Evaluation of Quality of Argentinean Sunflower Oil Used in High-Moisture Food Frying

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Abstract

Objective: To make evaluation of quality of Argentinean sunflower oil used in high-moisture food frying through parameters indicators of oil deterioration. Methods: The results were obtained after studying the effect of temperature-time and the type of food subjected to frying through Total Polar Compounds (TPCs) determination. The type of food selected was breaded food and potato chips. From calorimetric analysis (DSC) of frying oil was obtained crystallization temperature and the crystallization enthalpy. Also was determining fatty acid composition of the frying oil by gas chromatography. Findings: It was observed during the oil heating test at various times, that the TPC content increased over time. The highest the temperatures were, the most distinctive the rises were. During the frying of breaded food and potato chips the deterioration of the oil was accelerated, observing the greatest deterioration after the breaded frying process. The thermo grams obtained by DSC showed a well-defined crystallization peak that when heating treatment times were increased, it reflected in lower temperatures and a decrease in enthalpy. A high correlation was found between the concentration of total polar compounds, and the parameters obtained from thermo grams and the concentration of palmitic and linoleic acids. Novelty/Improvement: The results obtained provide useful information for food quality control in order to avoid variations of the sensory and nutritional characteristics of sunflower oil used in high-moisture food frying.

Keywords: Frying, High-Moisture Food, Oil, Quality, Total Polar Compounds

1. Introduction

The process of frying is considered one of the oldest methods in cooking food, it is used for both, treating food thermally and imparting flavors and textures that are unique to them1,2. The oil used is decisive in the quality and performance of this process. Argentina is the largest producer of sunflower in South America3. Sunflower produces oil rich in linoleic acid and vitamin E that is very appreciated by domestic consumption over other vegetable oils such as soybean, cottonseed, and rapeseed oils4 informed that in food industry, this product has been used for frying, showing similar performance to other oilseeds such as soybean and canola.

During the frying process, the oil is exposed to atmospheric oxygen and humidity at high temperatures (150-200°C). These high temperatures and repeated use of the oil increases the susceptibility to thermal and oxidative degradation. Chemical reactions such as hydrolysis, oxidation, and polymerization, lead to decomposition products, such as Free Fatty Acids (FFA), hydroperoxides, surfactants, and hydrocarbons. More than 400 different chemical compounds have been identified in the deterioration of the oil, including 200 volatile products5. Hydrolysis of lipids containing short chain fatty acids produces an unpleasant taste and aroma in the oil, whereas the presence of long chain fatty acids does not produce any perceptible changes in the taste or characteristics of the product. Free Fatty Acids (FFA),
which appears as a result of hydrolysis, may also undergo oxidation reactions. In the presence of oxygen, peroxides and hydroperoxides are formed, which decompose rapidly to form a variety of products such as aldehydes, ketones, alcohols, among others\textsuperscript{25}. The degradation products formed during the frying process include volatile compounds which are partially removed during process, and novel non-volatile compounds which accumulate therein as the process progresses and are incorporated into the food. These compounds possess a higher polarity than unaltered triglycerides and constitute the so-called polar compounds\textsuperscript{7,8}.

There are different standardized analytical methods to evaluate the oil stability as well as the quality and stability of the resulting fried product\textsuperscript{9,10}. Some of these methods include rapid analytical indicators such as free acidity; colorimetric methods based on redox indicators, viscosity measurements, and conjugated dienes, electronic noses, among others\textsuperscript{11,12}. The most general analytical method for evaluating the quality of frying oils is the determination of polar compounds which provides an accurate measurement of the percentage of compounds that contain a greater polarity than triglycerides. Most of these are degradation compounds that originated during the process. This method is also the most used in existing regulations to limit the alteration of fry oils and greases, which has been established around 25-27% as a criterion of deterioration\textsuperscript{14}.

The alteration of the grease by frying it also produces a significant increase in its dielectric constant. This technique was introduced in routine practice because of its low cost, quick, solvent free and good correlation with the amount of polar compounds. This advantage adds to the excellent correlation that it presents with the percentages of total polar compounds\textsuperscript{13,14}. There is different equipment, such as the FOS (Food Oil Sensor) or the Test 265 and 270, which can measure changes in the oil's dielectric constant and correlate them with the total polar compound content generated during degradation. Different authors have reported an adequate correlation between the values of the dielectric constant and other alteration parameters for different types of oils\textsuperscript{13,15} as well as in different temperature conditions and with or without the addition of antioxidants\textsuperscript{15,16,17}. Observed that the dielectric constant reflects the equilibrium between the polar and non-polar fractions of the frying oil and detected an increasing effect of such constant by increasing moisture, oxidized dimers, and oxidized volatile components\textsuperscript{18} argue the close relationships between percentage in weight of polar compounds and the composition expressed in terms of molar percentages of acyl groups in edible oils heated at frying temperature.

The Differential Scanning Calorimetry (DSC) has been widely used in the investigation of the thermal behavior of consumer products, especially in the food sector. For example, it is used to study the physical behavior during the processing and storage of proteins, carbohydrates, fats and oils. As a result of its advantages in terms of precision and sensitivity, Differential Scanning Calorimetry (DSC) has recently been used to evaluate the quality and stability of fats and oils\textsuperscript{19,26}. Used the differential scanning calorimetry to study the changes in the thermal properties of commercial oils (sunflower, colza and peanut) during a heat treatment of 10h at 180ºC. These authors reported that as the heating time increased, the crystallization peak shifted to lower temperatures and the enthalpy decreased.

The main objective of this study was to evaluate the deterioration kinetics of the quality of the sunflower oil used to fry food. This was achieved by measuring the formation of total polar compounds and other indicators of oil deterioration (parameters obtained by DSC and concentration of palmitic and linoleic acids), studying the effect of temperature, and indicating the type of food subjected to the frying process.

2. Materials and Methods

The oil subjected of study was sunflower oil of national origin (Argentina) acquired at the local supermarket. Potato chips and disks of breaded beef of 3.5 cm in diameter were used as food to fry.

To analyze the effect of the temperature on the oil used in the frying process, the sunflower oil was subjected to heating treatments at different temperatures (150ºC, 180ºC and 200ºC) for a period of 4 hours for the experiments at 180º and 200ºC and 7 hours for the experiment at 150ºC. The Total Polar Compounds (TPCs) were measured in the fryer oil for each temperature test, and at predetermined time intervals. Then, a sample was taken for Differential Scanning Calorimetry (DSC) analysis. At the end of the heating process at each temperature, a sample of oil was removed to analyze the fatty acid composition in order to compare it with the composition of the untreated sample.
In order to study the effect on the deterioration of the oil with different food, potatoes and breaded meat were fired at 180ºC in successive frying procedures during periods of 3 hours divided in cycles of 45 minutes. In each cycle, 4 groups of approximately 40 grams each of sample food were fried with a waiting time in the oil of 2 minutes per sample group. At the end of each cycle the TPCs were measured. Separate trials were performed for each sample type starting from fresh oil every time.

2.1 Determination of Total Polar Compounds

The content of Total Polar Compounds (TPC) was determined with a TESTO 265 capacitive type sensor (Testo Inc., USA). This device measures the dielectric constant of the oil and transforms this value directly into percentage in weight of polar compounds. Measurement is carried out by immersing the sensor in hot oil and provides the % in weight of polar compounds, together with the temperature.

2.2 Differential Scanning Calorimetry (DSC)

The thermo grams were obtained with the DSC Q100 device controlled by a 5000 TA module (TA Instruments, New Castle, Delaware, USA) with a cooling system triggered by an atmosphere of N₂ at a flow rate of 20 ml/min. Approximately 7-8 mg of sample oil was weighed into a precision electronic balance in an aluminum capsule and then sealed. TriPLICATE runs of the frying oil samples were run using an empty aluminum capsule as a reference. The thermo grams were obtained using a cooling program from 10 to -80°C at a rate of 2°C/min. From the thermo grams the thermal properties of the frying oil were obtained: Tc, the crystallization temperature (°C) and ΔH, the crystallization enthalpy (J/g) calculated as the area under the crystallization peak.

2.3 Determination of Fatty Acids

The fatty acid composition was determined by gas chromatography according to the AOAC method 965.49. First, the glycerides and phospholipids were saponified. Then, the released fatty acids were esterified in the presence of BF₃-methanol and after analyzed by gas chromatography (Agilent Model 6850, Buenos Aires, Argentina) equipped with a 100% capillary cyanopropyl silicone column (SPTM-2340 60 m with a 0.32 mm diameter and 0.25 mm thick). The oven temperature was set at 140°C for 5 minutes and then increased to 220°C at 4°C per minute. The temperatures of both, the injector and the detector, were 250°C. The identification of the methyl esters of fatty acids was based on the retention time of the standard esters (Sigma-Aldrich).

2.4 Statistical Analysis

All experiments were performed on triplicate samples. Analysis of Variance (ANOVA) was used to analyze the results obtained using the statistical program Info stat v2009 software (Argentina). Comparison of means by Fisher LSD mean was tested, and if P<0.05 the difference was considered statistically significant.

3. Results and Discussion

3.1 Effect of Temperature Treatment on Oil Deterioration

From the results obtained during the heating of the oil at different times, it was noted that the Total Polar Compound (TPC) content increased with the heating time, this increase being proportional to the temperature value. In other words, the increase was sharper the higher the temperature was. At 4 hours of treatment the TPC content reached values of approximately 15, 17, and 21% for 150º, 180º, and 200ºC respectively (Figure 1).

![Figure 1. Total polar compounds (%) formed in the oil during heating treatment at (▲) 150º, (●) 180º and (■) 200ºC.](image)
From the acquired results, zero order kinetics was proposed for the production of total polar compounds at each temperature (Equation (1)).

\[
\frac{dCPT}{dt} = k
\]  
(1)

Where \(k\) corresponds to the reaction rate constant of TCP formation.

Integrating Equation (1) gives the expression:

\[
CPT - CPT_0 = kt
\]  
(2)

Where \(CPT_0\) is the concentration of polar compounds at time 0 which corresponds to the time at which the oil reached the heating temperature used.

The mathematical relationship between the reaction rate constant of a chemical reaction and the temperature can be expressed by the Arrhenius equation (Equation (3)).

\[
k = k_{ref} \exp \left( \frac{Ea}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right)
\]  
(3)

Where \(k_{ref}\) is the value of \(k\) for a reference temperature \((T_{ref})\), \(R\) is the universal gas constant \((8.31 \text{ J} / \text{mol K})\) and \(Ea\) is the value of the activation energy. A normal procedure to determine \(Ea\) is to linearize Equation (3). This includes, taking logarithms followed by a linear regression of the values of \(k\) as a function of \(1/T\). But, in this case, the error in determining the value of \(Ea\) is quite large due to the low number of degrees of freedom \(n = 3 - 2 = 1\). A better way to estimate \(Ea\) is the nonlinear regression of all experimental results at once, since by combining the Equations (2) and (3), it becomes:

\[
CPT = CPT_0 + k_{ref} \exp \left( \frac{Ea}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right) t
\]  
(4)

In this case, the dependent variable is the concentration of total polar compounds while time and temperature are the independent variables. The parameters (constants) to be obtained by non-linear regression are \(TCP_0\), \(k_{ref}\) and \(Ea\). For this paper, the average of the temperatures used in the experiments \((175^\circ C)\) was chosen as the reference temperature. Using this procedure, the number of degrees of freedom was \(n = 18 - 3 = 15\). Therefore, the simultaneous analysis of all data is clearly preferable to the determination of \(Ea\) by linear regression of the values of \(k\) as a function of \(1/T\).

Anon-linear regression of the TPC values as a function of time and temperature (Equation (4)) resulted in an \(Ea\) value of 42.41 kJ/mol and a reaction rate constant at 175°C \((k_{ref})\) of 1.26% TPC/h, with a correlation coefficient \(R = 0.979\) (Figure 2). The values of \(k\) for 150°, 180°, and 200°C were 0.64, 1.42, and 2.30% TPC/h respectively.

In the thermo grams obtained by DSC, the fresh sunflower oil showed a crystallization peak at a temperature of -57.80 °C, with an enthalpy of 34.25 J/g (Figure 3). For the three heating temperatures observations show that as the heating time increased, the crystallization peak was transferred to lower temperatures and the enthalpy decreased. Figure 4 shows the thermo grams corresponding to oil samples with different heating times at 180°C. Table 1
describes the results of crystallization temperatures and enthalpy values obtained. These results are similar to those obtained by\(^2\) for soybean oil heated at 180°C.

Table 1. Crystallization and enthalpy temperature values during heating of sunflower oil at 180°C

<table>
<thead>
<tr>
<th>Heating Time (h)</th>
<th>Crystallization Temperature (°C)</th>
<th>Enthalpy (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>~60.71</td>
<td>29.30</td>
</tr>
<tr>
<td>0.75</td>
<td>~61.52</td>
<td>28.99</td>
</tr>
<tr>
<td>1.50</td>
<td>~62.87</td>
<td>26.01</td>
</tr>
<tr>
<td>2.25</td>
<td>~63.75</td>
<td>25.38</td>
</tr>
<tr>
<td>3.00</td>
<td>~65.44</td>
<td>21.10</td>
</tr>
<tr>
<td>4.00</td>
<td>~67.21</td>
<td>16.31</td>
</tr>
</tbody>
</table>

\(^a\)Time 0 corresponds to the heating time at which \(T = 180\,°\,C\), which was 10 min.

Figure 4. Thermograms obtained for sunflower oil at different heating times at 180°C. Time 0 corresponds to the heating time at which \(T = 180\,°\,C\), which was 10 min.

Table 2. Percent composition of fatty acids in fresh sunflower oil

<table>
<thead>
<tr>
<th>Fatty Acids</th>
<th>Relative Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palmitic (16 : 0)</td>
<td>5.81</td>
</tr>
<tr>
<td>Stearic (18 : 0)</td>
<td>3.16</td>
</tr>
<tr>
<td>Oleic (18 : 1)</td>
<td>22.44</td>
</tr>
<tr>
<td>Linoleic (18 : 2)</td>
<td>66.69</td>
</tr>
<tr>
<td>Others</td>
<td>1.90</td>
</tr>
</tbody>
</table>

The concentration of total polar compounds was linearly correlated with the parameters obtained from the thermograms and the concentration of palmitic and linoleic acids, obtaining correlation coefficients greater than 0.93 (Table 3). The high correlation found between the concentration of total polar compounds and the other measured parameters, suggests the possibility of using any of the analyzed parameters to study the quality of the oils used in the food frying process\(^7\) reported that when the quality of three oils subjected to heating treatment were assessed by DSC, the observed changes in thermal behavior correlated with conventional chemical modifications and the results were used to assess the oxidation status of the oil samples studied similar results were reported by\(^23\).
### Table 3. Relationship between total polar compound concentration (CPT) and other indicators of oil deterioration

<table>
<thead>
<tr>
<th>Indicator (Y)</th>
<th>Correlation Coefficient (R)</th>
<th>Number of Data (n)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc</td>
<td>0.937</td>
<td>11</td>
<td>Y = -48.97 - 1.023 CPT</td>
</tr>
<tr>
<td>H</td>
<td>0.962</td>
<td>11</td>
<td>Y = 66.50 - 2.86 CPT</td>
</tr>
<tr>
<td>16:0</td>
<td>0.985</td>
<td>4</td>
<td>Y = 5.43 + 0.03 CPT</td>
</tr>
<tr>
<td>18:2</td>
<td>-0.968</td>
<td>4</td>
<td>Y = 68.18 - 0.13 CPT</td>
</tr>
</tbody>
</table>

### 3.2 Effect of the Product Used in the Frying Process on Oil Deterioration

Oil deterioration was significantly accelerated while the potato chips and the breaded meat were being fried. The formation of polar compounds increased compared to the results from the heat treatment without sample food. The greatest deterioration was observed when the breaded meat discs were fried due to the increase in the residue content of the food in the oil. While at 2.25 h of heat treatment, the oil reached a TPC content of 14.5%. When potatoes were fried the value was 18.0%, and when breaded meat was used the value obtained was 19.0% (Figure 5).

Base on the values found, we calculated the reaction rate constants of polar compounds formation, which were 1.80 and 2.93% TPC/h for the fried potatoes and the fried breaded meat, respectively. In these frying conditions, the oil life (continuous treatment time until TPC = 25%) would be 7 hours for frying potato chips (37 fry batches) and 4 hours for breaded meat (21 fry batches). Continuous heating of the oil, after successive frying cycles, caused its degradation by oxidation (catalyzed by temperature, light, metal ions, instauration and oxygen) causing thermo oxidation, hydrolysis and polymerization. These results were similar to obtained by in cotton oil submitted to frying successive batches of potato chips in a temperature range of 155-195°C. The deterioration depends on, not only the temperature, but also the duration and the type of frying process, as well as the type of food, according to in unhydrogenated and partially hydrogenated soybean oils, who concluded that the rate of formation of the degradation compounds is given by the duration, temperature, and degree of hydrogenation of the oil concluded that heating time and frying cycles increased, all oxidation parameters including acid value, Total Polar Materials (TPM), Conjugated Dienoic Acid (CDA), and p-anisidine values increased significantly in vegetable oils during chicken frying. According to these results, the changes generated in the organoleptic properties of the oil are a limit in the useful life of the oil used was established, which would require the replacement when values of 25-27% TPC are reached. Establish the degree of oil oxidation can help predict the shelf life of fried foods, protect consumers’ health, and optimize the profit of food industries.

### 4. Conclusions

The deterioration of the quality of the frying oil was the result of the increase in the heating temperature, the duration of the frying process, and the type of product that was used.

It was established that the deterioration of the frying oil can be modeled with kinetics of order 0, obtaining the reaction rate constant which increased its value by increasing the heating temperature, which gained the highest value when frying breaded meat samples.

The high correlation found between the concentration of total polar compounds and the parameters obtained from the thermo grams (DSC) and the concentration of palmitic and linoleic acids suggests the possibility of...
using any of the analyzed parameters to study the quality of vegetable oils subjected to thermal stressing and frying as a quality control to verifying the thermal degradation.

5. Acknowledgements

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6. References