STUDY ON THE COMPOSITION AND OXIDATION STABILITY OF SUNFLOWER OIL – OLEIC TYPE DURING HEAT TREATMENT

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Abstract
The monitoring of physico-chemical changes in the oleic type of sunflower oil when frying potatoes in restaurant conditions by using a professional MModular fryer at 180 °C and comparison with the use of the linoleic type of sunflower oil was researched. In the oleic type of sunflower oil, there was a slight increase of the AV (acid value) observed till the second frying, after which there was detention within the limits of 0.15 to 0.20 % till the tenth frying. The peroxide value (PV, meqO₂/kg) increased significantly in both types of oil - oleic and linoleic, reaching the maximum at the fourth frying, and the value was close to the limiting value for vegetable oils from the linoleic type of sunflower oil - 10 meqO₂/kg. The induction period in the oleic type of sunflower oil was long - 22 hours, but it gradually decreased and after the tenth frying, it was 5 hours. In the linoleic type of sunflower oil, the induction period in the beginning was 8.55 hours, and after the fourth frying, it decreased to 4 hours. The color numbers according to Lovibond on 10 oil samples from repeated frying of products were determined and this indicator increased with the number of fryings over time. Chlorophyll content was not established. The oleic type of sunflower oil produced in Bulgaria, when frying fresh potatoes, was more stable to the oxidation than the traditionally used sunflower oil - linoleic type. It showed stability during storage and long frying time of the used products in real working conditions. This made it more suitable for the preparation of food products, culinary items, main courses, starters and garnishes that require longer thermal treatment. This type of product can be recommended for use when frying in the restaurant business and in the area of nutrition. The methods in our research can be used to control the degree of oxidation of frying oils with vegetable origin in their repeated use, by taking samples on the first, fourth and tenth day of frying at different loads of fryers and to test for acidity, peroxide number and color number.

Keywords: High oleic oil, frying process, fatty acids, peroxide value, color number.

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1. INTRODUCTION

In Bulgaria, the main type of fat used both for cooking and frying is sunflower oil - linoleic type. In recent years started the production of the oleic type of sunflower oil from high oleic varieties of sunflower seeds grown in Bulgaria. Several authors studied the physico-chemical changes in oils during frying. Methods for stabilization of various fats were also studied, which included taste stabilization as well (Warner, 2002). From a practical point of view, it is interesting how many fryings can be done with a certain type of oil, i.e. till when it can be fried without any change occurring in the quality of the oil (stability, acidity, peroxide value). The answer is not unambiguous, as various fats are used in
various frying conditions (Fritsch, 1981). Quality evaluation of oils can be made in various ways - sensory evaluation of food, determination of polar compounds, oxidation stability, etc.

During the time of storage and heat treatment, vegetable fats undergo a number of changes - hydrolysis, oxidation and polymerisation, which have an effect on the quality of the oil - the sensory and nutritional value of the food deteriorates (Ivanova et al., 2014; Trifonova et al., 2015; Ishrat et al., 2014; Dughaish, 2010). The change in the smell during frying is due to linoleic acid degradation. Its intensity decreases in oils with a lower content of linoleic acid. Priority in this case have oils rich in oleic acid or other monounsaturated fatty acids with a reduced content of linoleic FA (fatty acid) and a low content of saturated FAs (Nestel et al., 1994).

As compared to the unsaturated fatty acids, oleic acid is more stable to oxidation during storage, cooking and frying (Anon, 1998).

Low linoleic, high oleic oils, such as canola, olive or almond oils, are recommended for frying. They are quite stable during frying, but their high price does not allow wide usage. It is also recommended to use mixtures of oils where the main ingredient are oils with high oleic content. There is an increase in oxidation stability observed at that (Abdalbasit et al., 2006; Farmer and Sutton, 2002).

In scientific papers, there are data on the stability of sunflower oil - oleic and linoleic type during heat treatment in laboratory conditions, during continuous frying. This data show that the oleic type of sunflower oil has a higher stability expressed in terms of lower peroxide and acid values (PV 0.2 meq02/kg; AV 0.4 mgKOH/g and absorption: 0.610 A) as compared to those for the linoleic type (PV 1.1 meq02/kg; AV 0.5 mgKOH/g and 1.374 A232) (Angelova, 2005; Zhang et al., 2010).

There are also literary data known which indicates mainly the changes in organoleptic properties (color, smell), oxidation stability, peroxide value, acid value, viscosity and fatty acid composition of the linoleic type of sunflower oil and the products based on it, but no such data are available about the oleic type of sunflower oil (Cuesta, 2001; Warner, 2002).

There are data of using moringa oil when frying. This oil resembles olive oil by its fatty acid composition (Ramachandran et al., 1980) and it is used in various parts of the world for various purposes - for salads, cooking and frying (Dahot and Memon, 1985; Farmer and Sutton, 2002; Tsaknis and Lalas, 2002).

There are no data about studying the changes in oleic type sunflower oil during frying in restaurant conditions. This necessitates studies on the oxidation stability of this type of oil during thermal processing in restaurant conditions. For the practice, the issue of oxidation degree, before ranching has taken place, is important, i.e. before the by-products of oxidation have formed which give an unpleasant taste and smell to the oil.

In Bulgaria, the main type of fat used, both for direct consumption and for cooking and frying is sunflower oil - linoleic type. In recent years, the production of oleic type sunflower oil from high-oleic sunflower varieties grown in Bulgaria has begun.

The purpose of the present paper is to monitor the physico-chemical changes in the oleic type of sunflower oil when frying potatoes in restaurant conditions and to make a comparison with the use of the linoleic type of sunflower oil. And also to trace the physicochemical changes that occur mainly in oleic type sunflower oil before and after repeated frying of culinary products of the same species in an oil bath.
2. MATERIALS AND METHODS

Oleic type of sunflower oil produced by “Pappas Oil” JSC and linoleic type of sunflower oil produced by “Biser Oliva” JSC, were used for frying. Untreated fresh potatoes were fried. The heat treatment was carried out in a professional fryer - MMModular brand, with a capacity of 12 liters, and by uniform heating at 180°C. Fresh peeled potatoes were fried in 2 kg servings, in the course of 7 minutes. After each frying, two parallel samples of the oil were taken for analysis. The frying of 2 kg fresh potatoes (after peeling and cutting them to ellipses with a thickness of 4 mm) was carried out for 10 days in a two-nest fryer simultaneously in oleic sunflower oil (12 l in first basket of the fryer) and in linoleic sunflower oil (12 l in second fryer basket) under the same conditions: time of 7 minutes for each frying and temperature – 180 °C. Losses were reported daily, fresh oil was not added to take into account the real changes in both oils and their limit of oxidative stability and degree of use of vegetable oils when frying the same products in the same fat as the multiplicity of frying amount of oil duration of frying in days with equal load of fryers with products. Samples were taken daily with a zero sample for control (without heat treatment), and the other samples were marked from 1 to 10. Daily both types of oil after each frying of potatoes were drained from the baskets and stored under refrigeration conditions from 0 to 4 °C and filtered. Thus, samples of frying oils were collected daily for 10 days and analyzed by the indicators - peroxide value, acid number and monitoring of the period in which the oils will oxidize and become unsuitable for frying.

The physico-chemical characteristics and the fatty acid composition of the oil samples were determined by methods which were standard for the chemical nature of the lipids:

**The composition of fatty acids:** by capillary gas chromatography - ISO 5508 (2002). The fatty acid composition of oleic sunflower oil during the ten days marked as samples from 1 to 10, in order to correlate with the chemical indicators for oil stability were analyzed. Equipment used: Gas chromatograph: GC 17 A Shimadzu; Chromatography conditions: Injector temperature: 240 °C; Pressure: 65 atm; FID detector temperature: 250 °C; Column temperature mode: Initial T: 80 °C, retention time: 1 min, increase by 4 °C/min to 220 °C; retention time 20 minutes; increase to 240 °C with 10 °C/min; Column: Stabilwax - DA (fused silica), length: 30 m; inner diameter: 0.32 mm; movie category: 1 um. (Restek, USA) Carrier gas: nitrogen - 1 ml/min; Amount of sample injected: 1 µl; Split ratio: 1:100; Method of determination: Fat levels were determined in % by the "area normalization" method, i.e. the sum of all gives 100%.

The methodological work was performed by BNS EN ISO 5509 (2002) with used reagents: NaOH, methanol solution, 0.5 mol/l BF3, methanol solution, 12 to 15% (mass fraction). Isooctane NaCl, saturated aqueous solution NaSO4 anhydrous Nitrogen with an oxygen content of less than 5 mg/kg; Hexane with chromatographic quality; Methyl red, 1 g/l solution in 60% (v/v); ethanol Equipment Flasks of 50 ml or 100 ml with a grinder Reflux condenser Boiling aid 4 ml vial with screw cap; Separating funnel of 250 ml; Rotary vacuum evaporator; Analytical balance (accurate to 0.0001g). The test portion was placed in a suitable flask. The appropriate amount of 4 ml sodium methanol solution and boiling aid was added. The refrigerator was connected to the flask. If the fatty acids contain more than two double bonds, the air from the flask was removed by blowing with dry
nitrogen for a few minutes. The sample was boiled at reflux until the fat droplets disappeared, the flask was shaked in every 30 s for 1 minute to prevent the formation of a dense ring of sodium hydroxide. This lasted 5 to 10 minutes. The appropriate amount of boron trifluoride methanol solution 5 ml through the upper end of the refrigerator was added. Boiling lasted 3 minutes. 1 to 3 ml of isooctane were added to the boiling mixture through the upper end of the condenser. The flask was removed from the heat source and immediately was added 20 ml of sodium chloride solution. The flask was closed with a stopper and shaked vigorously for at least 15 s. Saturated sodium chloride solution was added so that the liquid level was brought to the neck of the flask. The two phases were separated in a separatory funnel. 1 ml to 2 ml of the upper isooctane layer was transferred to a 4 ml vial and added a small amount of anhydrous sodium sulphate to remove all traces of water. The isooctane solution thus obtained could be injected.

The results were worked in individual protocols reflected in table 1 of the ten days of frying of potato products;

The acid and peroxide values – acidity as a criterion for hydrolysis stability was determined titrimetrically after titration with 0.1 mol/l potassium hydroxide solution by EN ISO 3961 (2001) and ISO 3960 (2001).

The color value and the total amount of chlorophyll (a + b), ppm - directly by Lovibond (Model PFX/L) by ISO 15305 (1998). The determination of the color number by Lovibond was performed using Lovibond - colorimeter Model PFX/L that provides color data according to AOCS - Tintometric color scale, which is a special red - yellow version of the Lovibond scale. The apparatus operates in the range of 420 - 710 nm (ISO 15305, 1998).

Determination of total chlorophyll (a + b), ppm. The total amount of chlorophyll (a + b) was determined directly by Lovebond - colorimeter Model PFX 880/L.

The determination of oxidation stability was based on a conductometric measurement of volatile acid-dissociated products resulting from the accelerated oxidation of fats and on an automatic graphical plotting of the kinetic curve by "Rancimat 679 instrument of “Metrohm” AG Company (Switzerland). The oil samples of 2.7 g (3 cm³) were used with oxidation air feed rate of 20 dm³/h and temperature of 100 ºС (ISO 6886, 1996). Under these conditions, the oxidation process took place in two phases:

- First phase (induction period) was characterized by slow absorption of oxygen, which formed the primary products of oil oxidation - peroxides and hydroperoxides;

- Second phase (decomposition phase) was characterized by rapid oxygen absorption, in which the formed primary oxidation products under the influence of high temperature decomposed to aldehydes, ketones and low molecular weight fatty acids (formic and acetic). The latter were captured in a measuring vessel, where electrodes immersed in bidistilled water continuously record the change in the conductivity of the solution. The signal was transmitted to a computer with a printing device and graphically registered the change in conductivity over time, and hence oxidative stability. Calculation of the results: From the obtained graph the induction period (IP) was determined by the tangent method and was expressed in hours - the time from the beginning of the analysis to the moment when the concentration of oxidation products begun to increase rapidly.

Three consecutive measurements for each oil sample for 10 days from the same linoleic and oleic vegetable oil in which 2 kg of peeled and
sliced potatoes were fried daily were made and analyzed. The results were processed by mathematical - statistical method. Statistical analysis of the data was performed by determining the standard deviation (±SD), with three repetitions. It was performed with the help of Excel 2007 from the Microsoft package (Microsoft Corporation, USA).

**3. RESULTS AND DISCUSSION**

The suitability of oil was determined by its physico-chemical characteristics – acidity and peroxide value and by the changes which occurred in them in the process of frying. The fatty acid composition of oil samples during frying was also monitored. The results from the studies of the main physico-chemical characteristics - peroxide value, acid value of the two types of sunflower oil - oleic and linoleic are shown in Figure 1 and 2. From Figure 1, it can be seen that the acid value (AV, %) was increased with each frying with the linoleic type of sunflower oil within small limits - from 0.10 to 0.23 %, the highest value was obtained at the fifth frying. In case of the oleic type of sunflower oil, there was slight increase of the AV observed till the second frying, after which there was retention within the limits of 0.15 to 0.20 % till the tenth frying. The latter shown a certain stability of this type of oil as compared to the linoleic one, where acidity was increased with each frying. This proved that until the tenth frying, no significant hydrolysis processes took place in the oleic type of oil during the time of heat treatment.

From Figure 2, it can be seen that the peroxide value (PV, meqO₂/kg) was increased significantly in both types of oil - oleic and linoleic, reached the maximum at the fourth frying, and the value was close to the limiting value for vegetable oils of the linoleic type of sunflower oil - 10 meqO₂/kg (Hadjiiiski and Perifanova-Nemska, 1994). After that, there was a decrease observed in the frying process. For example, the oleic type of sunflower oil, after 4 consecutive fryings, has PV of 8.25 meqO₂/kg, and at the tenth frying, the value was 0.00 meqO₂/kg.

![Figure 1. Acidity during heat treatment of oleic- and linoleic types of sunflower oil](image-url)
This was due to the fact that during the frying process, the primary products of oxidation – hydroperoxides were decomposed into by-products of oxidation, such as aldehydes, ketones, mono- and dicarboxylic acids (ISO 5508, 2002; ISO 5509, 2002). These compounds, for their part, cannot be proved through determining the PV. The degree of oxidation was given by the oxidation stability through determining the change in the induction period, as shown in Figure 3. The induction period in the oleic type of sunflower oil was long - 22 hours, but it gradually decreased and after the tenth frying, it was 5 hours. In the linoleic type of sunflower oil, the induction period in the beginning was 8.55 hours, and after the fourth frying, it decreased to 4 hours.
Simultaneously with that, the colour properties and their change in the oil throughout the time of frying were studied. The colour value also changed during the frying process, and it was more strongly expressed in the linoleic type of oil - table 1. In the linoleic type of oil, the colour value increased from 1.90 to 6.50 and in the oleic one - from 1.10 to 2.10. The increase of the colour value during the frying process was probably due to the high temperature: the various colorants was chemically changed and this led to turbidity of the oil. No chlorophyll was found in either type of oil.

The main components of the oleic type of sunflower oil were: oleic acid - 74.25% and linoleic acid - 18.12%. There were no changes observed in the fatty acid composition of the oleic type of sunflower oils during the process of frying in the restaurant conditions - table 2. In the linoleic type of oil, the amount of linoleic acid prevails - 51.2 %, followed by the oleic acid - 36.5 % (Ivanova et al., 2014). Color properties of linoleic sunflower oil were not analyzed from the sixth to the tenth day, because it oxidized and became unsuitable for use and only the color indicators of oleic oil were analyzed, which showed stability until the tenth day of frying (Table 1).

The results of the research showed that the fatty acids Eicosenoic (C20:1) and Eicosatetraenic (C20:4) remained constant in the oleic type vegetable oil from the fifth to the tenth day of frying the potato slides and were not changed (Table 2). This proved the stability of this type of vegetable oil used for repeated frying.

Our main task was to monitor the changes in the degree of oxidation and oxidative stability of oleic-type sunflower oil during repeated frying and single use of frying fat and to compare it with the changes in linoleic-type sunflower oil.

Table 1. Colour properties of sunflower oils - linoleic and oleic types

<table>
<thead>
<tr>
<th>Color number by Lovebond</th>
<th>0 control sample fresh oil</th>
<th>1 sample 1 day of frying</th>
<th>2 sample 2 day of frying</th>
<th>3 sample 3 day of frying</th>
<th>4 sample 4 day of frying</th>
<th>5 sample 5 day of frying</th>
<th>6 sample 6 day of frying</th>
<th>7 sample 7 day of frying</th>
<th>8 sample 8 day of frying</th>
<th>9 sample 9 day of frying</th>
<th>10 sample 10 day of frying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic type of sunflower oil</td>
<td>R (red)</td>
<td>1.90 ±0.01</td>
<td>2.50 ±0.03</td>
<td>2.70 ±0.02</td>
<td>2.60 ±0.04</td>
<td>2.50 ±0.05</td>
<td>3.30± 0.08</td>
<td>3.10 ±0.03</td>
<td>3.80 ±0.05</td>
<td>4.40 ±0.07</td>
<td>4.90 ±0.04</td>
</tr>
<tr>
<td></td>
<td>Y (yellow)</td>
<td>9.70 ±0.07</td>
<td>16.00 ±0.10</td>
<td>19.00 ±0.09</td>
<td>21.00 ±0.03</td>
<td>21.00 ±0.20</td>
<td>23.50 ±0.05</td>
<td>24.00 ±0.40</td>
<td>28.80 ±0.06</td>
<td>33.00 ±0.80</td>
<td>46.00 ±0.60</td>
</tr>
<tr>
<td>Chlorophyll A, ppm</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Linoleic type of sunflower oil

| R (red)                  | 1.10 ±0.02               | 1.40 ±0.01               | 1.90 ±0.08               | 2.00 ±0.05               | 2.00 ±0.07               | 2.10 ±0.02               | -                        | -                        | -                        | -                        | -                        |
| Y (yellow)               | 7.90 ±0.01               | 11.00 ±0.05              | 14.00 ±0.03              | 18.00 ±0.02              | 19.00 ±0.07              | 21.00 ±0.04              | -                        | -                        | -                        | -                        | -                        |
| Chlorophyll A, ppm       | 0                        | 0                        | 0                        | 0                        | 0                        | 0                        | -                        | -                        | -                        | -                        | -                        |
Table 2. Fatty acid composition of sunflower oils - oleic type

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Samplea</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0</td>
</tr>
<tr>
<td>C 16:0</td>
<td>5.01±0.11</td>
</tr>
<tr>
<td>C 16:1</td>
<td>0.19±0.02</td>
</tr>
<tr>
<td>C 18:0</td>
<td>1.78±0.05</td>
</tr>
<tr>
<td>C 18:1</td>
<td>74.25±1.00</td>
</tr>
<tr>
<td>C 18:2</td>
<td>18.12±0.80</td>
</tr>
<tr>
<td>C 20:1</td>
<td>0.49±0.02</td>
</tr>
<tr>
<td>C 20:4</td>
<td>0.16±0.02</td>
</tr>
</tbody>
</table>

aResults are expressed as mean ± standard deviation of relative percentages of the compounds.

*After the ninth sample, 3 consecutive fryings were done and one sample was taken. AV – 0.2 %, PV – 0, oxidation stability - 4.95 h. This is sample 10*.

The results obtained from the measurements and reflected in the tables showed that oleic oil was stable until the tenth day of frying the product and had the potential to be used when loading the same product without changing the oil in the fryer. While the oxidation stability of linoleic sunflower oil was maintained until the fifth day of frying and then becomes unsuitable, therefore no data were reported from the sixth to the tenth day. As a result of our research, we recommend for widespread use in culinary practice, both from a health and economic point of view, the use of oleic sunflower oil for frying large quantities of products every day.

4. CONCLUSIONS

The oleic type of sunflower oil produced in Bulgaria, when frying fresh potatoes, was more stable to the oxidation than the traditionally used sunflower oil - linoleic type. Its showed stability during storage and long frying time of the used products in real working conditions. This made it more suitable for the preparation of food products, culinary items, main courses, starters and garnishes that require longer thermal treatment. This type of product can be recommended for use when frying in the restaurant business and in the area of nutrition. The methods in our research can be used to control the degree of oxidation of frying oils with vegetable origin in their repeated use, by taking samples on the first, fourth and tenth day of frying at different loads of fryers and to test for acidity, peroxide number and color number. Our study lasted for three months, repeating the frying cycles and loading the baths evenly and daily with an equal amount of potato semi-finished products and the results proved that the use of sunflower oil - linoleic type was suitable for use up to 5 days and oleic type was suitable for use up to 10 days as retained its good qualities and degree of oxidation.

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