Review

Effect of cooking on olive oil quality attributes

Carla S.P. Santos, Rebeca Cruz, Sara C. Cunha, Susana Casal *

REQUIMTE, Serviço de Bromatologia e Hidrologia, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

Abstract

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Virgin olive oil consumption, as final seasoning or within cooked foods, is increasing worldwide, mainly due to its recognized nutritional benefits. However, the maintenance of its quality and health attributes after thermal processing is frequently questioned. The aim of this article was to provide a careful review of published studies on the assessment of olive oil thermal processing, in order to ascertain the optimal settings for maximization of olive oil quality, while delaying the onset of oxidation products with detrimental health impacts.

Through the selection of a particular olive grade, such as extra-virgin, virgin or refined olive oil, distinct starting compositions may be achieved, particularly regarding bioactive and antioxidant compounds, with a direct effect on thermal performance and nutritional value of cooked foods. Furthermore, different cooking practices, from common frying to boiling and including microwave cooking, along with operating conditions, as time, temperature and food amounts, undoubtedly modify the olive oil chemical profile.

According to the compiled studies, in order to preserve virgin olive oil bioactive components heating time should be reduced to the minimum. Nevertheless, olive oil performance under prolonged thermal processing is usually equal or superior to other refined vegetable oils, due to its balanced composition regarding both major and minor components. However, as most of its bioactive components, including phenolic compounds, are gradually lost, it is economically advantageous to use lower olive oil grades and frequent replenishment under prolonged thermal processing. Future studies dealing with thermal degradation paths of minor olive oil components and their implication in human health will be of particular value to further clarify this issue.

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1. Introduction

Originally limited to the Mediterranean regions, where olive oil still remains as the main source of external fat, Olea europaea L. tree cultivation and olive oil consumption are expanding to other countries in Northern Europe, as well as United States, Argentina, Chile, Mexico and Australia, mainly as a result of its sensorial attributes and potential health benefits (Boskou, 2009; García-González, Aparicio-Ruiz, & Aparicio, 2008; Gustone, 2002).
Olive oil is usually obtained by cold-pressing of olive fruits, followed eventually by washing with water, filtering and centrifugation. In comparison with other common vegetable oils, obtained by solvent extraction and further submitted to diverse refining processes, this virgin olive oil (VOO) retains much of the original fruit components. Therefore, while most marketed vegetable oils are mainly triacylglycerol (TAG) mixtures, olive oil presents other natural fruit components, as pigments, phenolic compounds and volatile compounds. In addition to the health benefits of a rich monounsaturated fat, increasingly documented in the literature, the presence of these minor compounds endows an added value to olive oil, increasing its potential bioactivity (Stark & Madar, 2002; Waterman & Lockwood, 2007).

Several olive oil grades are commercially available. Its classification is usually based on sensorial attributes and chemical parameters that give a general overview on its quality and authenticity. These characteristics, namely the free fatty acids (FFA) as described in Table 1, are regulated by several organizations, including the European Commission itself, the International Olive Oil Council (IOC), or the Codex Alimentarius established by the Food and Agriculture Organization of the United Nations and the World Health Organization.

Extra-virgin olive oil (EVOO) and VOO are the most prized olive oil grades, being consensual that their quality attributes are maximized when consumed without being previously subjected to any thermal treatment. Therefore extra virgin oil should be preferably added as final seasoning in fresh salads, soups, or more elaborated dishes. Still, when olive oil is used as the cooking base, as in roasting, sautéing (pan-frying), stir-frying, or even deep-frying, thermal effects occur (Boskou, 2009; Waterman & Lockwood, 2007). Besides, in opposition to other refined vegetable oils, these effects will also disturb the minor olive compounds. Several authors have addressed this issue, in particular the heating effect on olive oil nutritional and biological properties. Such knowledge is essential if one intends to know the adequate temperatures for each olive oil category and processing method, the interaction with the food under cooking, the adequate rejection time or the shelf-life of the processed food, aiming the maintenance of the original nutritional features of crude olive oil.

The present review focuses on the most important studies dealing with olive oil heating, under laboratory simulation or, preferably, under real cooking conditions, while attempting to understand adequate processing conditions to preserve its quality and to reduce hazard formation. Moreover, the current work identifies those issues that require further research to reinforce olive oil correct use and to potentiate its health benefits.

### 2. Olive oil composition

In order to understand olive oil behavior under thermal processing conditions, it is fundamental to address some considerations into its chemical composition. In a brief way, as this is not the subject of the present review, some key points must be mentioned. First, olive oil is among the vegetable oils with higher monounsaturated fatty acids (MUFA) in its composition, being therefore less prone to oxidation than those with higher polyunsaturated fatty acid (PUFA) content. Second, VOO are not subjected to any refining process, keeping important olive fruit components, namely phenolic compounds (e.g. hydroxytyrosol, tyrosol and oleuropein), pigments (e.g. chlorophylls), hydrocarbons (e.g. carotenoids and squalene), sterols, phospholipids, mono- and diglycerides, fatty alcohols, waxes, and diverse aroma compounds, all with relevant functions in olive oil stability and flavor. Third, olive oil composition is dependent on several parameters including olive variety, edaphoclimatic conditions, harvesting period and technique, fruit ripening degree, leaf removal, extraction system, etc. (Firestone, 2005; Frankel, 2011; Gustone, 2002; Pellegrini & Battino, 2006), making each olive oil batch unique, and increasing the difficulties when attempting to standardize experimental conditions.

Compositional changes in the olive oil after thermal processing are expected. The most common degradations include TAG hydrolysis and polymerization, fatty acid and sterol oxidation, Maillard reactions with food components, among others. These reactions are common to all vegetable oils, each one with particular rates and susceptibilities, and are generally used to predict fat degradation (Warner, 2002). Therefore, the most usual parameters when testing vegetable oil thermal behavior include physical measurements (color, foam, density, etc.) and several chemical indicators such as FFA, polymerization degree, saturated/unsaturated fatty acid ratios, tocopherol and phenolic degradation.

Apart from the loss of beneficial substances during thermal treatment, a great concern regarding new formed compounds under thermal stress, including oxidized fatty acids and sterols or TAG polymers, and their possible impact on human health is rising. Nevertheless, due to its richness in other components than fatty acids, VOO represent a complex pool of possible thermal reactions, including degradation and interactions of those aforementioned substances.

The present review will focus on the behavior of the most important olive oil components under thermal processing, including fatty acids and several vital minor compounds. When available, comparisons with other vegetable oils will be established.

### 3. Cooking with olive oil

Olive oil, similar to other vegetable oils, is used in deep-frying, pan-frying, roasting, microwave cooking, etc. (Boskou, 2009; Waterman & Lockwood, 2007). Each thermal processing type has particular characteristics, namely regarding temperature and confection time. Tables 2 and 3 compile several studies with olive oil cooking, grouped by processing method. Within each group, real and simulated cooking are included and compared, being supported by the analytical parameters chosen by the authors to evaluate olive oil performance.

#### 3.1. Frying

Frying is one of the oldest methods of food preparation. It improves the sensory quality of food by formation of aroma compounds, attractive color, crust and texture, all highly appreciated by the consumers. However, the high level of incorporated fat is an undesirable outcome, increasing caloric intake (Echarte, Ansorena, & Astiasarraín, 2003; Pedreschi, 2012).

Due to the high temperature and prolonged time used on repeated frying, the oils are progressively degraded by a complex series of chemical reactions including oxidation, hydrolysis, and polymerization. These reactions, however, are not equivalent for all the vegetable oils, and there is a particular concern regarding olive oil since its bioactive attributes might be lost during this process, despite being highly resistant to thermal oxidation.

The most common frying methods are deep-frying, being the food totally immersed in hot oil, and pan-frying, when the food is cooked in a pan with little amounts of oil (Bognár, 1998; Boskou, Salta, Chioù, Troullidou, & Andrikopoulos, 2006; Sioen et al., 2006). Following consumer’s awareness to reduce fat intake, several electrical cooking systems are being developed, aiming to achieve products similar to the...
### Table 2
Literature review on olive oil under deep-frying and pan-frying studies.

<table>
<thead>
<tr>
<th>Type</th>
<th>Oil type</th>
<th>Food</th>
<th>Heating conditions</th>
<th>Free fatty acids</th>
<th>Peroxide Value</th>
<th>p-Anisidine value</th>
<th>Extinction coefficients</th>
<th>Fatty acid composition</th>
<th>Polar compounds</th>
<th>Phenolic compounds</th>
<th>Vitamin E</th>
<th>Antioxidant activity</th>
<th>Volatile compounds</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep-frying</td>
<td>VOO vs other</td>
<td>Potatoes</td>
<td>170 °C; 10 sessions (1 day); NR</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>Andrikopoulos et al., 2002</td>
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<tr>
<td></td>
<td>EVOO vs other</td>
<td></td>
<td>180 °C; 12 sessions (2/day); NR</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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<td>Gómez-Alonso et al., 2003</td>
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<td></td>
<td>ROO</td>
<td></td>
<td>180 °C; 75 sessions (10/day); FR</td>
<td>x</td>
<td>x</td>
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<td></td>
<td></td>
<td>x</td>
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<td>x</td>
<td>x</td>
<td>Romero et al., 2003</td>
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<tr>
<td></td>
<td>VOO vs others</td>
<td></td>
<td>170 °C; 8 sessions (1 day); NR</td>
<td>x</td>
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<td>Boskou et al., 2006</td>
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<tr>
<td></td>
<td>EVOO vs VOO vs</td>
<td></td>
<td>170 °C; 27 h (9 h/day); NR</td>
<td>x</td>
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<td>x</td>
<td>Casal et al., 2010</td>
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<td></td>
<td>OO vs other</td>
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<td>Transparent foods</td>
<td>x</td>
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<td>x</td>
<td>Romero et al., 2000</td>
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<tr>
<td></td>
<td>OO vs others</td>
<td></td>
<td>180 °C; 40 sessions (2/day); FR</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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<td>Bastida &amp; Sánchez-Muniz, 2002</td>
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<td></td>
<td>EVOO vs Potatoes vs simulation</td>
<td></td>
<td>180 °C; 40 sessions (10/day); NR</td>
<td>x</td>
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<td>x</td>
<td>Kalogianni et al., 2010</td>
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<td></td>
<td>VOO</td>
<td></td>
<td>180 °C; 5–25 h</td>
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<td>Brena et al., 2002</td>
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<td>EVOO vs OO vs others</td>
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<td>180 °C; 1–5 h and</td>
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<td>Fullana et al., 2004</td>
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<td></td>
<td>EVOO vs OO vs other</td>
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<td>240 °C; 2–7 h</td>
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<td>x</td>
<td>Carrasco-Pancorbo et al., 2007</td>
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<tr>
<td></td>
<td>EVOO vs CROO</td>
<td></td>
<td>170 °C; 3 h</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<td>x</td>
<td>x</td>
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<td>x</td>
<td>x</td>
<td>Cheikhousman et al., 2005</td>
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<tr>
<td></td>
<td>VOO</td>
<td>Mediterranean fish</td>
<td>180 °C; 10 min–60 min</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<td>x</td>
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<td>Procida et al., 2009</td>
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<td></td>
<td>VOO</td>
<td>Vegetables</td>
<td>180 °C; 30 min–60 min</td>
<td>x</td>
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<td>Uriarte &amp; Guillén, 2010</td>
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<td></td>
<td>EVOO vs others</td>
<td></td>
<td>190 °C; 40 h (8 h/day)</td>
<td>x</td>
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<td>Daskalaki et al., 2009</td>
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<tr>
<td>Pan-frying</td>
<td>VOO vs other</td>
<td>Potatoes</td>
<td>180 °C; 10 sessions (1 day); FR</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<td>Andrikopoulos et al., 2002</td>
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<td></td>
<td>VOO vs others</td>
<td>Mediterranean food</td>
<td>175 °C; 8 sessions (1 day); NR</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<td>x</td>
<td>x</td>
<td>Boskou et al., 2006</td>
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<tr>
<td></td>
<td>VOO</td>
<td>Mediterranean food</td>
<td>170 °C; 1 session by type</td>
<td>x</td>
<td>x</td>
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<td>x</td>
<td>x</td>
<td>x</td>
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<td>x</td>
<td>x</td>
<td>Kalogeropoulos et al., 2007a</td>
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<tr>
<td></td>
<td>EVOO</td>
<td>Simulated</td>
<td>180 °C; 15 min–60 min</td>
<td>x</td>
<td>x</td>
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<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>Messina et al., 2009</td>
</tr>
</tbody>
</table>

CROO — crude refined olive oil; EVOO — extra-virgin olive oil; FR — frequent replenishment; NO — new oil; NR — null replenishment; OO — olive oil; ROO — refined olive oil; VOO — virgin olive oil.
fried ones, from the sensorial point of view, with reduced oil amounts. Nevertheless, while frying is clearly the most studied cooking method, data regarding these new methodologies is still scarce. Indeed, the results found in the literature, and compiled in Table 2, include deep-frying and pan-frying, being then grouped by these procedures. Only the parameters evaluating the oil quality were included. Those regarding the food characteristics were not considered under the scope of this review.

Both frying methods were tested with several olive oil commercial grades, at temperatures ranging from 170 °C to 180 °C in real frying, and from 160 °C to 190 °C in simulated frying, i.e. being the olive oil heated without any food (Table 2). Some authors also compared the effects of adding fresh oil between frying sessions in the oil performance, as it will be discussed.

### 3.1. Deep-frying

Deep-frying is the most common frying method, particularly in restaurants and in the food industry. While in other cooking processes the oil is used for a reduced number of times, prolonged used is usually required when deep-frying is selected. The general guidelines include references to temperature, usually up to 180 °C, being the time in use conditioned by the degradation achieved, based on a clear visual and sensorial inspection or, latter, by the regulated limits on total polar compounds (TPC) (Bastida & Sánchez-Muniz, 2002).

The FFA, expressed as oleic acid, is an important measure for assessing the suitability of vegetable oils for human consumption, correlated with the global acidity perception. The FFA amounts are also directly related to the upper temperature limits due to their lower boiling points. This parameter is usually low in refined oils but, due to the absence of refining, can be higher in virgin olive oils. Indeed, acidity is an important parameter in the classification of EVOO and VOO, as detailed in Table 1. When acidity is higher than the limits imposed, as for instance in the European Commission Regulation (EU) no. 2568/91, 2568/91 (1991) and subsequent amendments, VOO must be industrially refined and sold as refined olive oil (ROO) or blended with virgin olive oil under the designation “olive oil” (OO). Under simulated conditions, heating at 180 °C does not increase TAG hydrolysis (Daskalaki, Kefi, Kotsiou, & Tasioula-Margari, 2009). However, probably derived from its moisture content in the presence of food, FFA increase slightly and proportionally with frying time, without achieving the maximum regulated limit for EVOO (Table 1) (Andrikopoulos, Kalogeropoulos, Falirea, & Barbagni, 2002; Casal, Malheiro, Sendas, Oliveira, & Pereira, 2010).

The fatty acid oxidation degree can be assessed by the primary oxidation products, the hydroperoxides, or by secondary ones, usually unsaturated aldehydes. The peroxide values (PV) constitute a standard determination for primary oxidation in olive oils, with maximum amounts of 20 meq/kg for VOO, and lower for the olive grades with higher acidity (Commission Regulation (EU) no. 2568/91, 2568/91), as these peroxides are reduced during refining. Daskalaki et al. (2009) reported an increase in the VVO PV for up to 60 min at 180 °C (Cheikhrouhouman et al. 2005) heated EVOO for an extended period (3 h; 170 °C) and reported a global PV reduction. Knowing that these primary products are highly unstable and will be converted to secondary ones, this maxim lead to the observation of low PV, though fatty acid oxidation still occurred. In the presence of food, an increase of PV was verified for VOO (Andrikopoulos et al., 2002), further confirmed by Casal et al. (2010) for different olive oil grades. Still, such increases were always inferior to the regulated limits for VOO, and significantly lower in comparison with sunflower oil, processed under the same frying conditions. As regards to the secondary oxidation products, evaluated by the a-anisidine value (PAV), equivalent trends and amounts were found for several EVOO or OO samples (Casal et al., 2010). Based on this parameter, the sunflower oil, used as comparison by the authors, presented an oxidation score after 3 h, equivalent to around 27 h of frying on all the olive oils tested (Casal et al., 2010).
The UV–Vis extinction titives also provide information on the oil degradation degree, particularly on changes induced by technological processes. The \( K_{232} \) indicates the formation of conjugated dienes of PUFA, while \( K_{270} \) is associated with the formation of conjugated trienes, and carbonyl compounds. These parameters increase under simulated frying (Daskalaki et al., 2009), as well as in the presence of food (Andrikopoulos et al., 2002; Casal et al., 2010), with no evident differences between the olive oil grades and frequently with no clear association with heating time. Therefore, despite being vital quality parameters for crude olive oil classification, the information provided by them is reduced in comparison with the abovementioned PAV evaluation, giving more consistent results.

Concerning, the olive oil fatty acid composition itself, it is known that such is only slightly altered during fresh potato frying at 180 °C, with a small reduction in the PUFA amounts (Andrikopoulos et al., 2002; Casal et al., 2010; Chatzilazarou, Gortzi, Lalas, Zoidis, & Tsaknis, 2006). A linear trans fatty acid increment with frying time was also observed, but below 0.5 g/100 g fatty acids even after 27 h of frying, and with similar amounts for all olive oil grades (Casal et al., 2010). Even for prolonged use, as performed by Romero, Cuesta, and Sánchez-Muniz (2003), with 75 frying sessions using EVOO for fresh potato cooking, the modifications were reduced. However, these authors used replenishment with fresh olive oil on each frying batch, contributing to the results achieved, as each session is refilled with a new pool of olive oil protective compounds. The main factor contributing for possible alteration in the fatty acid composition is the food itself. One cannot forget that the consumer can use pre-fried potatoes and their lipids will be blended with the olive oil, altering its thermal behavior. The same pattern applies to foods rich in lipids, including fish, whose high PUFA amounts may change olive oil frying performance.

A more accurate measurement of the oxidation and hydrolysis degree can be achieved by measuring TAG fractions, by size-exclusion chromatography, simultaneously with the evaluation of the polymerization degree, globally accounting for the polar compounds. The total polar compounds (TPC) represent all the fatty acid degradation products with higher polarity than the TAG, and comprise oxidized and polymerized TAG, and hydrolysis products as diglycerides and FFA. Their quantification is used as a global indicator of fat degradation. The TAG oligomers, in particular, are used in some countries to determine oil discarding, namely in Belgium, Czech Republic, German, Netherlands, as this fraction is known to be potentially toxic and actively absorbed (Gómez-Alonso, Fregapane, Salvador, & Gordon, 2003; Romero et al., 2003; Sánchez-Muniz & Bastida, 2003; Sánchez-Muniz, Bastida, & González-Muñoz, 1999). TPC linearly increase with frying time, but the amounts and rates are dependent on the oil composition. Under simulated frying conditions at 180–190 °C, the olive oil TPC formation was comparatively lower than that for other vegetable oils with increased unsaturation degree, supporting from 24 h to more than 33 h heating until the legal rejection point was achieved (Brenes, García, Dobarganes, Velasco, & Romero, 2002; Uriarte & Guillén, 2010).

Within the olive oils, a marked increase in the formation of TPC is also observed for those with higher polyunsaturation degree (Brenes et al., 2002). Under real frying conditions using a low food:oil ratio, equivalent results are obtained, with all tested olive oils presenting lower TPC amounts than more unsaturated vegetable oils, and with apparently no interference by the presence of food (Bastida & Sánchez-Muniz, 2002; Casal et al., 2010; Kalogianni, Karastogiannidou, & Karapantzi, 2010). For higher food:oil ratios, the performance seems to be aggravated (Kalogianni et al., 2010).

When the TPC fractions are detailed, EVOO presents lower susceptibility to the formation of oligomers in comparison with high-oleic sunflower oil (HOSO), despite the good frying performance presented by both oils (Romero et al., 2003). The formation of TPC in EVOO seems to increase after depletion of the phenolic compounds, suggesting a higher susceptibility to degradation for this point forward (Gómez-Alonso et al., 2003). The addition of fresh EVOO during frying, as suggested by Romero, Cuesta, and Sánchez-Muniz (2000) can contribute for an enhanced antioxidant capacity. Indeed, these authors compared real frying with and without replenishment, concluding that frequent replenishment allowed a higher number of fryings and a significantly \((p < 0.001)\) lower thermoxidative alteration, particularly regarding oligomer amounts.

Among the fatty acid degradation products, the formation of cyclic fatty acid monomers (CFAM) is also reported. Romero et al. (2000, 2003) studied CFAM formation during frying with EVOO and HOSO. Linear increments with the number of frying sessions were observed, being 12% lower when fresh oil was added between frying sessions. Also, 43% higher CFAM amounts were determined in HOSO, probably due to its greater linoleic acid content, which is more susceptible to their formation than oleic acid. The peroxidation of linoleic and arachidonic acid to trans,trans-2,4-decadienal, a volatile compound, has been identified and quantified in different vegetable oils during potatoes frying, with lower amounts formed EVOO was used in comparison with other vegetable oils. This compound is considered to be a major mutagenic and cytotoxic substance in oil fumes (Boskou et al., 2006).

The volatile fraction, formed during the heating process, apart from being important from the sensorial point of view, is rich in degradation compounds. The formation of low molecular weight volatile aldehydes has been studied under vegetable oil simulated deep-frying, olive oil included, with a clear dependence on the temperatures used, rather than frying time (Fullana, Carbonell-Barrachina, & Sidhu, 2004). Lower amounts of aldehydes, particularly the toxic acrolein, were invariably found in olive oil grades (EVOO and OO) in comparison to canola oil (Fullana et al., 2004). The high oleic acid content in olive oil, together with the presence of chlorophylls, phosphphtins and carotenoids, seems to contribute for a reduced acrolein formation (Procida et al., 2009).

More recently, Uriarte and Guillén (2010) also reported lower amounts of toxic monomeric hydrocarbons, alkylbenzenes and alkenylbenzenes, in olive oil, in comparison with other vegetable oils with higher polysaturated acyl groups.

The phenolic compounds are among those highly scored compounds in VOO, due to their antioxidant activity and potential health effects. These substances are eliminated during refining, being therefore absent in all commercial refined vegetable oils, and reduced in the olive oil mixtures with ROO. Hence, these are probably the most studied chemicals in olive oil, particularly under thermal processing, since it is important to maintain these potential bioactive attributes after processing. Some authors evaluated only total polyphenolic content, while others detailed the identity and amounts of each individual compound, giving further insights into their degradation mechanisms. Indeed, these substances are affected by thermal processing, but their loss is dependent on their chemical structure and probably on their antioxidant activity (Gómez-Alonso et al., 2003). The main components of olive oil phenolic fraction are hydroxytyrosol, tyrosol and their derivatives (secoiridoids). Hydroxytyrosol and their derivatives are extensively lost, with a 50% reduction in EVOO after frying fresh potatoes for only 10 min at 180 °C, and almost complete degradation is observed after 6 frying sessions. In opposition, tyrosol and its derivatives are less prone to degradation, retaining 80% of its original value even after 12 frying sessions (Gómez-Alonso et al., 2003). Knowing that hydroxytyrosol presents a higher antioxidant activity, one could justify its extensive loss with an effective activity during frying by protecting lipids from oxidation. On the other hand, tyrosol presents comparatively lower antioxidant efficiency, being therefore more retained during frying, and presenting a linear degradation rate with the frying sessions (Carrasco-Pancorbo et al., 2007; Cheikhousman et al., 2005; Daskalaki et al., 2009; Gómez-Alonso et al., 2003). These results confirm those achieved by Brenes et al. (2002), using two EVOO cultivars. Nevertheless, these observations cannot exclude the olive oil initial phenolic content that, being highly different between cultivars, will regulate the antioxidant capacity under thermal stress and the residual phenolic
oxidized phytosterols are also generated during frying, which seems to be dependent on the sterol structure, composition of the matrix, temperature, and amounts of non-oxidized sterols (Tabee, Azadmard-Šefidian, & Khaled, 2010). Also, some oil cultivars with higher linoleic acid, as “Arbequina” (Allouche, Jiménez, Gaforio, Uceda, & Beltrán, 2007; Brenes et al., 2002), might be less indicated for intensive thermal processing methodologies, as they will consume higher amounts of antioxidants. Romero et al. (2003) tested the influence of adding fresh oil and, despite confirming polyphenol degradation, 30% of the polyphenol content remained after 75 frying sessions. The refreshment of the olive oil antioxidants seems to promote a better oil stability. The phenolic compounds have also been implicated in the reduced formation of acrylamide during potato frying (Napolitano, Morales, Sacchi, & Fogliano, 2008) and heterocyclic aromatic amines in fried red meat (Persson, Graziani, Ferracane, Fogliano, & Skog, 2003), in comparison with other vegetable oils, both important from the health point of view.

Vitamin E is also an important antioxidant in all vegetable oils. Although being a minor compound in olive oil (Brenes et al., 2002; Procida et al., 2009), the higher oxidation stability of olive oil, mostly due to its low PUFA content, requires comparatively lower vitamin E amounts for effective protection. Some authors further confirm that polyphenols act as vitamin E stabilizers during olive oil heating, creating an effective balance of oxidative protection between these two antioxidant families (Pellegrini, Visioli, Buratti, & Brighenti, 2001; Valavanidis et al., 2004). Vitamin E degradation rate during heating at 170 °C (simulated frying) was lower than hydroxy-tirosol, but higher than tyrosol (Cheikhousman et al., 2005) counting with up to 70% losses after 3 h heating. Brenes et al. (2002) also reported high vitamin E losses, after 5 h at 180 °C, but a clear dependency on the cultivar was denoted, with the olive cultivar “Arbequina”, richer in PUFA, presenting a faster degradation rate. Indeed, after 10 h heating, only residual amounts of vitamin E were detected in this olive oil, while for “Picual” cultivar equivalent levels were found after more than 20 h of heating. Under fresh potatoes frying (170 °C), vitamin E loss is also fast, being depleted after 3 to 6 h, depending on the olive cultivar. Still, for other vegetable oils with increased tocopherol amounts, as sunflower oil, total depletion of vitamin E was perceived sooner, after only 3 h frying (Casal et al., 2010). Andrikopoulos et al. (2002) also tested fresh potato frying at 170 °C and after 10 frying sessions only 15% of vitamin E remained.

Finally, the phytosterols are a quantitatively relevant fraction in olive oil unsaponifiable compounds, with both health and technological effects. Indeed, some sterols are described as contributing for a higher protection of lipid degradation under thermal stress, particularly reducing the formation of TAG polymers (Singh, 2013). As these compounds are usually reduced by refining, unrefined oils as VO0 contain higher amounts of these substances. Also, they are partially transferred to food during frying, contributing for an increased consumption of phytosterols, which presents nutritional significance (Salta, Kalogeropoulos, Karavanou, & Andrikopoulos, 2008). Still, oxidized phytosterols are also generated during frying, which seems to be dependent on the sterol structure, composition of the matrix, temperature, and amounts of non-oxidized sterols (Tabee, Azadmard-Damirchi, Jägerstad, & Dutta, 2008; Tabee, Jägerstad, & Dutta, 2009). However, studies on this matter are scarce.

3.1.2. Pan-frying

Pan-frying is frequently used under domestic cooking, being characterized by a higher food:oil ratio. In comparison with deep-frying, potatoes pan-frying induced a higher VO0 degradation, with increased FFA, PV, UV-Vis readings, and TPC. Still, in comparison with other vegetable oils, the trends discussed for deep-frying remain similar, i.e. olive oil presents slightly higher FFA than the refined vegetable oils, while the latter presented higher thermoxidative degradation rates due to the increased PUFA content (Andrikopoulos et al., 2002). In fact, a PUFA loss was observed in all the tested oils, being lower under deep-frying when compared with pan-frying (Andrikopoulos et al., 2002). A higher olive oil phytosterol, phenolic compounds, and vitamin E loss were observed in pan-frying (Andrikopoulos et al., 2002; Kalogeropoulos, Mylona, Chiou, Ioannou, & Andrikopoulos, 2007a, 2007b; Messina et al., 2009; Salta et al., 2008), both with and without the presence of food.

The higher degradation under pan-frying conditions, observed for olive oil and other vegetable oils, can be explained by the higher food:oil contact surface, higher exposure to atmospheric oxygen, and lower temperature control under processing (Andrikopoulos et al., 2002). Still, in comparison with other vegetable oils, the fried food is enriched with olive oil antioxidants, as long as the olive oil is not extensively heated (Kalogeropoulos et al., 2007a, 2007b).

3.2. Roasting

Roasting with olive oil is common in both domestic and industrial food preparation in Mediterranean countries (Silva, Pinto, Carrola, & Paiva-Martins, 2010a). This procedure requires equivalent fat amounts to pan-frying, but the process is highly prone to oxidation due to the higher surface area exposed to conventional hot air and processing times.

Conventional oven with air-convection heating was tested in EVOO, VO0, OO, and ROO, with temperatures ranging from 180 °C to 230 °C, mostly under simulated heating (Table 3). When the primary oxidation degree was evaluated by the PV, variable results were achieved, either increasing with exposure time (Caponio, Pasqualone, & Gomes, 2003; Mahmoud, Dostalova, Pokorny, Lukeľová, & Doležal, 2009) or decreasing (Albi, Lanzón, Guinda, Pérez-Camino, & León, 1997a). Clearer oxidation trends were observed through K232, which increased with exposure time (Albi et al., 1997a; Allouche et al., 2007; Caponio et al., 2003; Mahmoud et al., 2009; Silva et al., 2010a). Still, when comparing with other vegetable oils with higher unsaturation degree, olive oil was clearly more resistant to oxidation under these heating conditions (Albi et al., 1997a; Caponio et al., 2003). In the presence of food, as tested by Silva et al. (2010a) for potatoes and meat roasting, lower oxidation degrees were observed for both primary and secondary oxidation products, highlighting the importance of studying heating effects under real cooking conditions.

The fatty acid composition was also affected by conventional heating with an increase in the saturated/polyunsaturated fatty acid ratios (Albi et al., 1997a; Allouche et al., 2007; Caponio et al., 2003; Mahmoud et al., 2009). Formation of minor amounts of trans-oleic acid, inferior to 0.2 g/100 g fatty acids was observed for all the olive oil grades, but lower than trans amount in other refined vegetable oils (Albi et al., 1997a; Caponio et al., 2003; Mahmoud et al., 2009).

The TPC increased with heating time as well, particularly the oligopolymers and oxidized TAG (Caponio, Pasqualone, & Gomes, 2002). However, lower amounts were reported by Albi et al. (1997a) for 2 h heating at 200 °C in comparison with Caponio et al. (2003) for higher temperature (230 °C) and reduced processing times (45 min). The temperature achieved seems to be a determinant factor in the formation of TPC, particularly the oxidation/polymerization ratios. In the presence of food, processed at 180 °C for 1 h, a minor increment of TPC was reported and no apparent differences were found between EVOO, OO, or ROO (Silva et al., 2010a). In opposition, the TPC clearly increased with vegetable oils with higher unsaturation degrees (sunflower and corn oil) being lower in the presence of food once again (Silva et al., 2010a).

As to the antioxidant compounds, both α-tocopherol and polyphenol contents decreased with roasting at 180 °C for 2 h (Albi et al., 1997a; Albi, Lanzón, Guinda, León, & Pérez-Camino, 1997b), being apparently influenced by cultivar (Allouche et al., 2007) and oil type (Silva et al., 2010a). Allouche et al. (2007) further examined other important minor olive oil compounds, concluding that even after 36 h of heating in a hot air oven (180 °C); the tested EVOO preserved important compounds as phytosterols, triterpenic alcohols and acids, and squalene.
3.3. Microwave

Only simulation studies were found in the literature, but covering several olive oil classes. All studies heated olive oil as is, usually for up to 15 min, and using domestic devices (Table 3). Such employed 2450 MHz frequencies but, depending on the equipment, distinct powers were tested, from 500 W (Brenes et al., 2002; Mahmoud et al., 2009) to 1100 W (Caponio et al., 2002, 2003). Most authors were unable to provide accurate data for the temperatures achieved, since this is difficult to measure in these devices, requiring instrumental adaptation. Mahmoud et al. (2009) measured the temperature immediately after processing and compared with conventional heating, reporting a lower temperature course for microwave samples and final temperatures around 200 °C (500 W, 15 min). Albi et al. (1997a, 1997b) used an equivalent power (120 min) and reported temperatures of 170 ± 10 °C. For 1100 W and 15 min, Caponio et al. (2003) reported temperatures of 206 ± 8 °C. However, Cerretani, Bendini, Rodriguez-Estrada, Vittadini, and Chiavaro (2009) presented significantly higher and alarming temperatures (720 W; 15 min; 313 °C). The results achieved will be discussed on the basis of the chemical parameters evaluated, as compiled in Table 3.

Olive oil oxidation was evaluated by all the authors, commonly using fast methods, for instance PV, PAV and UV–Vis readings. As regards to PV, Albi et al. (1997b) found a minor increase in VOO and OO, while Mahmoud et al. (2009) observed a higher increment in EVOO compared to ROO. Malheiro et al. (2009) verified a small increase in EVOO and VOO up to 10 min (1000 W), increasing above 20 meq/kg at 15 min for VOO. Both Cossignani, Simonetti, Neri, and Damiani (1998) and Caponio et al. (2003), reported significant increases in the PV with microwave heating, being equivalent to the ones observed with conventional heating (230 °C) and a half of those achieved with sunflower or peanut oil, under the same processing conditions. Notwithstanding, Cerretani et al. (2009), observed a decrease in the first 6 min followed by constant values thereafter. Indeed, PV is not a good index for the measurement of oxidation because hydroperoxides are unstable on heating at high temperatures, due to the reduction of oxygen availability and changes in the oxidation reaction balance towards a greater formation of secondary oxidation products (Cerretani et al., 2009), as previously discussed. Also, in accordance to Tan, Che Man, Jinap, and Yusoff (2001), the formation of hydroperoxides is higher at low-power settings than in the medium and high-power settings, supporting Cerretani et al. (2009) outcomes. On the contrary, PAV, which measures secondary oxidation products in a stable way, is a better indicator of the fatty acid oxidation. Indeed, Cerretani et al. (2009) found a generalized increase for all the olive oil categories. Both \( K_{232} \) and \( K_{370} \) are kept constant during the first 5–10 min, increasing significantly afterwards (Mahmoud et al., 2009; Malheiro et al., 2009). For standard cooking times, no absorbance differences were verified after microwave and conventional heating (Caponio et al., 2003). For increased processing times, outside the usual cooking ranges, higher outcomes were reported for microwave heating (Albi et al., 1997a). Still, when comparing with other vegetable oil, once again figures are lower for olive oil (Caponio et al., 2003).

Regarding fatty acid composition, such was only evaluated by some authors. All have verified a reduction of the unsaturated fractions (MUFA and PUFA) (Caponio et al., 2003; Cossignani et al., 1998; Mahmoud et al., 2009) and an apparent increase in the trans fatty acid content. These values, were however similar to the ones observed for conventional heating (Albi et al., 1997a; Caponio et al., 2003; Mahmoud et al., 2009), and lower than the ones reported for sunflower oil, high-oleic sunflower, peanut oil and lard. Cossignani et al. (1998) further detailed the fatty composition of each glyc eride fraction with no significant alterations. Still, the stereospecific analysis of the TAG fraction revealed that the fatty acids in the sn-2-position were more stable towards oxidation, which is of important nutritional significance.

Hydrolysis under microwave heating for simulated cooking is usually reduced, as reported by Albi et al. (1997a). Malheiro et al. (2009) tested two EVOO and one VOO, also describing minor FFA increases up to 15 min heating (1000 W). Cerretani et al. (2009) compared EVOO, OO and pomace oil and observed that the FFA content was quite constant up to 10 min (720 W), increasing significantly thereafter, particularly for EVOO. Moreover, the authors stated that the elevated water content in EVOO, due to the absence of refining, could promote TAG hydrolysis at temperatures higher than 300 °C, being this out of the usual cooking range. In comparison with refined vegetable oils, olive oil acidity is slightly higher, supported again by the absence of chemical refining. Still, all these studies were performed under simulating conditions, in the absence of food. Therefore, depending on food moisture, an increase in the hydrolysis degree can probably be expected, as well as lower effective temperatures due to water evaporation during the cooking process. Real cooking studies are then mandatory for effective conclusions.

Caponio et al. (2002) observed a higher oxidation degree by microwave heating than by conventional heating, simulating heating times for a pizza cooking at 1100 W (15 min). TPC as high as 26.8% were achieved (203 °C), in opposition to 18.6% under 45 min of conventional heating (230 °C). This increase occurred at expenses of TAG oligomers and oxidized TAG, both significantly higher in microwave heating. This fact confirms the previous results obtained by Albi et al. (1997b), with higher TAG modification in microwave heating in comparison with conventional, particularly polymerization. Brenes et al. (2002), using EVOO and only 10 min heating at 500 W, found a lower TPC increase (up to 6%), indicating that power rather than heating time influences TAG degradation. In comparison with other vegetable oils, TPC verified in olive oil (VOO and OO) were lower than those obtained for sunflower oil and HOSO (Albi et al., 1997b).

Olive oil phenolic compounds were also evaluated by some authors. Generally, minor losses were reported after microwave heating for a short processing period. Brenes et al. (2002), using EVOO and gentle processing conditions (10 min, 500 W), reported lower losses than those achieved during frying. In opposition, a huge decrease on total polyphenols in VOO and OO (>85%) was reported by Albi et al. (1997b), for prolonged heating (120 min, 500 W). Cerretani et al. (2009), using high temperatures, reported similar decreases for EVOO and VOO, particularly for more than 6 min heating (>255 °C). These observations suggest that, for prolonged/intense microwave cooking, lower olive oil grades could present economic advantages, since most phenolic compounds are degraded.

Microwave heating also causes a decrease in olive oil α-tocopherol (Brenes et al., 2002), or its complete disappearance (Albi et al., 1997b; Malheiro et al., 2009). The same pattern is observed for chlorophylls and carotenoids, particularly for more than 10 min heating (1000 W) (Malheiro et al., 2009). The sterolic fraction was not altered but a slight reduction in squalene (<27%) was observed by Albi et al. (1997a).

In general, the results demonstrated an apparent higher oxidation when compared with conventional heating, despite being probably lower than those achieved with other vegetable oils (Malheiro, Casal, Ramalhosa, & Pereira, 2011). Still, as previously mentioned all studies were performed without the presence of food, requiring real processing conditions for correct inferences.

3.4. Boiling

Studies dealing with the behavior of olive oil under water boiling conditions are scarce as well. In some countries, there is a common practice of cooking vegetable in water in the presence of small amounts of olive oil. These include soup preparation and stewing, using temperatures around 100 °C or a little higher while using pressure cookers, but lower than all the aforementioned methods. Therefore, rather than the oxidative stress imposed by temperature, hydrolytic reactions should
be expected by the presence of water, as well as leaching of water soluble components.

Brenes et al. (2002) used VOO to simulate several cooking conditions, including boiling. Three different pHs were tested (4, 5 and 6) in order to simulate the usual pH of vegetables, and olive oil was added at 2.4%. After cooking for 30 min, the water and oil phases were analyzed separately for phenolic compounds by high-performance liquid chromatography. The authors confirmed the hydrolysis of hydroxytyrosol and tyrosol aglycons as well as the migration of hydrophilic polyphenols from the oil into the water phase. Still, no losses of total phenolics compounds (water plus oil) were observed at pH 6, but a clear degradation was visible for lower pH values. Therefore, boiling acidic vegetables in the presence of olive oil might reduce its phenolic content. Still, one cannot forget that the vegetables themselves also have phenolic compounds, and these will inevitably diffuse into the boiling water and possibly interact. The tocopherol content and fatty acid composition were also evaluated with no significant changes, indicating that olive oil is not oxidized during water boiling.

Silva, García, and Paiva-Martins (2010b) complemented the abovementioned study using real cooking conditions, with vegetables (potatoes, carrots and onions), and 2% and 5% of each EVOO and OO. The olive oils were added in the beginning of the cooking process or just at 15 min from conclusion. The presence of the vegetables in the cooking water increased dramatically the polyphenol loss. The authors suggested that this loss could be a consequence of the presence of metals (Fe and Cu) in some vegetables. The losses were also dependent of the processing time, being advantageous to add the olive oil only at 15 min from concluding. An interesting observation from these authors was that EVOO, despite presenting more phenolic compounds, showed similar amounts to OO after processing with vegetables. This can question the benefits of using EVOO in vegetables boiling processes. As to fat oxidation, the authors evaluated the primary oxidation products by the K232, the secondary ones by the PAV, and tocopherol content, concluding, similar to Brenes et al.’s (2002) finding that fat was not oxidized and kept its anti-oxidant properties.

4. Conclusions and recommendations

Olive oil degradation under thermal processing is a complex issue from the chemistry point of view, due to the huge amount of different compounds in its composition, as well as from the potential health effects perspective, derived from the reactions and interactions taking place under thermal stress. This problem has been tentatively evaluated in diverse published studies, using a multitude of analytical methods, some of reduced specificity and apart from real domestic cooking conditions relating to time, temperature and food presence. Thus, for viable conclusions, reliable methodological protocols and testing methods are needed to address the real cooking effect on olive oil composition and therefore its potential bioavailability and health effects.

Based on the results achieved for olive oil cooking under different processing conditions, one can conclude that, in comparison with other vegetable oils, such has a good thermal resistance in general. This is a direct consequence of its high MUFA profile, but even on a direct association with other vegetable oils with equivalent oleic acid amounts, as HOSO, olive oil reveals an improved stability. This enhancement is mostly attributed to the antioxidant capacity of the phenolic compounds in combination with vitamin E, providing a balanced protection under thermal stress. The heating conditions (temperature, time, cooking process and food presence) as the initial olive oil composition will determine the degradation rate, as well as the time taken to consume the antioxidant pool.

The temperature achieved during cooking is a determinant factor for most vegetable oils and for VOO in particular. Indeed, the higher acidity of VOO, due to the absence of refining, reduces their upper thermal limits as a consequence of the lower boiling point of the FFA released. Still, when processed under normal cooking conditions, with temperatures up to 180–190 °C as usual in frying and roasting, olive oil performance is comparable or better than other vegetable oils. Nevertheless, under microwave heating, the temperatures achieved are uncontrolled and, on the basis of published results, all vegetable oils are rapidly degraded. Though, no data was found in the literature for real microwave cooking conditions, as for other cooking methods. The presence of food, particularly its moisture release, will certainly reduce the thermoxidative effects of microwave heating, but effective studies, with variable potencies/times, are needed to understand the microwaves effect on vegetable oils and olive oil, in particular. Under water boiling conditions, hydrolysis and leaching of phenolic compounds into the water phase are significant but the heating time and the presence of food constitute the main contributor to their effective degradation. Therefore, when possible, olive oil should be added more closely to the final cooking process.

According to the most recent legislation, oil degradation is usually evaluated by the TPC or TAG oligomer fractions. In comparison with other vegetable oils, olive oil has a lower formation rate of these compounds. Nevertheless, based on the detailed analysis of olive oil components, the phenolic compounds and tocopherols are almost depleted after a short heating period. From that point forward, most olive oil advantages, in comparison with other vegetable oils, are lost, behaving as a mixture of MUFA. Apart from the apparent tolerance of the regulated limits for oil discharge, if one intends to use olive oil for its potential health attributes, it should be used only for a limited period of time. If the purpose is to accomplish a high cost-effectiveness, namely in the food industry, two strategies can be implemented: the use of mixtures of refined and virgin olive oil, the “olive oil” grade, and periodic refreshment with fresh oil to rebalance the antioxidant pool and reduce oil deterioration. The same approach should be applied under domestic cooking, with no advantages proven from the use of EVOO for thermal processing, in opposition to olive oil, as their attributes are rapidly lost.

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