Effects of Antioxidant Capacity and Peroxide Value on Oxidation Stability of Sunflower Oil

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ABSTRACT

Sunflower oil is one of the most consumed types of oils worldwide. Its fatty acid composition consists of about 90 % unsaturated fatty acids and this makes sunflower oil more susceptible to oxidation. In this study; the effects of total antioxidant capacity and peroxide value on oxidation stability of four kinds of refined sunflower oil were determined. The oxidative stability was monitored by peroxide value (PV) and Rancimat induction period (IP). The antioxidant capacities of the samples were determined using DPPH (2,2-diphenyl-1- picrylhydrazyl). The values of the induction period of four samples were determined as 1.46 h, 1.63 h, 2.12 h and 2.35 h, respectively. Radical scavenging activities were ranged between 56 % and 65 %. Peroxide values were determined between 5.0 and 9.0. Peroxide values are a bit higher when compared with previous studies and according to these results the samples cannot be defined as “fresh”, whereas they are acceptable to legal limitations.

1. Introduction

The sunflower which can be grown in limited areas due to soil properties and climatic requirements, is the fourth common oil seed in the World, after soybean, palm and canola [1]. Russia and Ukraine are the largest producers of sunflower and they provide more than 50 % of the total World production [2]. It is the most cultivated oilseed in Europe [3] and Turkey could be mentioned as one of the considerable sunflower producers with 0.93 million tons of seed in 2012, coming after China and USA [2]. Traditional sunflower seed contains about 35-50 % oil [4], whereas by sunflower breeding created hybrids, oil content rises up to 45-50 % [2]. Fatty acid composition and tocopherol, sterol content are some of the main parameters in defining oil quality. An essential fatty acid; linoleic acid (18:2) forms 70 % of the standard sunflower oil. The next one is oleic acid (18:1), it exists 20 % and with breeding programmes oleic acid content may rise more than 90 %. It was proven by clinical and animal studies that both of these fatty acids decrease serum cholesterol. Nevertheless, high content of these unsaturated fatty acids make vegetable oils more prone to thermo-oxidation [2]. Oxidation is a kind of reaction series yielding undesirable products affecting odor and taste. It also causes losses of nutritional value of oil. Tocopherols, considered as natural antioxidants, have protective effect against many diseases such as cardiovascular diseases, cell and DNA damage by free radicals, cancer and Alzheimer [5]. Total tocopherol content of sunflower oil is about 700-1000 mg/kg. In spite of expressing maximum in vivo activity, α-tocopherol’s in vitro protection of extracted oil is limited [2]. Besides, it was proposed that total tocopherol content decreases significantly during refining processes [6]. Lipid oxidation is the main cause of deterioration of oils and fats. Long storage times, presence of heat, metal ions and exposure to light may induce oxidation. Sunflower oil commonly used as cooking oil and salad dressing. It is also used in food processing industry and non-food industries. Widespread usage brings along good quality necessity likewise in all food item. Oxidation stability is one of the most important parameters of edible oils. The main aim of this study was to determine the effects of total antioxidant capacity and peroxide value on oxidation stability of refined sunflower oils sold in Turkey markets prevalently.

2. Material and Method

Four commercial brands (A, B, C, D) of refined sunflower oil were selected as samples which have high availability in the major markets in Afyonkarahisar.

2.1 Rancimat test

Accelerated oxidation tests are commonly used for assessment of oxidation stability. Some of them are Rancimat test and OSI (Oxidative stability index) [7]. In rancimat assay, induction times are observed for the determination of oxidative stability. Sunflower oil (3 g), was exposed to the rancimat test by Rancimat model 743 Metrohm, at 120 °C at an airflow of 20 L/h. The samples are oxidized in elevated temperature under a
stream of air. Volatile, secondary reaction products are formed in oxidized oil sample. These volatile oxidation products are trapped in deionized water. Electrical conductivity of the water is measured by Rancimat and the conductivity increase is associated with the oxidative stability of the sample. Induction time is the period of time until secondary reaction products are detected in the measurement of the electrical conductivity of the solution due to the absorption of the reaction products [8]. The most stable oil samples have the highest values of induction period.

2.2 DPPH Radical Scavenging Activity

DPPH, ABTS and FRAP are common in vitro methods to analyze the antioxidant activities of oils, extracts etc. [9]. In present study, radical scavenging capacity was measured using DPPH method. DPPH is a purple colored stable free radical and by abstracting one electron, it turns into yellow colored non-radical form. It means electron donation capacity of antioxidants specifies the transform of DPPH to non-radical form [10]. 0.5 g sunflower oil was taken and the volume was completed to 3 ml with ethyl ether. 1 ml aliquot of a methanolic solution of DPPH (0.02 %) was added on it. The mixture was shaken vigorously and incubated in the dark for 30 minutes. The absorbance of the solution was measured at the end of the 30. minute at 517 nm against a blank. The antioxidant activity was calculated using the following equation [11]:

\[
\% \text{ Radical Scavenging Act.} = \frac{A_s - A_v}{A_s} \times 100 \quad (1)
\]

\(A_s\) is the absorbance of value of the sample and \(A_v\) is the absorbance value of the blank (methanol).

2.3 Analysis of Peroxide Value (PV)

Peroxide value is the quantity of the total primary oxidation products present in edible oils and it is widely used as a measure of oil quality and to evaluate the storage properties of oils and fats. It measures the concentration of peroxides and hydroperoxides in the initial stages of lipid oxidation [12]. 5 gr sunflower oil were dissolved in 30 ml of acetic acid: chloroform (3:2, v/v). 0.5 ml of saturated solution of potassium iodide was added to mixture and the mixture was shaken by hand swiftly. The mixture was kept in dark for 5 minutes. After the addition of 30 ml distilled water, 2 ml starch indicator (1%) was added subsequently. The mixture was titrated against sodium thiosulfate (0.1 M) until white color appeared. The peroxide value was calculated using the following equation:

\[
P V \left( \frac{\text{mg}}{\text{kg}} \right) = \left( V - V_0 \right) \frac{m}{C} \times 1000 \quad (2)
\]

V and V0 are the volume of sodium thiosulfate consumed by sample and blank, respectively (mL); \(m\) is the weighed portion of oil in grams and \(C\) is the concentration of sodium thiosulfate (M).

3. Results and Discussion

Induction periods of samples were detected as 1.46; 1.63; 2.12; and 2.35 h, respectively. Sample D followed by sample C were the most stable ones, showing the highest induction periods (Table 1). In contrast sample A and B have lower induction periods, indicating poor oxidative stability.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Induction period(h)</th>
<th>Abs. values at 517 nm</th>
<th>DPPH (RSA %)*</th>
<th>Peroxide Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.46</td>
<td>0.554</td>
<td>56</td>
<td>9.0</td>
</tr>
<tr>
<td>B</td>
<td>1.63</td>
<td>0.514</td>
<td>59</td>
<td>8.0</td>
</tr>
<tr>
<td>C</td>
<td>2.12</td>
<td>0.451</td>
<td>64</td>
<td>7.0</td>
</tr>
<tr>
<td>D</td>
<td>2.35</td>
<td>0.435</td>
<td>65</td>
<td>5.0</td>
</tr>
</tbody>
</table>

*RSA: Radical Scavenging Activity

Radical scavenging activities of A, B, C and D are 56 %, 59 %, 64 %, and 65 % respectively as shown in Table 1. As expected, a positive relationship was observed between the amounts of oxidative stability and radical scavenging activities. Peroxide values of samples ranged between 5.0–9.0.

Figure 1. Changes in induction periods versus peroxide values and radical scavenging activities

When all the datas are turned into a polynomial graphic, we obtain the shown equations in Figure 1 and R2 values as 0.9459 and 0.9996. In Figure 1, first curve shows the changes in peroxide values versus induction period and the second one show the changes in induction period versus radical scavenging activities.
4. Conclusion

In present study induction periods are between 1.46-2.35 h. Chinprahast et al. [13] applied the crude extract of pigmented Thai rice cultivar as natural antioxidant and BHA as antioxidant to sunflower oil and compare their effects on oxidative stability. Induction period of control sample determined as 3.02 h whereas antioxidant added ones had induction values between 3.23 h and 3.77 h. These results indicate higher oxidative stability than our samples have. It was specified that sunflower oil was used within 7 days after manufacturing date and this means that samples did not exposed to marketing conditions; this may be the reason of the higher oxidative stability. The results also show that natural and artificial antioxidants fortify the oxidative stability of oil. Radical scavenging activities of our samples range between 56 % and 65 %. Positive relationship between the amounts of oxidative stability and radical scavenging activities is obvious. In other words, oil sample with higher oxidative stability, also has higher radical scavenging activity. Anusuya et al. [12] searched about the impact of polyphenols from 3 banana cultivars on sunflower oil stability and they determined that 3 different Indian banana cultivars exerted 49.01 % – 80.86 % DPPH radical scavenging ability. On the other hand, synthetic antioxidants BHT and BHA had radical scavenging activities ranged between 85.21 % and 95.68 %. All of these radical scavenging activities are higher than our values. This means that addition of any kinds of antioxidants provide higher oxidation stability to sunflower oil. Peroxide values of our samples are acceptable as Turkish Food Codex permits to peroxide values for edible refined oils till 10 meq/kg [14]. Janu et al. [10] investigated commonly used vegetable oils physicochemical parameters. They determined the peroxide value of sunflower oil they analyzed as 1.2 meq O₂/kg oil. Castelo-Branco et al. [15] investigated the quality and stability of vegetable oils in Rio de Janeiro, similarly. They reported the peroxide value of sunflower oil 1.14 meq O₂/kg oil and induction period 4.91 h. Both of these values point out high oxidative stability.

Differences between brands in present study and other studies mainly arise from the variations in process parameters during refining. As Castelo-Branco stated [15]; These may be process time, temperature, chemicals etc. Transport and storage conditions are also important post-process factors effecting food stuff. Storage time, temperature and illumination conditions in markets may cause significant changes in oils.

This market analysis study proves the fact that direct proportion between radical scavenging activity and rancimat induction period. Oils with high radical scavenging activity have lower peroxide values. Comparing with previous studies, it is obvious that addition of any kinds of antioxidants provide higher oxidation stability to sunflower oil. Addition of these different antioxidants may also contribute to desirable aroma.

References