ABSTRACT
The purpose of this study was to investigate changes in TPCs, acid value and peroxide value as well as fatty acids composition in edible oils during french fries production. Lower TPCs content was found in rapeseed oil (3.3%) and the threshold (24%) was reached on the fourth day. The total time for the deterioration of deep-frying rapeseed oil was 23\(^\circ\) hours. On the contrary, in fresh sunflower oil at the first day was TPCs content 5.5% and the limit of 24% was reached on the third day. The total time for the deterioration of deep-frying sunflower oil was 17\(^\circ\) hours. The results indicated significant differences (\(<0.05\)) in TPCs content between rapeseed and sunflower oils during deep-frying process. At the beginning of deep-frying French fries in rapeseed oil, the acid number was 0.374 mg KOH·g\(^{-1}\) and 1.271 mg KOH·g\(^{-1}\) at the fourth day of deep-frying. The measured peroxide value was 4.3 mEq O\(_2\)·kg\(^{-1}\) at the beginning and at the end of deep-frying 10.5 mEq O\(_2\)·kg\(^{-1}\). The initial peroxide and acid values were higher in sunflower oil compared with rapeseed oil, respectively. It should be note, then the acid values and peroxide values, respectively, in the two fresh oils used in this study were below the limit of refined oil according to Slovak legislation (peroxide value – not more than 10 mEq O\(_2\)·kg\(^{-1}\), acid value – not more than 0.6 mg KOH·g\(^{-1}\)). However, detected values varied during deep-frying process. Monounsaturated fatty acids were predominantly observed in fresh rapeseed oil (61.22%) wherever in sunflower oil they were much lower (29.77%). A slight increase of MUFA was found in both oils. The initial content of saturated fatty acids in rapeseed oil was 6.94\%, in fresh sunflower oil was observed slightly higher content of SFA (10.37\%). The major groups of fatty acids in fresh sunflower oil were polyunsaturated fatty acids (PUFA) which have in principle a significant effect on oil deterioration. A slight decrease of PUFA was observed in both oils throughout the frying period. The content of PUFA was reduced by about 9.42\% in rapeseed oil and by 10.8\% in sunflower oil. The initial content was 28.14\% and 58.91\%, respectively.

Keywords: plant oil; deep-frying; total polar compound; peroxide and acid value; fatty acid methyl ester; oil deterioration

INTRODUCTION
Frying is a unit operation in which food is heated in oil to alter its eating quality, and destroy microorganisms to make safe of food, and for some foods to extend their shelf-life (Romero et al., 2006; Tabee et al., 2009; Fellows, 2017).

Frying is a more efficient process in comparison with other cooking methods and has gained a high popularity both in restaurants and in industry. The benefits of the frying are its speed and operational simplicity. Even though deep-frying is an old and popular process, it is still poorly understood (Ziaifar et al., 2008; Zeleňáková et al., 2012; Gertz, 2014).

Temperatures used at frying are in the 150 – 200 °C range. In contrast to boiling in hot water the preparing of foods at elevated temperatures provides a desirable appearance (color), texture (crispness) and taste (Erickson, 2007; Sebastian et al., 2014; Neethu et al., 2016).

Deep frying is a cooking method in which food is submerged in hot fat, for example oil. Normally, a deep fryer or chip pan is used for this; industrially, a pressure fryer or vacuum fryer may be used (Aladedunye and Przybylski, 2013; Srivastava and Semwal, 2015).

Deep frying food is a process where food is completely submerged in hot oil at temperatures typically between 350 °F (177 °C) and 375 °F (191 °C). Deep frying is commonly used for food preparations such as frozen pre-fried foods, snack foods and fast foods (Fellows, 2009; Chen et al., 2013).

The nature and rate of decomposition products during frying depend mainly on the composition of the oil (fatty acids pattern, unsaponifiable matter content), the mode of frying (intermittent or continuous, shallow- or deep-frying), frying temperature, length of frying process, and type of food being fried. Many laboratory tests have been proposed for quality assessment of frying oils. There are also used a number of quick tests to screen oils easily at
the frying process is a complex system depending on the chemical reactions like oxidation, polymerization of triglycerides (TAGs), and hydrolysis where the physical and chemical properties of the heated fat are altering. It is difficult to estimate the extent of influence of each factor and to keep the frying conditions at an optimum level. Excellent reviews are published in the scientific literature describing the oxidative and hydrolytic changes during frying process. Moisture in foods induces and accelerates oxidation with the hydrolytic compounds (Gertz 2014; Perkins and Erickson 2007; Tkáčová et al., 2015; Nieva-Echevarría et al., 2016).

Hydrolysis of TAGs occurs due to the presence of moisture from foods, releasing free fatty acids (FFAs), monoglycerides (MAGs) and diglycerides (DAGs). Unsaturated fatty acids in glycerides are prone to be oxidized under high temperature, generating oxidized glyceride compounds (Dobarganes and Márquez-Ruiz, 2006). In addition, dimeric and oligomeric triglycerides are generated in the polymerization reactions (Firestone, 2007; Choe and Min, 2007; Bansal et al., 2010).

TPCs content in deep-fried oils is a reliable indicator of oxidative degradation of frying oils (Zribi et al., 2014; Aladedunye and Przybylski, 2013; Aioniowska and Kita, 2016). Several authors (Matthäus, Haase and Vosmann, 2004; Mareček et al., 2010; Sebastian et al., 2014; Crosa et al., 2014; Li et al., 2017) have determined relative content of fatty acid methyl esters in vegetable oils such as soybean oil, sunflower oil, rapeseed oil, olive oil, coconut oil as well as palm oil (in fresh state and during deep-frying, respectively). Many of them have examined the effects of fatty acids profile on the formation of polar compounds and their retention in French fries, over deep-frying process.

The contents of free fatty acid (FFA) and total polar compounds is usually used for initial oil quality assurance and after-use frying oil quality assessment, respectively (Lee, 2009; Chen et al., 2013).

In context with the above mentioned, the aim of this study was to examine the thermo-degradative changes of rapeseed and sunflower oils during deep-frying French fries.

Scientific hypothesis

The purpose of this study was to investigate thermo-degradative changes of rapeseed and sunflower oils during deep-frying French fries. In this context the purpose of our experiment was to examine the effect of deep-frying process on fatty acids composition, acid value, peroxide value and content of TPCs in used oils.

MATERIAL AND METHODOLOGY

Material

Deep-frozen French fries were purchased at a local supermarket and stored in the freezer at -18 °C until being analyzed. The total quantity of French fries that were used in the experiment was 2.5 kg. For deep-frying French fries were used edible rapeseed and sunflower oils bought from market. Both oils have wide spectrum of using in long-term and short-term thermal preparation of food (cooking, steaming, frying, baking) as well as in cold kitchen (salads, marinades, sauces etc.).

Deep frying French fries

A commercial deep-fat fryer (Siemens TG 15001/01 Kreis Pinneberg, Germany) of capacity 2 L was used for the frying of French fries’ samples. Fresh rapeseed oil and sunflower oil was loaded into the fryer separately and heated to 170 °C before frying. The same batch of French fries (100 g) was deep-fried and the same frying conditions (4 min, 170 °C) were applied. Afterwards, the French fries were placed in a plate and extra oil was sucked using tissue paper. The frying procedure was held constantly for 4 continuous days (6 h per day according to reached 24% TPCs content). At the end of each day of frying the deep fryer was shut off and the oil was cooled down. Then, the oil was filtered to remove the solid residues. Time of oil sampling was different according to examined parameters (explained below). All experiments were done at least in duplicates. All analyzes oil samples were carried out at Department of food hygiene and safety, FBFS, SUA in Nitra and at Department of animal nutrition, FAFR, SUA in Nitra as well.

Experimental determinations

Examined parameters: TPCs – total polar compounds, acid value, peroxide value, fatty acids composition.

Measurement of TPCs content by oil tester Testo 270

TPCs estimation was based on dielectric constant changes directly measured on hot oil with deep frying oil tester Testo 270. The following measurements were performed with the Testo 270:

• Temperature of the deep-frying oil: Indicator for correct setting of the deep-fryer.
• TPCs content: Indicator for the deterioration of the deep-frying oil. The sensor works on a capacitive basis and determines the total amount of polar materials in % as the reading.

For quality analysis used oil samples (fresh and deep-fried) were taken every 30 min throughout the deep-frying process. Measurement of TPCs content in oils was carried out at an oil temperature 130 °C. Analyses were terminated when the TPCs content reached ≥24%, which means oil wear.

For quality analysis used oil samples were taken in fresh state as well as deep-fried every 30 min throughout the deep-frying process.

Determination of peroxide value according to ISO 3960:2007 (EN)

The oil samples were dissolved in isooctane and glacial acetic acid, and potassium iodide was added. The iodine liberated by the peroxides was determined iodometrically (visually) with a starch indicator and a sodium thiosulfate standard solution. The endpoint of the titration was determined iodometrically (visually). The peroxide value (PV) expressed in milliequivalents of active oxygen per kilogram (mEq O2.kg⁻¹) was calculated by the following equation:
\[ pV = \frac{V - V_0}{c} \times \text{ctho} \times c\text{stand} \times 1000 \]

where:
\( V \) – is the volume of the 0.01 N sodium thiosulfate standard solution used for the determination, in millilitres.
\( V_0 \) – is the volume of the 0.01 N sodium thiosulfate standard solution used for the blank test, in millilitres.
\( c\text{stand} \) – is the exact concentration of the 0.01 N sodium thiosulfate standard solution, in moles per litre.
\( \text{ctho} \) – is the approximate concentration of the 0.01 N sodium thiosulfate standard solution, in moles per litre (= 0.01)
\( m \) is the mass of the test sample, in grams.

**Determination of acid value according to ISO 660:2009 (EN)**

Acid value of fat was determined after dissolution of fat in the extract ethanol-diethyl ether in a 1:1 alkalimetric titration against phenolphthalein. The extracted fat was slightly heated, and fat was dissolved in 25.0 mL of ethanol-ether. The content in extraction flask was titrated with a few drops of the indicator with the potassium hydroxide solution until it turned to slight pink colour. An acid number of fat was expressed in mg KOH per g (mg KOH\cdot g\(^{-1}\)). A fat acid value is the number of mg of potassium hydroxide required to neutralize free fatty acids per gram of fat extracted from the extracting agent.

For quality analysis used oil samples were taken in fresh state as well as deep-fried every 60 min throughout the deep-frying process.

\[ AV = \frac{56.1 \times V \times c}{m} \]

Where:
\( AV \) : acid value
\( V \) – is the volume of the potassium hydroxide standard solution, in millilitres.
\( c \) – is the exact concentration of the potassium hydroxide standard solution, in moles per litre
\( m \) is the mass of the test sample, in grams.

For quality analysis used oil samples were taken in fresh state as well as deep-fried every 60 min throughout the deep-frying process.

**Determination of fatty acids composition by gas chromatography according to ISO 12966-1:2014**

0.1 g oil samples were dissolved in 5 mL hexane; 1 mL 2 M KOH in methanol was added. The tubes were capped and stirred for 30 min to separate into two phases. The upper phase was analysed using gas chromatography. A 6890 GC with a Multi-Mode injector, a 7683B automatic liquid sampler and flame ionization detection (Agilent Technologies, Palo Alto, CA) were used. Separation was performed with a (60 m × 0.25 mm i.d. × 0.15 μm DB-23) column (Agilent 6890 GC). The temperature programme was an initial 50 °C with a 1 min hold, ramp 25 °C per min to 175 °C, then 2 °C per min to 230 °C with a 5 min hold, then 120 °C per min to 245 °C with an 8 min hold. Injector temperature was 250 °C. Carrier gas was H2 with a pressure of 238.96 kPa (2.225 mL.min\(^{-1}\)). Fatty acid analysis was performed by auto injection of 1 μL of each sample at a split ratio of 1.10\(^{-1}\), constant flow mode, velocity 20.4 cm.s\(^{-1}\). The flame ionization detector temperature was 280 °C with H2 35 mL.min\(^{-1}\), air 350 mL.min\(^{-1}\), and N2 make-up gas flow rates of 30 mL.min\(^{-1}\), respectively. The run time for a single sample was 32 min. The fatty acid methyl esters were identified by comparing their retention times and mass spectrum with a mixture standard FAME.

For quality analysis used oil samples were taken in fresh state as well as deep-fried every day after 6-hour of deep-frying process.

**Statistical analysis**

Mathematical and statistical evaluation of the results was realized by the SAS Enterprise Guide Version 1.5 system program. Measurements of duplicate samples were expressed as means ± standard deviation. The data were subjected to the analysis of variance (ANOVA) in the general linear models (GLM), t-test, Scheffe’s test and Pearson correlation coefficients (rxy). The level of significance associated to the statistical test was 0.05.

**RESULTS AND DISCUSSION**

Deep frying is cooking method in hot-fat. Typically, deep frying cooks foods quickly: all sides of a food are cooked simultaneously as oil has a high rate of heat conduction (Koh and Surh, 2015). However, only very few researches related to the influences of oil and food types on frying oil quality can be found.

Both goal setting and implementation of the experiment itself were based on requirements of Slovak legislation (Decree No. 125/2017). It requires that deep-fat frying be carried out in accordance with good manufacturing practice and frying fats should not be heated above 180 °C (not longer than 24 hours of continuous frying). The law specifically forbids preparation of fried foods in equipment not provided with temperature control. However, practice shows that, especially, operators of fast food restaurants often violate these requirements and use “frying” oils for several days.

Our research was focused on analysis of thermo-degradative changes of rapeseed and sunflower oils during deep-frying French fries. The following indicators of excessive oil deterioration were investigated: content of total polar compounds, peroxide and acid value, fatty acids composition.

**TPCs in oils during deep-frying French fries**

The polar compounds were identified as oligomeric triglycerides, dimeric triacylglycerol, oxidized triacylglycerols, diacylglycerols, and free fatty acids (Alađedunye and Przybylski, 2013; Aniołowska and Kita, 2015). Recommended and widely accepted limits are 24% for TPCs and 12% for PTG.

When oxidative alterations strongly predominate over thermal alterations, sensory defects can appear before TPCs and PTG reach recommended values. In that case additional parameters like anisidine value, carbonyl value, or epoxy fatty acids should be considered. There are many available physical and chemical rapid methods. Despite the limited informative value and the possibility of error of rapid tests, they are essential for fryer operators, because
they deliver information about fat quality in real-time (Weisshaar, 2014).

Since the degradation of frying oil is greatly accelerated by foods, the frying condition should be controlled carefully. As is shown in Figure 1, TPCs values measured by Testo 270 grown in both oils continuously since the first deep-frying. Lower TPCs content was found in rapeseed oil (3.3%) and the threshold (24%) was achieved on the fourth day. The total time for the deterioration of deep-frying rapeseed oil was 23½ hours. On the contrary, in fresh sunflower oil at the first day was TPCs content 5.5% and the limit of 24% was reached on the third day. The total time for the deterioration of deep-frying sunflower oil was 17½ hours.

The results in this study indicate significant differences (p <0.05) in TPCs content between rapeseed and sunflower oils during deep-frying process (Table 1). The statistical analysis (Scheffe’s test) showed comparable results in both oils between days and hours of deep-frying French fries. TPCs content was similar or lower at 8 o’clock compared to previous day (at 14 o’clock). However, this finding was not statistically significant (p >0.05). Deeper analysis using Pearson correlation coefficients (rxy) by Cohen (1988) showed that between days and hours of deep-frying French fries in rapeseed oil was found high positive linear correlation (p <0.01) between A08 and B08; C14; B08 and C14; B14 and C08. The other linear correlations were other medium negative (p >0.05) or none. However, high positive linear correlation (p <0.001) according TPCs content in sunflower oil during deep-frying time was found at the end of the first frying day and B08, C14, as well as at the beginning of the second frying day and C14 (at the end of the third frying day). In other results were no linear correlations. However, it can be said that deep-frying process directly increases TPCs content (p <0.05).

Similar research was realized by Zeleňáková et al. (2012). Two kinds of rapeseed vegetable oils were used for continuously deep-frying French fries and outside deep-frying process were stored in the room temperature and in the refrigerator, respectively. The both rapeseed oils were from different producers and had different composition related to fatty acid. These factors have significantly affected achieved TPCs amounts. The oil with higher content of oleic acid achieved the 24% TPCs after 22 hours (at room temperature) and 26½ hours (in the refrigerator) of deep-frying. The low erucic acid rapeseed oil was less stable (19 hours and 22½ hours, respectively). For public health concerns, the content of total polar compounds in frying oil is regulated at not more than 25%, in Taiwan (Lee, 2009). Chen et al. (2013) published that the contents of TPCs in soybean oil and palm olein, respectively, were shown to exceed the limit of 25% after 48 h of frying with foods.

Table 1 Changes in TPCs, peroxide value and acid value in sunflower and rapessed oils during deep-frying French fries.

<table>
<thead>
<tr>
<th>Oil sampling time</th>
<th>TPCs (%)</th>
<th>Peroxide value (mEq O2 kg⁻¹)</th>
<th>Acid value (mg KOH g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rapeseed oil</td>
<td>Sunflower oil</td>
<td>Rapeseed oil</td>
</tr>
<tr>
<td>A08</td>
<td>3.33 ±0.29a</td>
<td>5.50 ±0.01</td>
<td>4.33 ±0.50b</td>
</tr>
<tr>
<td>A14</td>
<td>8 ±0.02a</td>
<td>10.83 ±0.29</td>
<td>5.73 ±0.70a</td>
</tr>
<tr>
<td>B08</td>
<td>7.33 ±0.29a</td>
<td>10.83 ±0.29</td>
<td>4.20 ±0.20b</td>
</tr>
<tr>
<td>B14</td>
<td>12.83 ±0.29a</td>
<td>16.50 ±0.02</td>
<td>6.67 ±0.23b</td>
</tr>
<tr>
<td>C08</td>
<td>12.83 ±0.29a</td>
<td>17.00 ±0.01</td>
<td>5.00 ±0.20a</td>
</tr>
<tr>
<td>C14</td>
<td>17.83 ±0.29a</td>
<td>24.33 ±0.29</td>
<td>7.80 ±0.53c</td>
</tr>
<tr>
<td>D08</td>
<td>18.50 ±0.03</td>
<td>-</td>
<td>8.07 ±0.61</td>
</tr>
<tr>
<td>D14</td>
<td>24.50 ±0.02</td>
<td>-</td>
<td>10.53 ±0.70</td>
</tr>
</tbody>
</table>

Note: Least square means and standard deviations of the variables analysed according to period of deep-frying. Lowercase letters indicate significant differences between means of the rapeseed and sunflower oil according to examined indicators by t-test a(p <0.001), b(p <0.01), c(p <0.05), d(p >0.05). Oil sampling time: A/B/C/D – first/second/third/fourth day of deep-frying 08/14 – at 8 am/at 2 pm.

Figure 1 Determination of TPCs content in rapeseed (R) and sunflower (S) oils during deep-frying French fries.
The same batch of <e>e</e>, which quantifies the M 310 was more suitable for <e>monitoring</e> the quality of soybean oil. Polar compounds and TAG oligomers which created during frying determine. This formation starts at temperatures above 120 °C and the maximum rate takes place at temperatures higher than 170 – 180 °C (Pedreschi and Moyano, 2005; Knol et al., 2009). The batch of French fries (100 g) was deep-fried and the same frying conditions (4 min, 170 °C) were applied in our research. As it was mentioned, over the frying process, TPCs increased linearly with the frying time in both oils. The progress of each linear function was defined by regression equation and the reliability of all determinations was expressed by determination coefficients (R²). As shown Figure 1, level of detection reliability (99.4 and 99.1%, respectively) was comparable for both oils. In context with Figure 1, level of detection reliability (99.4 and 99.1%, respectively) was comparable for both oils. As shown Figure 1, level of detection reliability (99.4 and 99.1%, respectively) was comparable for both oils. As shown Figure 1, level of detection reliability (99.4 and 99.1%, respectively) was comparable for both oils. As shown Figure 1, level of detection reliability (99.4 and 99.1%, respectively) was comparable for both oils. As shown Figure 1, level of detection reliability (99.4 and 99.1%, respectively) was comparable for both oils. As shown Figure 1, level of detection reliability (99.4 and 99.1%, respectively) was comparable for both oils.

Table 2a Parameters of linear regression for TPCs in sunflower and rapessed oils during deep-frying French fries.

<table>
<thead>
<tr>
<th>Summary output</th>
<th>TPCs (%)</th>
<th>Sunflower oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>y = 3.04 + 0.7942x</td>
<td>y = 5.43 + 0.9357x</td>
</tr>
<tr>
<td>Multiple R (r)</td>
<td>0.997</td>
<td>0.995</td>
</tr>
<tr>
<td>R Square (R²)</td>
<td>0.994</td>
<td>0.991</td>
</tr>
<tr>
<td>p – value</td>
<td>5.24.10⁻⁷</td>
<td>3.92.10⁻⁹</td>
</tr>
<tr>
<td>Intercept</td>
<td>3.04</td>
<td>5.429</td>
</tr>
<tr>
<td>Slope</td>
<td>0.794</td>
<td>0.936</td>
</tr>
</tbody>
</table>

Table 2b Parameters of linear regression for peroxide value in sunflower and rapessed oils during deep-frying French fries.

<table>
<thead>
<tr>
<th>Summary output</th>
<th>Peroxide value (mEq O₂ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>y = 3.48 + 0.2481x</td>
</tr>
<tr>
<td>Multiple R (r)</td>
<td>0.933</td>
</tr>
<tr>
<td>R Square (R²)</td>
<td>0.937</td>
</tr>
<tr>
<td>p – value</td>
<td>4.49.10⁻¹³</td>
</tr>
<tr>
<td>Intercept</td>
<td>3.48</td>
</tr>
<tr>
<td>Slope</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 2c Parameters of linear regression for acid value in sunflower and rapessed oils during deep-frying French fries.

<table>
<thead>
<tr>
<th>Summary output</th>
<th>Acid value (mg KOH·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>y = 0.31 + 0.038x</td>
</tr>
<tr>
<td>Multiple R (r)</td>
<td>0.886</td>
</tr>
<tr>
<td>R Square (R²)</td>
<td>0.785</td>
</tr>
<tr>
<td>p – value</td>
<td>3.71.10⁻¹⁰</td>
</tr>
<tr>
<td>Intercept</td>
<td>3.11</td>
</tr>
<tr>
<td>Slope</td>
<td>0.038</td>
</tr>
</tbody>
</table>

As was discussed in the (EFL, 2011) for fresh oils, the acid value is routinely used as a selective indicator for the degradation status. Oxidation may be initiated by the formation of lipid peroxides. Initial phases of lipid oxidation can be detected by measuring the peroxide value, which quantifies the levels of peroxides and hydroperoxides formed at that stage (Bennett et al., 2014).
Throughout the deep-frying process were in rapeseed oil and sunflower oil measured acid values and peroxide values. At the beginning of deep-frying French fries in rapeseed oil, the acid number was 0.374 mg KOH g\(^{-1}\) and 1.271 mg KOH g\(^{-1}\) at the fourth day of deep-frying. The measured peroxide value was 4.3 mEq O\(_2\) kg\(^{-1}\) at the beginning and at the end of deep-frying 10.5 mEq O\(_2\) kg\(^{-1}\). The initial peroxide and acid values, respectively, were higher in sunflower oil compared with rapeseed oil. The initial acid value in deep-fried sunflower oil was 0.598 mg KOH g\(^{-1}\) and at the end of deep-frying French fries (third day) 1.497 mg KOH g\(^{-1}\). The measured peroxide value was 0.7 mEq O\(_2\) kg\(^{-1}\) at the beginning and at the end of deep-frying 12.7 mEq O\(_2\) kg\(^{-1}\). It should be note, that the acid values and peroxide values, respectively, in the two fresh oils used in this study were below the limit of refined oil according to Slovak legislation (Decree No. 424/2012). This regulation laying down requirements for edible vegetable fats and edible vegetable oils and their products (peroxide value – not more than 10 mEq O\(_2\) kg\(^{-1}\), acid value – not more than 0.6 mg KOH g\(^{-1}\)). However, detected values varied during deep-frying process.

Peroxides are known to be unstable and volatile, as can be seen from Figure 2. It follows that sunflower oil is responsible to thermal degradation and is not suitable for long-term heat treatment.

As it was mentioned, over the frying process, TPCs increased linearly with the frying time in both oils. The linear regression was also used in evaluating the reliability of peroxide and acid value detection (Figures 2 and 3). However, unlike TPCs detection, in these detections was found a lower reliability indicated by \(R^2\). The determination coefficients were 0.8711 (peroxide value) and 0.7847 (acid value) in rapeseed oil and 0.4749 (peroxide value) and 0.5175 (acid value) in sunflower oil. The other parameters of linear regression for both values are shown in the Table 2. This finding is explained by many authors (Alander and Lidefelt, 2007; Nieva-Echevarría et al., 2016; Li et al., 2017).

During deep-frying process (125 °C), rapid oxidation occurs (accumulation of hydroperoxides) and peroxide value increased. However, but upon further heating at high frying temperatures, the peroxide value again decreases, because accumulated hydroperoxides are decomposed.
more rapidly and other secondary degradation products are formed. The rise of the peroxide value therefore occurs at a time when the oil cools and is not used.

It can be concluded that measurement of the peroxide value is more suitable for measuring the quality of fresh oil than for measuring the quality of oil during frying and deep-frying, respectively (Koh and Surh, 2015; Naz et al., 2005; Juárez et al., 2011). For public health concerns, the acid value in frying oil is regulated at not more than 2.0 mg KOH·g⁻¹, in Taiwan (Lee, 2009).

From the results of Chen et al. (2013) soybean oil contained 0.03 mg KOH·g⁻¹ of acid value, while palm olein contained slightly higher acid value (0.071 mg KOH·g⁻¹).

Table 3a Fatty acids composition (%) of deep-fried oils during frying process (rapeseed and sunflower oil).

<table>
<thead>
<tr>
<th>FAMEs (wt %)</th>
<th>Rapeseed oil</th>
<th>Sunflower oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh oil</td>
<td>after 1 day</td>
</tr>
<tr>
<td>palmitic acid C16:0</td>
<td>4.52 ±0.00</td>
<td>4.64 ±0.00</td>
</tr>
<tr>
<td>stearic acid C18:0</td>
<td>1.49 ±0.00</td>
<td>1.55 ±0.00</td>
</tr>
<tr>
<td>oleic acid C18:1 cis n9</td>
<td>59.64 ±0.00</td>
<td>59.97 ±0.01</td>
</tr>
<tr>
<td>linoleic acid C18:2 cis n6</td>
<td>18.96 ±0.00</td>
<td>19.00 ±0.00</td>
</tr>
<tr>
<td>arachidic acid C20:0</td>
<td>0.52 ±0.00</td>
<td>0.52 ±0.00</td>
</tr>
<tr>
<td>cis-11-eicosenoic acid C20:1 n9</td>
<td>1.23 ±0.00</td>
<td>1.23 ±0.00</td>
</tr>
<tr>
<td>behenic acid C22:0</td>
<td>0.31 ±0.00</td>
<td>0.31 ±0.00</td>
</tr>
<tr>
<td>lignoceric acid C24:0</td>
<td>0.11 ±0.01</td>
<td>0.12 ±0.00</td>
</tr>
<tr>
<td>caprylic acid C8:0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>myristic acid C14:0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>palmitoleic acid C16:1</td>
<td>0.22 ±0.00</td>
<td>0.22 ±0.00</td>
</tr>
<tr>
<td>α-linolenic acid C18:3 n3</td>
<td>9.19 ±0.00</td>
<td>8.58 ±0.00</td>
</tr>
<tr>
<td>erucic acid C22:1 n9</td>
<td>0.13 ±0.00</td>
<td>0.13 ±0.00</td>
</tr>
<tr>
<td>cis-13,16-docosadienoic acid C22:2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PUFA polyunsaturated fatty acids</td>
<td>28.14</td>
<td>27.58</td>
</tr>
<tr>
<td>MUFA monounsaturated fatty acids</td>
<td>61.22</td>
<td>61.56</td>
</tr>
<tr>
<td>SFA saturated fatty acids</td>
<td>6.94</td>
<td>7.14</td>
</tr>
<tr>
<td>ratio Σ3/Σ6</td>
<td>0.48</td>
<td>0.45</td>
</tr>
<tr>
<td>ratio Σ6/Σ3</td>
<td>2.07</td>
<td>2.22</td>
</tr>
</tbody>
</table>

Table 3b Fatty acids composition (%) of deep-fried oils during frying process (rapeseed and sunflower oil).

<table>
<thead>
<tr>
<th>FAMEs (wt %)</th>
<th>Sunflower oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fresh oil</td>
</tr>
<tr>
<td>palmitic acid C16:0</td>
<td>6.13 ±0.00</td>
</tr>
<tr>
<td>stearic acid C18:0</td>
<td>3.05 ±0.00</td>
</tr>
<tr>
<td>oleic acid C18:1 cis n9</td>
<td>29.51 ±0.01</td>
</tr>
<tr>
<td>linoleic acid C18:2 cis n6</td>
<td>58.82 ±0.00</td>
</tr>
<tr>
<td>arachidic acid C20:0</td>
<td>0.22 ±0.00</td>
</tr>
<tr>
<td>cis-11-eicosenoic acid C20:1 n9</td>
<td>0.16 ±0.00</td>
</tr>
<tr>
<td>behenic acid C22:0</td>
<td>0.73 ±0.00</td>
</tr>
<tr>
<td>lignoceric acid C24:0</td>
<td>0.25 ±0.01</td>
</tr>
<tr>
<td>caprylic acid C8:0</td>
<td>-</td>
</tr>
<tr>
<td>myristic acid C14:0</td>
<td>-</td>
</tr>
<tr>
<td>palmitoleic acid C16:1</td>
<td>0.11 ±0.00</td>
</tr>
<tr>
<td>α-linolenic acid C18:3 n3</td>
<td>0.09 ±0.00</td>
</tr>
<tr>
<td>erucic acid C22:1 n9</td>
<td>-</td>
</tr>
<tr>
<td>cis-13,16-docosadienoic acid C22:2</td>
<td>-</td>
</tr>
<tr>
<td>PUFA polyunsaturated fatty acids</td>
<td>58.91</td>
</tr>
<tr>
<td>MUFA monounsaturated fatty acids</td>
<td>29.77</td>
</tr>
<tr>
<td>SFA saturated fatty acids</td>
<td>10.37</td>
</tr>
<tr>
<td>ratio Σ3/Σ6</td>
<td>0.00</td>
</tr>
<tr>
<td>ratio Σ6/Σ3</td>
<td>628.64</td>
</tr>
</tbody>
</table>
Other studies (Gerde et al., 2007; Tabee et al., 2009) also showed that the acid value in palm olein were higher than those in soybean oil.

Table 1 lists the acid value and peroxide value in both analysed oils with statistical evaluation. The influence of oil type on the peroxide value in used oil was significant ($p < 0.05$), but the effect of oil type on acid value was not observed ($p > 0.05$).

Our results partially correspond with those from Chen et al. (2013), who used palm and soybean oil for frying French fries. They found significant influence of oil type on acid value in these oils.

The One-way ANOVA test was used to determine the statistical significance between two types of frying oils according to changes of peroxide value and acid value during the frying time. Post-Anova (Scheffe’s test) was used where the F value was significant.

No significant differences in the peroxide value of rapeseed oil were observed in the first two days of frying. The first significant differences were found between B14 and A08, B08. Interestingly, no significant differences in the peroxide value were observed at the beginning of the third frying day and A08, A14, B08 and B14, but there were significant differences at the end of the third frying day and A08, A14, B08, C08. At the beginning of the last frying day, there were observed significant differences compared with A08, A14, B08 and C08. The peroxide value was significant different at the end of the last frying day compared with the first three frying days.

In sunflower oil, there is a significant difference in peroxide value measured at the beginning of frying (A08) and all other measurements. There were observed no significant differences between A14, B08, B14, C08, C14.

In the determination of acid value in both oils, there were no significant differences among days and hours of deep-frying rapeseed oil and sunflower oil, respectively.

**Fatty acid methyl esters composition in oils during deep-frying French fries**

Fatty acids composition is one of the most crucial factors determining the oxidative stability of oil. Fatty acids profile changed during frying process.

In the present study, fatty acids profiles in rapeseed and sunflower oil were analysed and compared over the deep-frying process of French fries at temperature 170 °C. As is shown in the Table 3, the content of PUFA, MUFA, and SFA in fresh oils was different but other changes in quantity due to the deep-frying in these oils were comparable (increasing and decreasing, respectively).

Monounsaturated fatty acids (MUFA) were predominantly observed in fresh rapeseed oil (61.22%) wherever in sunflower oil they were much lower (29.77%). A slight increase of MUFA (from 61.22 to 62.1 and from 29.77 to 32.03%) was found in both oils. Moreover, the saturated fatty acids (SFA) in fresh oils were determined and the trend of increasing due to deep-frying was quite similar to MUFA. The initial content of saturated fatty acids in rapeseed oil was 6.94%, over the deep-frying process increased to 7.14, 7.33, 7.59 and 8.03%. In fresh sunflower oil was observed slightly higher content of SFA (10.37%) and it increased with the increase of frying time (to 13.63%).

The major groups of fatty acids in fresh sunflower oil were polyunsaturated fatty acids (PUFA) which have in principle a significant effect on oil deterioration. A slight decrease of PUFA was observed in both oils throughout the frying period. The content of PUFA was reduced by about 9.42% in rapeseed oil and by 10.8% in sunflower oil. The initial content was 28.14% and 58.91%, respectively.

The impact of the fatty acid composition on lipid oxidation was evaluated by measuring the relative percentage of unsaturated, polyunsaturated and saturated fatty acids. Roman et al. (2013) reported a higher reactivity of PUFA than MUFA (-linolenic acid > linoleic acid > oleic acid) in sunflower oil, as had previously been shown by different studies (Parker et al. 2003; Martin-Polvillo et al., 2004). The major fatty acid in fresh rapeseed oil was oleic acid (59.64 ±0.00%) while in fresh sunflower oil dominant linoleic acid (58.82 ±0.00%). A slight increase of oleic acid (C18:1) was observed in both fried oils examined. At the end of frying period, oleic acid increased by 1.5% in rapeseed oil and by 7.79% in sunflower oil. Initial content of oleic acid in sunflower oil was 29.51 ±0.01%.

In contrary, amount of oleic acid decreased slightly from 38.70% to 32.06% in palm oil over the frying process. However, oleic acid content in the other two kinds of oils (palm kernel oil and coconut oil) remained unchanged (approximately 17% and 8%, respectively) during frying period (Li et al., 2017). The high oleic acid is reported as a better oil compared to regular sunflower, soybean, corn and peanuts oils due to its good thermal and oxidative stability during traditional frying (Smith et al., 2007; Marmesat et al., 2012). Chemometric analysis showed, that there was no correlation between the polar compounds level and saturated fatty acids profile. It can be also assumed that high-oleic oils show a lower polar compounds level after a period of deep-frying compared to the oils with less oleic acid (Abdulkarim et al., 2007; Zribi et al., 2014). Among frying oils, those with high oleic acid content such as palm olein have better health profile and heat stability (Tabee et al., 2009).

In the case of palmitic (C16:0) and stearic acids (C18:0), they increased with the increase of frying time as well in both kinds of oils (from 4.52 to 5.11% and 1.49 to 1.75%, respectively, in rapeseed oil; from 6.13 to 8.59% and 3.05 to 3.43% in sunflower oil). Notably, even though no caprylic acid was observed in fresh rapeseed and sunflower oils, it increased to 0.12% and 0.17%, respectively, at the end of the frying procedure. The similar results were found in content of myristic acid (C14:0).

Caprylic acid and capric acid were observed reduced in refined palm kernel oil and refined coconut oil. The medium-chain fatty acids are volatile under the high temperature (Amri, 2011). According to Zribi et al. (2014), the fatty acids composition influences the generation of polar compounds over the frying process. Higher percentage of unsaturated fatty acids (UFAs) in the oils resulted in a higher level of polar compounds during the frying process. However, this was inconsistent with the present study.
In our study fresh rapeseed oil was found to have 18.96% of linoleic acid (C18:2) and 9.19% of linolenic acid (C18:3). The level of linoleic acid in fresh sunflower oil (58.82%) was higher than this in the rapeseed oil analysed. On the contrary, fresh sunflower oil contained only 0.09% of linolenic acid. The linoleic acid content was almost unchanged during frying process in rapeseed oil. Slight decrease was found in sunflower oil (from 58.82 to 52.55%).

It is necessary to note, that linolenic acid concentration was not detectable from the second day of deep-frying French fries in sunflower oil. The deterioration of (α) linolenic acid was more pronounced, with its contents being decreased by 30.25% in the last day of deep-frying French fries in rapeseed oil. Similar results were found by Chen et al. (2014) who detected by 20.86% lower linolenic acid content in palm oil. Aladedunye and Przybylski (2009) reported decreases of 13.3% in linoleic acid and 47.1% in linolenic acid when fresh canola oil was heated at 215 °C for 7 days.

Fresh soybean oil was reported to have 21.5% of oleic acid (C18:1), 53.4% of linoleic acid (C18:2) and 5.1% of linolenic acid (C18:3) and saturated fatty acid (Juárez et al., 2011). It is important to note that soybean oil is commonly used for deep fat frying by Korean school meal services.

In our study, rapeseed oil has n-6/n-3 ratio around 2. This result is similar to this from Dubois et al. (2007) who analysed soybean oil (around 6). Flaxseed oil stands out for containing high levels of n-3, and sunflower oil stands out for introducing high n-3 values. The mixture of these oils can result in a mix with higher concentrations of polyunsaturated fatty acids and different n-6/n-3 ratios. Recent studies have been demonstrated that mixtures of vegetable oils might modify the fatty acid profile and improve the stability of oils (Wang et al., 2006; Meinhart et al., 2017).

Industrial food producers should understand the thermo oxidative changes in their frying oils, especially below 15% polar compounds. In fast food restaurants where the products are prepared for the direct consummation the limits of degradation are much higher (i.e. 24% polar materials) and may be monitored by units that measure and related dielectric constant to the degree of degradation (EFL, 2011).

Finally, there is a discussion of the effect of frying on the sensory characteristics of foods, changes to their nutritional value, healthy concerns over fried foods and methods to reduce their fat contents.

CONCLUSION
Good understanding of the frying process helps in optimizing the manufacturing processes with regard to quality of food and use life of fat and of energy consumption. To guarantee a good quality of the fried end product it is necessary to install a management system which includes all critical points of the frying process. Variables involved in the process include frying conditions, replenishment of fresh oil, original oil quality, food materials, and fryer type. Oil for frying should be selected by its performance during the frying process. Nowadays, besides thermal-oxidative stability, handling (good melting profile), availability and price, the
nutritional-physiological features (good fatty acid balance, low trans-fatty acids, no allergens, no GMO) are important points of decision. There is no ideal fat suitable for all frying applications.

Our results, supported by other studies, provided the basis for choosing the suitable vegetable oil as well as rapid-measuring device to control the quality of frying oil in restaurants.

Based on our findings, we suggest:
• for frying and deep-frying to use only oils for that purpose,
• to keep the set temperatures and time with respect to the type of food,
• to keep the established ratio between food and oil,
• to filter the used oil at the end of the frying day to remove food debris,
• to store the oil in a dark and cool place,
• regularly check the oil quality,
• immediately to change oil showing the deterioration (exceeded smoke point and TPCs of 24%).

REFERENCES
Decree of the Ministry of Agriculture and Rural Development of the Slovac Republik no. 424/2012 laying down requirements for edible vegetable fats and edible vegetable oils and their products, including requirements for their production, labeling and division.
Decree of the Ministry of Health of the Slovac Republik no. 125/2017 which amends Decree no. 553/2007 laying down requirements for mass caterers.
Potravinarstvo Slovak Journal of Food Sciences


Nieva-Echevarria, B., Goicoechea, E., Manzanos, M. J., Guillén, M. D. 2016. The influence of frying technique, cooking oil and fish species on the changes occurring in fish lipids and oil during shallow-frying, studied by 1H NMR. Food Research International, vol. 84, p. 150-159. https://doi.org/10.1016/j.foodres.2016.03.033


Romero, A., Bastida, S., Sanchez-Muniz, F. J. 2006. Cyclic fatty acid monomer formation in domestic frying of frozen foods in sunflower oil and high oleic acid sunflower oil without oil replenishment. Food and Chemical Toxicology, vol. 44, no. 10, p. 1674-1681. https://doi.org/10.1016/j.fct.2006.05.003


Oxidative stability of chicken meat during storage influenced by the feeding of alfalfa meal. Potravinárstvo, vol 9, no. 1, p. 106-111. https://doi.org/10.5219/444


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