Advantages of thermal stability of virgin olive oil over canola and frying oil

Saeed Keshavarz Moghadamb, Maryam Moslehishadb, *a

a Nutrition and Food Sciences Research Center, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran
b Department of Food Science & Technology, Safadasht Branch, Islamic Azad University, Tehran, Iran

A B S T R A C T

The aim of this study was to investigate the suitability of virgin olive oil in comparison with canola oil and frying oil for thermal processing of virgin olive oil, canola oil and frying oil on chemical oxidative indices (peroxide, p-anisidin value and oxidative stability), acid value and fatty acid compositions. The oil samples were exposed to heat treatment at 180 °C and qualitative parameters were determined at 0, 60, and 90 min after thermal processing. The results indicated that the parameters of acidity, p-anisidin value increased over time (p < 0.05). Oxidative stability at 110 °C was also analyzed using Rancimat. Resistance to oxidation in frying and canola oils reduced (p < 0.05) faster than that in virgin olive oil due to presence of sterolic compounds with antioxidant properties in olive oil that is activated at high temperatures and increases stability of olive oil. Therefore, the virgin olive oil regarding to its nutritional properties, being rich in oleic acid (67%) and containing natural antioxidant compounds might be a good choice to be in the basket of goods of families for domestic frying.

Keywords: Thermal processing, Virgin olive oil, Canola, Frying oil

1. Introduction

In recent years, frying is a rapid, convenient and energy efficient process which has increased dramatically in industrial countries (Inanc & Maskan, 2014). Frying is the process of soaking food in hot oil in relationship with air and food at high temperature (around 140-190 °C). Frying improves palatability of food products due to the desired taste, odor and texture of the fried food (Marinova et al., 2012; Chiou & Kalogeropoulos, 2017).

Besides the desired changes, during thermal processing, a set of chemical reactions such as hydrolysis, oxidation, thermal decomposition and polymerization occurs. Oxidation can cause to increase health hazard especially cardiovascular diseases, some unwanted physiochemical changes and also can cause to reduce nutritional and organoleptic characteristics of food products (Soriano et al., 2000; Marinova et al., 2012; Inanc & Maskan 2014). Typically, during thermal process, there are optimal conditions under which the desired quality of food is obtained. Certainly, many factors affect the deterioration of oil and oxidation process during thermal process such as the type of frying oil, initial oil quality, time and temperature, the amount of antioxidants and oxygen content (Shyamala et al., 2005; Choe & Min 2007; De Alzza et al., 2018).

The choice of frying oil depends on many factors such as availability, price, frying performance, flavor and oxidative stability of fried oil. Ideal frying oil should be inexpensive, high stability and fatty acid profile that is low in saturated and trans fatty acids (Sulieman et al., 2006). Fatty acid components are the most important factor in oxidative stability of edible oils. Furthermore, it has been reported that high content of monounsaturated fatty acids (MUFAs) reduce the risk of cardiovascular disease and decrease low density lipoprotein (LDL) cholesterol and triglycerides. Monounsaturated fatty acids (MUFAs) such as oleic acid have high resistance to oxidation (Covas, 2007; Kim et al., 1999; Silva et al., 2010). Therefore, virgin olive oil and canola oil were selected as a good source of oleic acid content as well as they are abundant in the market and can be easily prepared. Although synthetic antioxidants are used in commercial oils especially in frying oil to prevent oxidative rancidity; application of these additives has been limited due to their detrimental effects on human health. Besides, hydrogenation has also been performed in production of frying oil to increase thermal stability of oil. However, hydrogenation can cause to increase saturated, trans fatty acid or metallic flavor, and it can cause to oil quality and increase the risk of heart disease (Choe & Min, 2007; Chiou & Kalogeropoulos, 2017; De Alzza et al., 2018).

The aim of this study was to investigate the suitability of virgin olive oil in comparison with canola oil and frying oil for thermal
processing. Due to the health hazards of synthetic antioxidants added to canola oil and especially frying oils at high concentration, to increase the level of public health, the use of virgin olive oil which has natural antioxidant compounds (phenolic compounds, sterols, tocopherol) and high oleic acid content has been considered in this study.

2. Material and Methods

2.1. Oil samples and Materials

Commercially available oil samples of frying, canola and virgin olive oils were purchased from local market and transferred to laboratory under proper transportation conditions. All oil samples were kept in sealed dark glass bottles and stored at 20 ºC.

All of the chemicals used in this research were analytical grade. Potassium iodide, sodium thiosulfate, ammonium thiocyanate were purchased from sigma-aldrich. KOH, n-hexane, chloroform, methanol, phenolphthalein, diethylether, acetic acid was used from Merck, Germany.

2.2. Frying treatment

250 mL of the oil samples were poured into a 500 mL beaker and heated at 180 ± 2 °C in an oven. The samples were taken at 0, 60, and 90 min after heat treatment and the following experiments were conducted at above-mentioned time intervals.

2.3. Determination of acid value

Acid value was measured using AOCS standard method 3d-63 (AOCS, 1990). Oil samples were completely dissolved in ethanol-chloroform and vigorously stirred. After adding phenol-phthaleine indicator, the contents of flask were titrated with 0.1 normal standard of hydroxide solution. The acidic value was expressed in terms of mg potassium hydroxide per g of oil.

2.4. Determination of peroxide value

Measurement of peroxide value was performed by iodometric method based on AOCS Cd 8-53 standard method. The amount of peroxide value was calculated in terms of milli-equivalents of active oxygen per kg oil.

2.5. Determination of para-anisidine value

In order to determine the para-anisidine value (p-AV) of the oil samples, AOCS Official Method Cd 18-90 was utilized. Based on this, 1 g of oil was mixed with 100 mL isooctane. The absorption of the solution was determined by spectrophotometric assay.

2.6. Determination of totox value

Totox value considering measurement of peroxide and para-anisidine values was calculated by the following formula to indicate overall oxidation state of fried oil samples:

Totox value = 2 peroxide value + Anisidine value

2.7. Determination of Oxidative stability

To determine the oxidative stability of oil samples, Rancimat device (Metrohm; Herisau, Switzerland) was used based on ISO 6886 (2006). For this purpose, 2.5 g of the sample was placed in each container of the device and the container temperature was raised up to 110 ºC. A stream of air was passed over the samples at 20 L/h. According to the oxidative stability diagram of the samples at these conditions, the oxidative stability of samples was expressed as the time duration of induction phase per hour.

Table 1. Change of fatty acid composition (mean values ± SE) during frying at 180 ºC

<table>
<thead>
<tr>
<th></th>
<th>Frying oil</th>
<th>Virgin olive oil</th>
<th>Canola oil</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>C12:0</td>
<td>0.15±0.07</td>
<td>0.15±0.14</td>
<td>0.14±0.14</td>
</tr>
<tr>
<td>C14:0</td>
<td>0.75±0.07</td>
<td>0.74±0.08</td>
<td>0.75±0.08</td>
</tr>
<tr>
<td>C14:1c</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C16:0</td>
<td>2.6±0.20</td>
<td>2.3±0.10</td>
<td>2.65±0.70</td>
</tr>
<tr>
<td>C16:1c</td>
<td>0.1±0.21</td>
<td>0.2±0.07</td>
<td>0.4±0.28</td>
</tr>
<tr>
<td>C17:0</td>
<td>0.05±0.07</td>
<td>0.1±0.00</td>
<td>0.5±0.07</td>
</tr>
<tr>
<td>C18:0</td>
<td>4.8±0.20</td>
<td>4.7±0.20</td>
<td>4.5±0.05</td>
</tr>
<tr>
<td>C18:1c</td>
<td>0.1±0.14</td>
<td>0.5±0.07</td>
<td>0.1±0.21</td>
</tr>
<tr>
<td>C18:1c</td>
<td>37.9±0.60</td>
<td>18.2±0.60</td>
<td>17.6±0.60</td>
</tr>
<tr>
<td>C18:2c</td>
<td>0.3±0.14</td>
<td>0.2±0.28</td>
<td>0.4±0.00</td>
</tr>
<tr>
<td>C18:2c</td>
<td>24.8±0.20</td>
<td>23.6±0.79</td>
<td>23.5±0.80</td>
</tr>
<tr>
<td>C18:3s</td>
<td>0.2±0.07</td>
<td>0.2±0.05</td>
<td>0.2±0.07</td>
</tr>
<tr>
<td>C18:3c</td>
<td>2.7±0.10</td>
<td>2.6±0.20</td>
<td>2.7±0.20</td>
</tr>
<tr>
<td>C20:0</td>
<td>0.4±0.07</td>
<td>0.4±0.07</td>
<td>0.4±0.07</td>
</tr>
<tr>
<td>C22:0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C22:1c</td>
<td>-</td>
<td>0.1±0.21</td>
<td>0.1±0.21</td>
</tr>
<tr>
<td>C24:0</td>
<td>-</td>
<td>0.05±0.07</td>
<td>0.1±0.14</td>
</tr>
<tr>
<td>C24:1c</td>
<td>-</td>
<td>0.2±0.14</td>
<td>0.2±0.14</td>
</tr>
<tr>
<td>SFA</td>
<td>32.6±0.90</td>
<td>32.5±1.55</td>
<td>32.2±0.80</td>
</tr>
<tr>
<td>UFA</td>
<td>67.4±5.90</td>
<td>67.5±3.55</td>
<td>68.3±0.50</td>
</tr>
<tr>
<td>MUFA</td>
<td>38.4±0.90</td>
<td>38.2±0.95</td>
<td>38.2±0.95</td>
</tr>
<tr>
<td>PUFAs</td>
<td>29±0.95</td>
<td>28.6±0.70</td>
<td>29±0.95</td>
</tr>
<tr>
<td>SFA/UFAs</td>
<td>0.45±0.02</td>
<td>0.45±0.02</td>
<td>0.45±0.02</td>
</tr>
<tr>
<td>C18:1c/C18:2c</td>
<td>1.67±0.01</td>
<td>1.49±0.02</td>
<td>1.47±0.01</td>
</tr>
</tbody>
</table>
2.8. Preparation of fatty acid methyl esters

To determine fatty acid profile of oil samples, methyl esters of fatty acids were prepared based on AOCS Ch 2-91.b and ISO 5508 (1999). Initially, around 1 g of the oil samples was mixed with 7 mL of solvent and stirred vigorously. Thereafter, 2 mL of KOH was added and stored at 50-60 °C for 15 min. Then, 1 µL of the top phase of the prepared samples was injected to a gas chromatography.

2.9. Gas chromatography analysis

Methyl esters of fatty acids were analyzed using gas chromatography (YL6500GC, Young-Lin Inc., Korea) with a capillary column Cp-Sill 18 (60 m × 0.25 mm and outer diameter: 0.33 mm) and detector type of Flame Ionization Detector (FID). The injector and detector temperature was 250 °C and 280 °C, respectively. The process was Isothermal at 180 °C. The carrier gas was hydrogen, and injection volume was 1 µL with a flow rate of 4 mL min⁻¹. The relative percentage of each fatty acid was expressed as final result.

2.10. Statistical analysis

One-way analysis of variance (ANOVA; p < 0.05) was used to compare the data using SPSS 20.0 software (SPSS INC., Chicago, IL, USA, 2002). The significant difference was calculated by Duncan’s New Multiple Range Test. The data are shown as mean values plus standard errors of mean.

![Graph](Image)

Fig. 1. Changes in Acid (AV) value against the frying time of oil samples. Different small letters show significant differences at p < 0.05 for behavior of oil against time during frying. Different capital letters show significant differences at p < 0.05 for oils together at a same time.

3. Results and Discussion

3.1. Acid value

As shown in Fig. 1, the results of this study revealed that acid value of oil samples increased slightly during heat treatment which was in accordance with previous studies (Frega et al., 2012). Note that since heating oil samples has been done in the absence of food product and due to lack of humidity, the hydrolysis reaction is trivial and a slight increase in acid value occurs. Ghavami et al. (2002) also stated that free fatty acid of semi- and non-hydrogenated sunflower oils is temperature dependent and prolongation of the process time results in increase percentage of free fatty acids. They, however, did not observed a fully ascending trend for free fatty acid contents due to volatility of free fatty acids that might leave the frying oil along with the water vapor of food products. The similar findings were previously obtained by Rahnamon et al. (2010), during investigation of the efficiency of grape seed oil as a frying oil, they observed that as the heating time to the grape seed oil increases at 180 °C (from 0 to 90 min), acid value is magnified significantly. These observations have also been reported in relation to heating of different types of olive oil by other researchers (Nawar, 1985).

Increased level of free fatty acids during heating process at high temperatures might be attributed to the role of high temperature in accelerating the separation of fatty acids from triacylglycerols. Furthermore, the free fatty acids themselves are able to emulsify water and oil and to intensify the hydrolysis process resulting in increased value of free fatty acids (Nawar, 1985; Frega et al., 1999). However, they stated that increased acid value is not only due to hydrolysis of triacylglycerol and part of it can be attributed to the carboxyl within the polymeric or oxidative products. Based on Codex alimentarius standard, the maximum acidic value of frying oil is 2% and it is indeed regarded as a disposal point for the oil. According to this standard, it seems that olive, canola oil investigated in this research have not exceeded the standard of interest after 90 min of heating at 180 °C (Kaviani et al., 2012).

![Graph](Image)

Fig. 2. Changes in peroxide value (PV) against the frying time of oil samples. Different small letters show significant differences at p < 0.05 for behavior of oil against time during frying. Different capital letters show significant differences at p < 0.05 for oils together at a same time.

![Graph](Image)

Fig. 3. Changes in oxidative stability index (OSI) against the frying time of oil samples. Different small letters show significant differences at p < 0.05 for behavior of oil against time during frying. Different capital letters show significant differences at p < 0.05 for oils together at a same time.

---

Keshavarz Moghadam and MoslehiShad

JFBE 3(1): 41-46, 2020

---
3.2. Peroxide value and oxidative stability

Fig. 2 and 3 presents the peroxide value and oxidative stability of olive oil, canola and frying oil, respectively. At the beginning of the thermal process of olive oil, peroxide value was significantly ($p < 0.05$) higher than that of frying and canola oils, the oxidative stability of olive oil was also significantly ($p < 0.05$) lower than that of canola and frying oil. Note that peroxide value of olive oil is in accordance with IOOC standard ($\leq 20$ in milleq. oxygen per kg oil) (IOOC, 2011). During heat treatment the oxidative stability of virgin olive oil increases that might be due to the presence of sterolic compounds of Δ5-avenasterol and Δ7-avenasterol in citrostadienol of the virgin olive oil. These compounds at high temperatures exhibited antioxidant activity (Wang et al., 2002). Furthermore, the oxidative stability of olive oil is also due to the higher amount of α-tocopherol, compared with the other three oils (Chatzilazarou et al., 2006).

The formation rate of hydro-peroxides (preliminary products of oxidation) significantly ($p < 0.05$) increases. Regarding to higher amounts of monounsaturated fatty acids of olive oil compared with the frying oil, the higher peroxide value of olive oil was predictable. Decomposition of hydro-peroxides implies production of free radicals followed by launching or accelerating of the oxidation reaction and eventually transition of the fatty molecules oxidation from the slow or induction phase to the quick or accelerated phase. For this reason, hydro-peroxides have a great potential for launching and intensifying the oxidation activity. The reflection of the phase transition rate in the oxidation process or the decomposition rate of peroxides can also be observed in other parameters such as anisidine index, oxidative stability and totox value (Fig. 4). Accordingly, the progression of oxidation is larger than that of fresh frying oil or canola compared with olive oil. Consequently, it can be concluded that preliminary products of oxidation in olive oil have been decomposed to secondary compounds. The lower oxidative stability of the olive oil compared with that of frying oil or canola can also be regarded as an evidence for this claim. In another research, conducted on the examination of the effect of temperature and time on production and decomposition of hydro-peroxides in canola and soy oil, it has been reported that at $160 \, ^{\circ}C$, the peroxide index of canola oil changed until the first 6 hours with an ascending trend, while thereafter no specific variation was observed in the level of production for these compounds. However, the changes in soy oil did not follow any specific patterns and indicated fluctuations over this time period (Nawab & Ghavami, 2011). Rahnamon et al. (2010) also suggested that the degree of peroxide index of grape seed oil has a significant increase during the first hour of the thermal process, but in the final 30 min decreases significantly. For investigation of heat stability of rice bran oil during thermal treatment at $173 \, ^{\circ}C$, found that during heating of oil at 3-min cycles, the peroxide value experiences a significant increase until the first two cycles, however thereafter no significant increase was observed in the amount of this acid (Debnath et al., 2012). Such observations regarding the trend of changes in the peroxide index during thermal process have been reported in many studies. What is similar in almost all of these studies is the instability of the ascending trend of production of peroxide compounds in parallel with increased prolongation of the thermal process. The stability of the oxidation of the semi- and non-hydrogenated rapeseed oil has been investigated during thermal process of potato for 15, 20-min cycles at $180 \, ^{\circ}C$. They reported that due to fluctuations in the degree of the peroxide value during the frying process and lack of a certain trend because of decomposition of hydro-peroxides with prolongation of the process time, one cannot use it as an index for the comparison of oxidative stability of these two types of oil (Hazuka et al., 2000). As mentioned previously, as the preliminary products of the oxidation process, hydro-peroxides are relatively unstable, where the energy required for splitting the oxygen-oxygen bond in these compounds (R-O-O-H) is around 44 kcal/mol, considered as a fairly weak bond (Kaviani et al., 2012). Accordingly, during the frying process, these compounds are usually decomposed to different compounds and hence it is expected that the amount of these compounds does not increase with the progression of oxidation. However, that the amount of these compounds decreases immediately after a certain period of time, but they may decompose with production of hydro-peroxides. Similarly, after a certain period of time, an almost constant trend may be seen. This phenomenon can also be observed to some extent in the changes that occur in the trend of peroxide index of the studied frying oil in this research. Accordingly, the peroxide index is not a very reliable index for investigation of oxidation progression in an oil sample or at least it is not possible to judge oxidative stability of oil samples. Nevertheless, the peroxide index is still used as an index for specifying the disposal point of oil. Based on Codex standard, the maximum allowable amount of peroxide for vegetable frying oil is 5 meq. active oxygen per kg of oil. Based on the findings presented in this study, the amount of peroxide in frying oil in the worst case, 90 min, was around 4.9 meq active oxygen per kg of oil. However, during 90 min of heating the olive and canola oil, the amount of peroxide exceeds far greater than the standard limits.

![Fig. 4. Changes in Totox value against the frying time of oil samples.](image)

3.3. para-anisidine value ($p$-AV)

Due to the instability of peroxide compounds (preliminary products of oxidation) and their decomposition during frying, the contents of aldehydes ($p$-AV) as secondary oxidation products were determined (Inanc & Maskan, 2014). The changes in the $p$-AV of oil samples during frying are presented in Fig. 5. Obtained data revealed that there were significant differences ($p < 0.05$) among $p$-AV of oil samples before heat treatment. However, the $p$-AV of olive and canola oil samples was higher than that of frying oil. In other words, the presence of these compounds can be regarded as the consequence of oil oxidation during harvesting of oil recovery sources, its transportation, maintenance, and eventually the extraction and treatment processes (Nawab & Ghavami, 2011). The $p$-AV of all the oil samples increased with the increase in heating.
In the current study, the $p$-AV of the frying, olive and canola oil was determined after 90 min at 180 °C. These findings are in agreement with those reported by Silva et al. (2010), Turani et al. (2012) and Inanc and Maskan (2014). In another study about the investigation of heat stability of soy and olein palm oils, they suggested that the value of the $p$-AV of these oils after 6 hours of thermal process at 185 °C was 104.1 and 46.25, respectively (Abdulkarim et al., 2007).

The results showed the concurrence of decreasing trend of peroxide value and the onset of increasing rate $p$-AV of olive oil sample during thermal process. Rahnamon et al. (2010) also reported that exactly at the time when the peroxide value of the frying oil starts its decreasing trend the $p$-AV grows more dramatically.

3.4. Fatty acid composition

As shown in Table 1, the predominant fatty acid of frying, olive, and canola oil isoleic acid (C18:1). Note that, the oleic acid content of olive oil accounting for around 67% that is significantly ($p < 0.05$) the highest one compared with canola (55%) and frying oil (37%). After oleic acid, linoleic acid (C18:2) stands in the second place with 25% in frying oil and 23% in canola oil, greater than that in olive oil (12%).

Other fatty acids identified in the oil samples had lower amounts including C18: 3, C20: 1, C16:1, C20:0, and C20:2. Fatty acid profile is an important determining factor in oxidative and heat stability of oil samples during heat treatment due to the fact that energy required for separation of hydrogen from the carbonic chain of that polyunsaturated fatty acid diminishes, followed by acceleration of fatty acid participation in oxidation, isomerization, polymerization, and cyclation. Consequently, organoleptic and frying quality of oil decreases and toxic and harmful compounds increases (Boskou, 2011). Therefore, it is expected that frying oil possess higher heat and oxidative stability since saturated fatty acids account for about 32% of its fatty acids, while these values are 17% and 11% for the olive and canola oils, respectively as well as this stability is also related to the presence of high amounts of synthetic antioxidants. In a comparative study of oxidative stability of soy, olein palm, and corn oils during deep frying, researchers found that the olein palm oil had the highest heat stability because of containing the highest amount of saturated fatty acids among the three oils of investigation. However, saturated fatty acids are not the only criterion for heat stability, the type of unsaturated fatty acids and the degree of their unsaturation are also of great significance such that the oxidation rate of linolenic acid with three dual bonds is 1.5 times the oxidation rate of linoleic acid with two dual bonds and 15 times the oleic acid with one dual bond (Shahidi, 2005). Kim et al. (1999) and De Alzza et al. (2018) reported that higher stability of olive oil oxidation compared with that of grape seed, canola oil and soy oil. They attributed this to the lower polyunsaturated fatty acid content of olive oil compared with the two other oils. Monounsaturated fatty acids accounted for around 65% of the frequency of fatty acids of olive oil investigated in the present research. However, this amount was about 33% and 57% for the frying and canola oils, respectively. The ratio of monounsaturated to polyunsaturated fatty acids for olive, canola, and frying oil was 5.83, 3.42, and 1.64, respectively.

Normand et al. (2006) suggested that the degree of formation of free fatty acids in typical sunflower oil during 72 h of the thermal process is higher compared with modified sunflower seed with higher oleic acid content. However, the extent of formation of polar compounds was similar in both oils. Furthermore, the degree of destruction of tocopherols compounds with antioxidant properties was more intense in typical sunflower oil compared with modified oil. Based on this, they stated that it is not possible to judge heat stability of oil only by relying on the composition of fatty acids. However, the comparison of the nutritional quality and oxidative stability of these oils can be a basis for preferring one to another.

The results of epidemiological research indicate that consumption of oils containing saturated fatty acids results in sclerosis of vein walls and in turn increased risk of cardiovascular diseases (Daniel et al., 2005). Accordingly, olive oil due to high oleic acid content seem to be more suitable oil for frying compared with frying oil containing lower saturated fatty acids and it had been shown antihypertensive activity and LDL cholesterol lowering effects as well as it has high heat and oxidative stability (Psaltopoulou et al., 2004).

4. Conclusion

Considering the results obtained, although both frying and canola oils had almost the minimum requirements for frying oil, the virgin olive oil is suggested as suitable oil for thermal processing due to high nutritional value, natural antioxidant compounds, high amount of $\alpha$-tocopherol and acceptable oxidative stability and being in standard range during frying. The ratio of monounsaturated fatty acids to polyunsaturated was also higher for olive oil, a reason for its oxidative stability. At the end of the thermal processing, the oil stability indices of virgin olive oil revealed that it is suitable for thermal processes. Therefore, one can benefit from virgin olive oil as domestic frying.

Acknowledgment

The support of Pharmaceutical Sciences Branch, Islamic Azad University (IAUPS) and Institute of Standards and Industrial Research of Iran are gratefully acknowledged. The authors would like to gratefully thank Dr. Masoud Homapour for his kind support in this research.

Conflict of interest

The authors declare that there is no conflict of interest.
References


