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NATURAL ANTIOXIDANTS USED IN FRYING OILS TO MINIMIZE THE ACCUMULATION OF TOXIC COMPOUNDS

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Abstract

The objective of this experiment was to determine if the quality of sunflower oil enriched with mixtures of two antioxidants of rosemary extracts was improved during frying. The enriched oils have been subjected to frying process at a temperature of 180 ° C ± 1°C and held for about seven hours per day, for a period of 10 days. Samples of frozen cooked potatoes were fried in these oils seven times a day, every hour. Quality evaluation of the oils took place every day of the experiment, as far as refractive index, acidity, p-anisidine value, K232 and K270 and polar and oxidation compounds were concerned.

***Key words**: rosemary antioxidants, frying process, oil quality, toxic compounds, food safety, sunflower oil, rapid methods.*

INTRODUCTION

Fat or oil frying is one of the most common and the oldest methods developed and used by man for the preparation of food. Recent consumer interest in “healthy eating” has raised awareness of the need to limit the consumption of fat and fatty foods (Ghiduruş et al., 2013).
The fast food industry is adopting various methods designed to maintain the quality and increase the useful life of frying oils. Among those they include the use of antioxidants (Paul and Mittal, 1997). As it is known, the phenolic compounds have capacity to act as antioxidants (Zayova et al., 2016). The antioxidant properties of herbal products are mainly attributed to phenolic compounds such as flavonoids and polyphenolic derivates (Nikita et al., 2016). Among the antioxidant compounds, polyphenols have gained importance due to their large array of biological action that include free radical scavenging, metal chelation and enzyme modulation activities (Popa et al., 2016). When added to foods, antioxidants control rancidity development, retard the formation of toxic oxidation products, maintain nutritional quality, and extend the shelf-life of products (Shahidi and Ambigaipalan, 2015).
According to Chammem et al. (2015) the addition of the rosemary extract in the mixture of soybean and sunflower oil reduced the peroxide value by 38% after 30 h of heating. This oil resists to oxidation and conserves the higher amount of unsaturated fatty acids even after 30 h of heating.
The frying temperature recommended for specific foods in different studies varies from 160 to 200^0C, with the optimal frying temperature depending on the type of food, its size, the fat turnover, the size of the frying vat, the number of the frying vats used (Mehta and Swinburn, 2001). Natural antioxidants are usually used in low-temperature conditions. In foods exposed to high temperatures (i.e., potato chips) little information is available on the effectiveness of natural antioxidants. Potato chips oxidize easily, thus losing commercial value and health properties (Lalas and Dourtoglou, 2003). Higher temperatures, especially over 200^0C, accelerate oxidative and thermal alterations and increase the rate of formation of decomposition products (Soriano et al., 2002).

MATERIALS AND METHODS

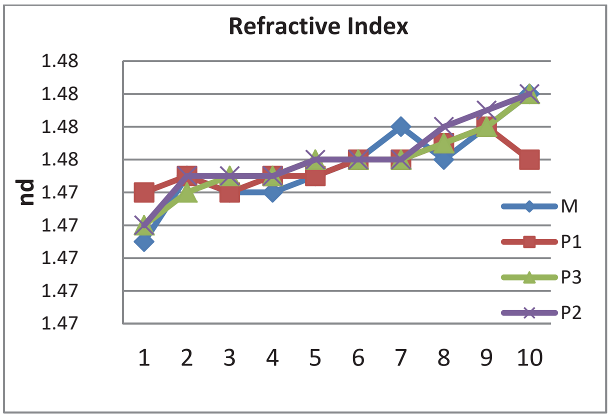
The experiment was conducted in such a manner to determine if the quality of sunflower oil enriched with mixtures of two antioxidants of rosemary extracts was improved during frying. In this respect the vegetable oil samples

were placed in four deep fryers, as follows: 1st deep fryer contained a control sample (M) - normal sunflower oil (reference sample); 2nd contained sample 1 (P1) - sunflower oil with added antioxidant, INOLENS 4 manufactured by Vitiv, 500 ppm rosemary extract; 3rd contained sample 2 (P2) - sunflower oil enriched with INOLENS 4 containing 1000 ppm antioxidant as rosemary extract; 4th fryer contained sample 3 (P3) - sunflower oil 1000 ppm antioxidant SyneROX HT as rosemary extract manufactured by Vitiv, which contains citrate as well. The enriched oils have been subjected to frying process at a temperature of 180°C ± 1°C and held for about seven hours per day, for a period of 10 days, and the total number of frying hours being 68. The oils were heated 10 minutes to reach the first predetermined temperature, without frying potatoes. Samples of frozen cooked potatoes weighing 50 g were fried in these oils seven times a day, every hour, each sample, except the first day when frying took place only 5 hours. The methods used for quality evaluation of the oilsare the AOAC standard methods for refractive index, acidity, p-anisidine value, K232 and K270 and a sensor for polar compounds (FOM-Food oil monitor). Fritest and Oxifrit, rapid methods, were used to asses qualitatively the oils as far as the total oxidation compounds are concerned.
The extracts of rosemary used had a polyphenol content of 42 ± 1 mg/g, expressed as carnosic acid and carnosol.

RESULTS AND DISCUSSIONS

As can be seen in Figure 1 both the refractive index and the percentage of solids in the oil samples increased from 1.47 in the fresh oil to about 1.48, however the differences between the three samples of the oil enriched with antioxidant extract and the control oil sample was not significant.
The results are in agreement with those published by other authors in the literature: Yoon et al., (1987), Al-Harbi (1993), Al-Kahtani (1991), who argue that IR values of oils were used to fry, are higher than those of fresh oil. IR values change in relation to the three stages of autooxidation.

During induction the peroxide formation is low, the refractive index remains constant.



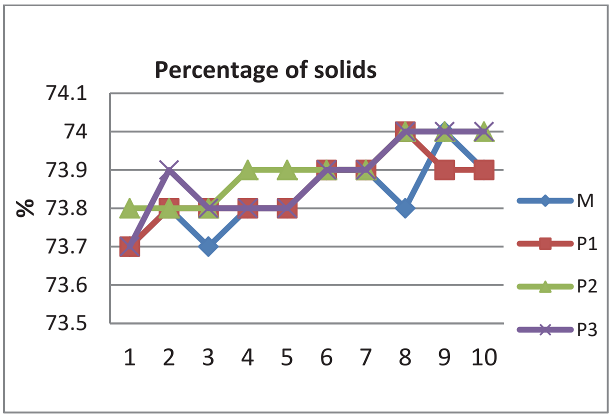


Figure 1. Refractive index and the percentage of solids values of oil samples enriched with antioxidants from rosemary oil, used in 10 days frying process

During the 2nd stage when forming relatively more peroxides, IR increases rapidly until the maximum amount of peroxide is continuing to grow in the third stage peroxides decompose, but not as much as in stage second.
Regarding the acid indexes and the percentage of oleic acid, the highest values were recorded for both parameters in P3, test sample which was containing sunflower oil with 1000 ppm antioxidant SyneROX HT, who reached a value of index acid of 1.253 after 10 days of experiment, the initial value being 0.269 so we observed an increase of 4.66 fold as compared to day one.
The minimum value was recorded in P1 sample, which contained sunflower oil with added antioxidant INOLENS 4, as rosemary extract, 500 ppm, where the acid value was 0.981 on the tenth day (Figure 2).

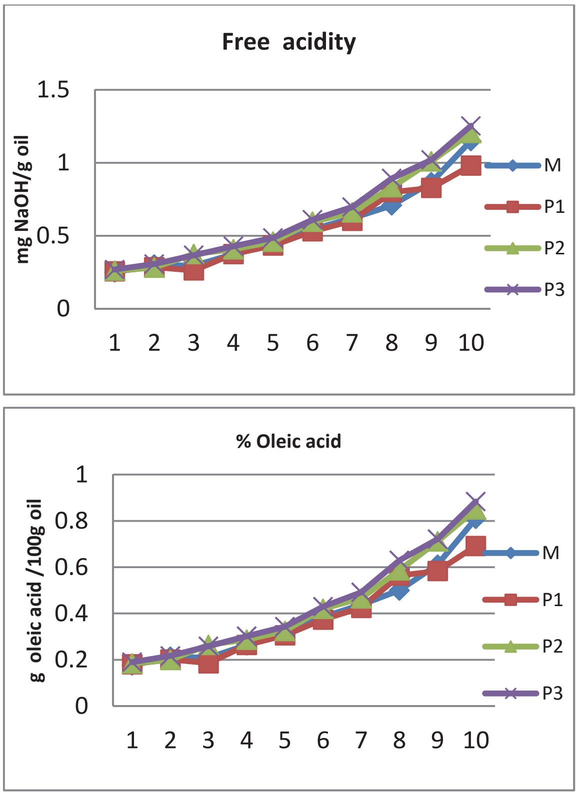


Figure 2. Free acidity and oleic acid percentage values of oil samples enriched with antioxidants from rosemary oil, used in 10 days frying process

It can be concluded that an amount of 500 ppm antioxidant INOLENS 4 is more efficient than 1000 ppm antioxidant HT SyneROX in the accumulation of free fatty acids during the 10 days of the experiment, representing 68 h hours of heat treatment at a temperature of 180^0C ± 1^0C. The value of p - anisidine is a measure of the presence of certain oxidation by-products (primarily aldehydes) and has a good ability to discriminate between samples with different degrees of oxidation.
The results of the experiment reveals the fact that P3 sample with 1000 ppm antioxidant SyneROX HT had the smalest p-anisidine values throughout the experiment with a value of 16.61 at the end of first experimantal day and 43.38 in day 10, therefore p anisidine value in P3 incresed 2.83 times compared to day one. Higher values recorded P2 sample, which contained sunflower oil with added antioxidant INOLENS 1000 ppm as rosemary extract, at the end of the 10^{th} day of the experiment (Figure 3).

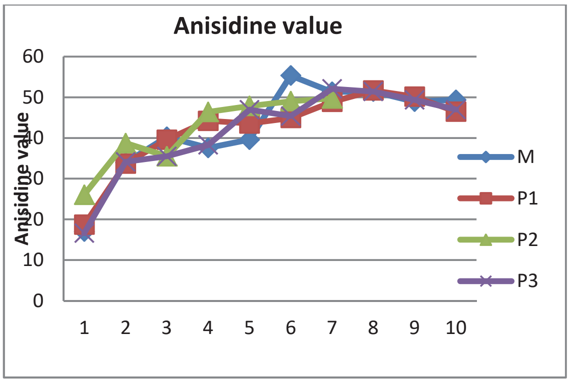


Figure 3. P- Anisidine values of oil samples enriched with antioxidants from rosemary oil, used in 10 days frying process

It was observed the fact that the frying process increased the extinction values at 232 nm and 270 nm, which indicates the formation of compounds such as conjugated dienes and trienes following the removal of double bonds during frying (Figure 4). These findings are consistent with results obtained by Al Kahtani in 1991. Most of frying oils that have a high percentage of polar compounds have a high content of diene and triene. Although these compounds may form polymers, there is a balance between the rate of conjugated diene formation and the rate at which these compounds form polymers during the frying process (Yoon et al., 1987).
In conclusion these two antioxidant extracts and different concentrations, both INOLENS 4 and SyneROX HT did not affect the development of both 232 nm and 270 nm extinction over a period of 10 days of the experiment, 68 h hours of heating treatment at a temperature of 180^0C ± 1^0C, except for the first two days in which the samples P1 and P2 have had lower extinction, the following days the differences were not significant.
Figure 5 shows the increase in percentage of total polar compounds (TPC) of the samples containing oils enriched with antioxidants in rosemary extracts that have been used in continuous frying processes. Of all the physical and chemical analysis, the content of TPC is one of the most objective and valid criteria for the evaluation of the deterioration of oils and fats used for frying processes. However, the standard method for the measurement of TPC by column chromatography on silica gel may be correct, but it is time-consuming and relatively expensive.

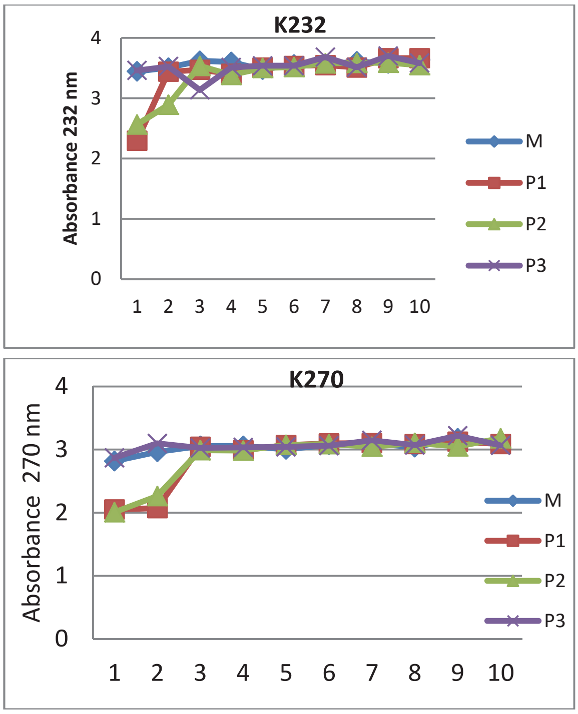


Figure 4. K232 and K270 values of oil samples enriched with antioxidants from rosemary oil, used in 10 days frying process

During the frying process, the oil decomposes into peroxides, acids and other radicals that are formed in the frying oil. This induced polarization of oil molecules. TPC increased in oils during frying experiment being correlated with frying time. Once frying time has progressed, it was observed that the growth rate in TPC was relatively lower in sunflower oil samples enriched 1000 ppm SyneROX HT and INOLENES 4 samples P3 and P2 respectively. After the first day of frying to 180^{0}C the TPC content of the control samples was 6.75%, TPC of P1 was 6%, 6.5% of P2 and 5.5% of P3. At the end of ten days, the TPC increased to 17% in M, 16% in P1, 15% in P2 and 15.25% in P3.

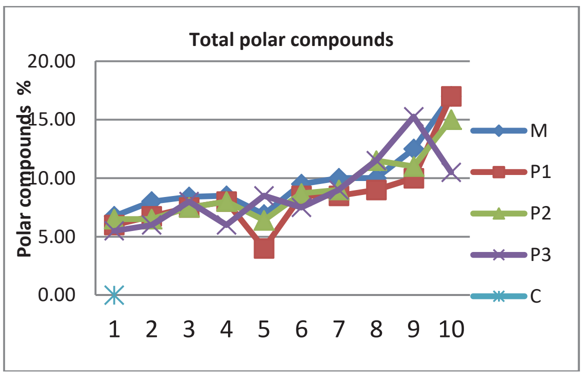


Figure 5. TPC values of oil samples enriched with antioxidants from rosemary oil, used in 10 days frying process (C refers to TPC value of fresh oil)

Although TPC content was the highest in the tenth day, these oils were acceptable after 68 h of the heat treatment conditions of experiment, given that many countries have established a maximum acceptable level for 25-27% TPC content.

After using Oxifrit kit for total oxidized compounds the results showed that all the samples were marked "good" (first colour - 1) on the scale of 4 colors of the kit even in the 9th day of the experiment; changes occurred on day 10 of the experiment the sample P3, sample containing sunflower oil with 1000 ppm antioxidant SyneROX HT which recorded a value of 2 (blue-green) meaning the oil is still good.

The results obtained from the use of the colorimetric test kit FRITEST, which is sensitive to carbonyl compounds, where the analysis consist of comparing the reacted sample mixture to a scale consisting of a choice of three colors from yellow to orange, showed that after 10 days of experiment or 68 hours of frying, the samples had a value of 2. A value of 2 or higher obtained from Fritest indicates that the oil should be replaced. An exception was exhibited by P1, sample containing sunflower oil with added antioxidant INOLENS 4, 500 ppm as rosemary extract, who recorded a value of 1, the color remains almost unchanged after ten days of experiment.

CONCLUSIONS

Both the refractive index and the percentage of solids in the oil samples taken during the frying experiment increased, the differences between the three samples of the oil enriched with antioxidant extract and the control oil sample were not significant. An amount of 500 ppm antioxidant INOLENS 4 is more effective than the 1000 ppm antioxidant SyneROX HT in the accumulation of free fatty acids during the 10 days of the experiment (representing 68 h hours of heat treatment at a temperature of 180^{0}C ± 1^{0}C). The amount of p-anisidine in P3 sample, 1000 ppm antioxidant SyneROX had the lowest values throughout the 10 days of frying.

TPC of oils used in frying increased during the experiment being correlated with frying time; there was relatively slower growth rate of TPC in sunflower oil samples enriched with 1000 ppm SyneROX HT and INOLENES 4 in samples P3 and P2. Although TPC content was highest in the tenth day, these oils were acceptable after 68 h of heat treatment, under the conditions of the experiment, given that many countries have established a maximum acceptable level for 25-27% of TPC content.

In conclusion, the value of p - anisidine, UV analysis of the lipid and the percentage of total polar compounds may be used as a complementary method to determination of free acidity level, to control the quality of vegetable oil during continuous frying processes. In addition, the combination of acid index value and some of these parameters provides additional information regarding the quality of oil that can be used to determine more accurate and efficient quality control methods for fried products.

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