ^f	0.04 ± 0.01 ^b
	SO	N.D.	0.48 ± 0.67 ^a	0.48 ± 0.67 ^a	0.48 ± 0.67 ^a	0.48 ± 0.67 ^a	0.48 ± 0.67 ^a
8	HO	N.D.	1.41 ± 0.01 ^d	5.55 ± 0.01 ^d	1.46 ± 0.00 ^a	1.21 ± 0.01 ^d	1.26 ± 0.01 ^f
	SO	N.D.	1.54 ± 0.48 ^b	1.54 ± 0.48 ^b	1.54 ± 0.4 ^b	1.54 ± 0.48 ^b	1.54 ± 0.48 ^b
10	HO	N.D.	1.41 ± 0.01 ^{d,c}	3.36 ± 0.01 ^b	1.45 ± 0.00 ^a	0.72 ± 0.02 ^a	0.00 ± 0.00 ^a
	SO	N.D.	1.66 ± 0.44 ^b	1.66 ± 0.44 ^b	1.66 ± 0.44 ^b	1.65 ± 0.44 ^b	1.66 ± 0.44 ^b
12	HO	N.D.	1.42 ± 0.01 ^c	6.06 ± 0.01 ^g	1.50 ± 0.01 ^b	0.84 ± 0.01 ^c	0.40 ± 0.01 ^c
	SO	N.D.	0.45 ± 0.38 ^a	0.45 ± 0.37 ^a	0.44 ± 0.38 ^a	0.45 ± 0.38 ^a	0.45 ± 0.38 ^a

Mean values (± standard deviation) abcdef – (different superscript letters within the same column indicate significant difference (p < 0,05); HO- hydrogenated oil ; SO - sunflower oil)

During the frying process, statistically significant differences can be observed between the content of tested metals in frying oils in 4, 6, 8, 10 and 12 h of frying, however, these values did not increase linearly, which is probably conditioned by the arrival of metals in oils from fried food, and oil absorption into some kinds of food (Table 2). The highest concentrations found for the tested metals are 1.740 mg/kg of oil for copper, 6.06 mg/kg of oil for iron, 1.54 mg/kg of oil for manganese 1.30 mg/kg of oil for nickel, and 6.22 mg/kg of oil for zinc (Table 2).

4. CONCLUSION

The frying oil quality parameters obtained in this research showed very high concentrations of oil oxidation products during the frying process, and a high metal content in the frying oils, which further enhance the oil oxidation reactions. Considering the potential toxicity of oxidation products recorded in high concentrations in the tested oils, and considering the high concentrations of metals in the oils after 12 h of frying, these oils can be considered a risk to the health of consumers of this food.

Due to the fact that Bosnia and Herzegovina has not adopted special legislation on oil quality that would be used exclusively for frying food in deep oil, in commercial restaurants, which would describe the limit values of hydrolysis, oxidation products and products of other reactions that occur during food frying, as well as the limit values of metals present in frying oil. In addition, such legislation would prescribe the frying process parameters, primarily the maximum frying temperature, the frequency of oil changes in fryers, i.e. the total allowed frying time, and other measures that would improve the health of fried food consumers, and public health in Bosnia and Herzegovina in general.

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