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Original article

Effect of potato presence on the degradation of extra virgin olive oil during frying

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Summary This work investigates the effect of potato presence on the degradation of extra virgin olive oil (EVOO) during repeated frying. For this reason the performance of EVOO during frying was compared with its performance during heating at frying temperatures. In order to make meaningful comparisons the temperature profiles obtained during the frying experiments were replicated during the heating experiments by means of a high energy exchange rate cooling/heating system. The effects of potato-to-oil ratio (1/7 and 1/35 $kg_{potatoes}/L_{oil}$) and number (N) of batches (N = 0, 1, 0, 20, 30, 40) were examined. EVOO was analysed using high performance size exclusion chromatography (HPSEC). It was found that polymerisation products increased linearly during frying and heating and that they were not affected by potatoes presence at low ratio. The effect of potato presence became statistically significant (yet not remarkable) at the high ratio. Decomposition products increased during frying whereas they decreased during heating.

Keywords Decomposition, extra virgin olive oil, frying, frying load, heating, HPSEC, polymerisation, potatoes, potato-to-oil ratio, temperature profile.

Introduction

Frying is a popular method for food preparation worldwide. Despite the alarm from nutritionists, the consumption of fried products continues to increase (Stier, 2004). Therefore, there is a need for finding appropriate oil types that do not serve only technological aspects (such as long term stability) but have an advantage for human health as well. Almost all oil types have been used for frying around the world, this depending on availability, economic aspects and tradition. Around the Mediterranean sea, olive oil is traditionally used for domestic frying. Nevertheless, commercial applications of olive oil for frying are extremely limited. This is mainly due to its high price and relatively low mass production compared to other oil types (e.g. palm oil).

Virgin olive oil is one of the few oil types that is consumed without any chemical treatment. It has been argued that olive oil is a key element of the famous Mediterranean diet (Harwood & Yacoob, 2002). It exhibits a high resistance to oxidation mainly due to the high monounsaturated-to-polyunsaturated fatty acid ratio and a group of minor compounds having antioxidant activity (Kiritsakis, 1990). The high percentage of monounsaturated fatty acids makes olive oil a good alternative for human nutrition compared to other frying media that consist mainly of saturated fatty acids. In addition, it has been shown that olive oil has protecting properties against cardiovascular disease and positive effects on the immune and endothelial functions and coagulation pathways (Harwood & Yacoob, 2002).

Upon frying, olive oil shows good chemical performance. Some of the minor constituents of olive oil responsible for its positive health effects, such as squalene, are rather stable during frying and their content in fried olive oil is about two orders of magnitude greater than in other oil types even when they are fresh (Kalogeropoulos & Andrikopoulos, 2004). There is also evidence that olive oil has a greater resistance to oxidation during frying than other oil types (Fedeli, 1988; Naz *et al.*, 2005). This resistance to oxidation has been positively correlated with several health aspects in rats such as oxidative stress in the liver and iron metabolism (Péres-Granados *et al.*, 2000; Battino *et al.*, 2002). Apart from oxidation (which is the most frequently studied chemical reaction in olive oil during frying) frying also causes hydrolysis and polymerisation of the frying medium (Belitz *et al.*, 2004).

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Polymerisation products constitute the major part of new products generated during frying (Dobarganes & Márquez-Ruiz, 1996). Therefore, they should not be neglected when assessing an oil type for frying. However, information on polymerisation during frying with olive oil is extremely limited (Romero *et al*., 1995; Bastida & Sánchez-Muniz, 2002; Kalogeropoulos *et al*., 2007) compared to the extensive literature dedicated to olive oil.

There is a vast literature coping with the effect of heating and frying of food on the composition of several oil types. A survey of this literature demonstrates that the factors affecting the chemical composition of an oil or fat during frying include processing variables (e.g. time and temperature) the composition of the frying medium (fatty acid composition and minor constituents) as well as the composition of the food being fried (Fedeli, 1988; Tyagi & Vasishtha, 1996; Houhoula *et al*., 2003). It has also been established that the presence of food plays a significant role to the degradation of the frying medium (Belitz *et al*., 2004). Nevertheless, information on the net effect of the food being fried (separated from the effects of time and temperature) is rather limited. Recently, Kalogianni *et al*. (2009) investigated the effect of potato sticks frying in palm oil compared to sheer heating of palm oil under the same temperature profile. These authors found that potato frying induced higher polymerisation rates in palm oil compared to those induced by simply heating the fat. In addition, it was found that the potato-to-oil ratio affected polymerisation but only after a certain frying time, i.e. number of repeated frying batches. We were also able to identify only two studies (Fedeli, 1988; Dana *et al*., 2003) which systematically examined the effect of individual food constituents on the chemical changes induced during frying. In the rest of the relevant studies the time–temperature profile between frying and heating experiments (i.e. between experiments with and without food submerged in the frying medium) was different. This limited information on the net effect of food presence in the chemical degradation of an oil or fat during frying despite the vast literature devoted to frying is not due to lack of interest on the subject but mainly due to experimental difficulties: adding food to a fryer causes a considerable drop of oil temperature, which cannot be easily replicated in the absence of food. But then, if the time–temperature profile is different between food frying and sheer oil heating experiments no safe comparisons can be made. This is not only because there is a quantitative effect of temperature on chemical changes [increasing the temperature, in general increases the rate of chemical reactions (Tyagi & Vasishtha, 1996)] but also because different chemical reactions are promoted at different temperatures (Gertz *et al*., 2000).

The present study investigates the performance of extra virgin olive oil (EVOO) during frying of potato sticks (referred to as potato chips in UK English or French-fries in US English). Potatoes are employed as the fried food since they are the most popular food commodity around the globe. Results obtained during frying are compared with those from experiments where just the oil is exposed to a time–temperature profile similar to that of frying but without potatoes in the fryer. We name these latter experiments as heating/quenching experiments because the oil is initially heated and then rapidly cooled down (quenched) in order to replicate the temperature profile of an actual frying batch. This is obtained experimentally with the use of a high-precision temperature controller in combination with a heating/cooling system offering exceptionally high exchange rates of energy which has been especially built for the experiment. In addition, this work demonstrates how the potato-to-oil ratio (frying load) affects chemical changes during frying and how the temperature profile affects chemical changes during oil heating/quenching in the absence of potatoes.

Materials and methods

Materials

EVOO was purchased from a local producer at the time of production and kept at −18 °C until used. Angria variety potatoes were bought in the local market, conditioned at a final temperature of 15.5 ± 1 °C and 95% relative humidity (Lisińska & Leszczyński, 1989). Only potatoes with specific gravity between 1.07 and 1.10 were selected.

Frying and heating/quenching experiments

Four series of experiments were performed: two series of repeated frying experiments and two series of EVOO heating/quenching experiments in the absence of food. Frying was conducted in temperature-controlled fryers using raw potato sticks (1 cm × 1 cm × 8 cm) (Fig. 1a). Potatoes were equally spaced apart in the oil volume by using a custom-made wire basket divided in compartments. This kept the temperature across the fryer homogeneous as verified in preliminary measurements (Kalogianni, 2007). In the intervals between frying batches temperature homogeneity was assisted by gently stirring with a three beam paddle impeller (not shown in Fig. 1a but the same as in Fig. 1b). Frying experiments are divided into two series of experiments, in each series a different frying load (potato-to-oil ratio) was applied: high frying load (1/7 $kg_{potatoes}/L_{oil}$) and low frying load (1/35 $kg_{potatoes}/L_{oil}$). The high potato-to-oil ratio was similar to potato-to-oil ratios used in industry whereas the low potato-to-oil ratio was similar to those used in

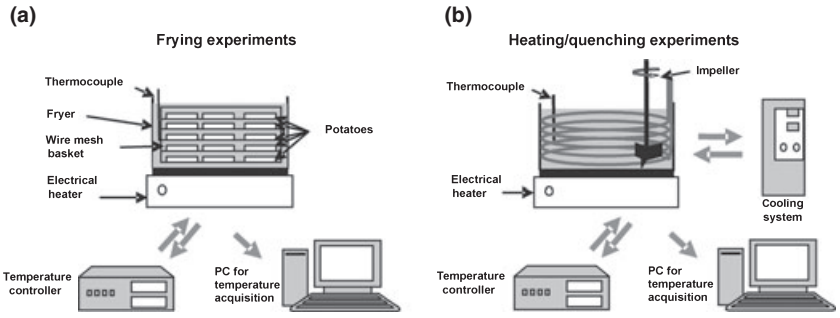

Figure 1 Experimental set-up used during frying (a) and heating/quenching (b) experiments.

the catering/restaurants sector. In order to make meaningful comparisons between heating/quenching and frying series parameters were optimised to replicate the temperature profile of the oil during the frying experiments in the experiments without potatoes (oil heating/quenching). This was implemented by employing a custom made cooling system which can remove high amounts of heat in short time. In order to achieve such high cooling rates without temperature gradients in the oil a submerged impeller was used to enhance heat transfer between the oil and the cooling coil and assure temperature homogeneity in the fryer (Fig. 1b).

Each repeated frying experimental series was performed by forty frying batches conducted in four consecutive days. Initially the oil was heated up to 180 ± 2 °C and was further kept at this temperature for 30 additional minutes before adding the potatoes (Blumenthal, 1991). The total time that the oil was kept at elevated temperatures in each experimental series was 46 h including the time spent for heating up and the time in-between frying batches. Experiments were carried out without replacing oil between batches (Arroyo *et al*., 1992; De Marco *et al*., 2007). Frying time for each batch was 12 min corresponding to the high load and 3 min for the low load due that the EVOO temperature profile was significantly different between both potato-to-oil ratios (Fig. 2a and b). The duration of frying was decided in preliminary tests (Kalogianni, 2007).

Series of forty heating/quenching batches were performed under the same conditions (time and temperature) used by the frying process (Fig. 2c,d).

Since there was no oil replacement between frying or heating/quenching batches, the quantity of oil in the fryers decreased progressively along each experimental series due to oil absorption by the potatoes and/or sampling. However, the potato-to-oil ratio was kept constant throughout the frying series. This was done by measuring the oil volume at 180 °C after each frying batch and adding the appropriate potato weight in the next one. Because of the progressive decrease in the oil volume, the temperature profile in the oil bath would tend to change gradually between frying batches (this was noticed during preliminary experiments). In order to overcome this problem the oil temperature (and heat supply) was controlled separately during each frying batch in order to achieve similar temperature profiles in all batches.

The absence of replacement demanded high initial oil quantities, in order to have enough oil for forty batches. To save some oil the following scenario was employed: two fryers were used at the beginning of each series containing 4 L of EVOO each. The two fryers were operated simultaneously for the first half of the frying series then the oil of the two fryers was mixed and the frying series went on in only one fryer.

Repeating the same experimental conditions in the two initially employed fryers was not a trivial task.

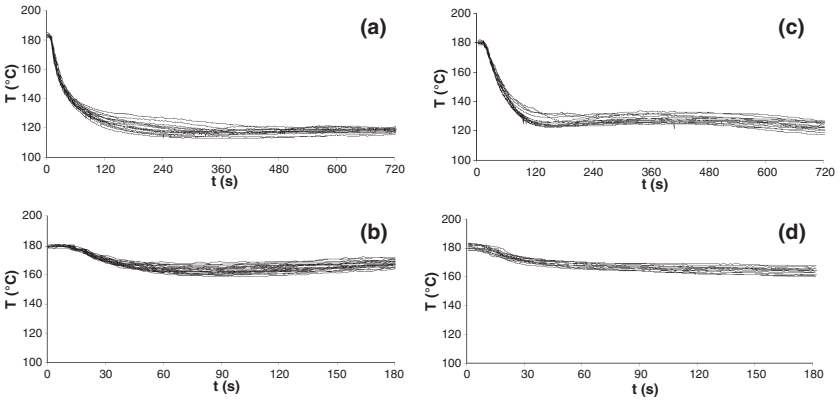

Figure 2 Indicative temperature profiles obtained during different potato frying batches at high (a) and low (b) frying load. Results for both fryers are shown. (c) and (d) present indicative temperature profiles obtained during different heating/quenching batches simulating the temperature profiles obtained during frying at high and low load, respectively.

Machado *et al*. (2007) showed that conducting repeated frying experiments in identical fryers (with identical temperature control systems) could not assure the repeatability of experiments. This was attributed to possible differences in the time–temperature profile (not recorded in their experiments). In our experiments the resemblance of experimental conditions was checked by comparing records of on-line temperature measurements and analysing a few samples from both fryers separately.

Temperature recording

For recording on-line the oil temperature, a 3-mm T-type (OMEGA Engineering Inc., Stanford, CT, USA) thermocouple was immersed in each fryer as shown in Fig. 1. The thermocouples were interfaced to a PC with the aid of an Adam 4018, 16bit A/D board (Advantech, Cincinnati, OH, USA). Representative temperature profiles obtained during the frying and heating/quenching batches are shown in Fig. 2a–d. In addition, analysis of the oil of both fryers before mixing (halfway the frying series) gave the same quantitative results in the HPSEC chromatogram (standard deviation between total polymerisation products lower than 0.7% in all cases).

Sampling and storage

Extra virgin olive oil samples were collected at the beginning (t_0), at the end of the initial 30-min heating period (t_{30}) and at different numbers (N) of frying batch or heating/quenching series (N_1, N_{10}, N_{20}, N_{30}, N_{40}) during four consecutive days. On the other hand samples were also collected at the end of each of the three intermediate days for frying process as well as at the beginning of the next day. Samples were kept at −26 °C under nitrogen, airtight close and in dark-coloured glass bottles.

Chromatographic analysis of the whole EVOO and of its polar fraction

The analysis of the whole (non-fractionated) EVOO and its polar fraction were conducted by HPSEC following the IUPAC methods (Wolff *et al*., 1991; Dobarganes *et al*., 2001). HPSEC analysis was performed using a stainless steel of 300 mm × 7.5 mm i.d., PL-gel 100 Å (polystyrene–divinylbenzene co-polymer in toluene) column with 5-μm packing (Polymer Laboratories Ltd, Shropshire, UK), connected to a PL-gel guard column (Polymer Laboratories Ltd). The column and guard column were operating in a column oven set at 35 °C and connected to an injection valve equipped with a 20-μl sample loop. Tetrahydrofuran (HPLC-grade; Merck, Gibbstown, NJ, USA) was used as the mobile phase. For the analysis of the polar fraction the modifications proposed by Gertz (2001) were followed. Extensive details on the analysis and quantitative determination can be found in Kalogianni *et al*. (2009). Two to three samples were analysed and the average and standard deviation are presented for each case. However, the standard deviation is very small (in most cases less than 0.2% weight and never above 0.4% weight) therefore in some cases it cannot be resolved in the figures.

The method used here for the determination of polymer compounds is not recommended by IUPAC for quantitative determination of polymer contents below 5% (Wolff *et al*., 1991). Yet, in some European countries (i.e. France) this lower limit is set to 3% (Wolff *et al*., 1991). Therefore, in this work polymer content values below 5% are displayed for qualitative comparison reasons and should not be taken as accurate quantitative values. Besides small amounts of polymerisation products ($< 5\%$) have been determined by this method also by other authors (Gertz *et al*., 2000).

Statistical analysis

Linear regression analysis and analysis of variance was employed in order to assess whether there was a linear dependence of total polymerisation products in the samples on the number of frying batches or heating/quenching batches for each frying series (Petridis, 1997). Furthermore, multiple linear regression analysis and analysis of variance was applied in the results of total polymerisation products. In this analysis we made use of 'dummy variables', allowing us to examine possible differences in the rate of polymerisation among frying series. The method can be found in Draper & Smith (1981). Both regression analysis and analysis of variance were conducted using the Minitab 14 (Minitab Inc., State College, PA, USA) software.

Results and discussion

HPSEC chromatograms

Figure 3 presents the indicative HPSEC chromatograms of EVOO samples (whole oil and polar fraction) taken from fresh EVOO and from that at the end of the high frying load series (potato-to-oil ratio: 1/7 $kg_{potatoes}/L_{oil}$). In the whole fresh EVOO (Fig. 3a) a large peak is observed (T) corresponding to triglycerides and a second smaller one (F) corresponding to a lower molecular weight compound. In the chromatograph of the polar fraction of fresh EVOO (Fig. 3c), three distinct peaks are identified (To and D and F). To corresponds to the oxidised triglycerides while D corresponds, according to literature (Dobarganes *et al*., 1988; Gomes, 1992), to diglycerides. It should be noted that the D peak is largely masked in the whole oil chromatograms from the

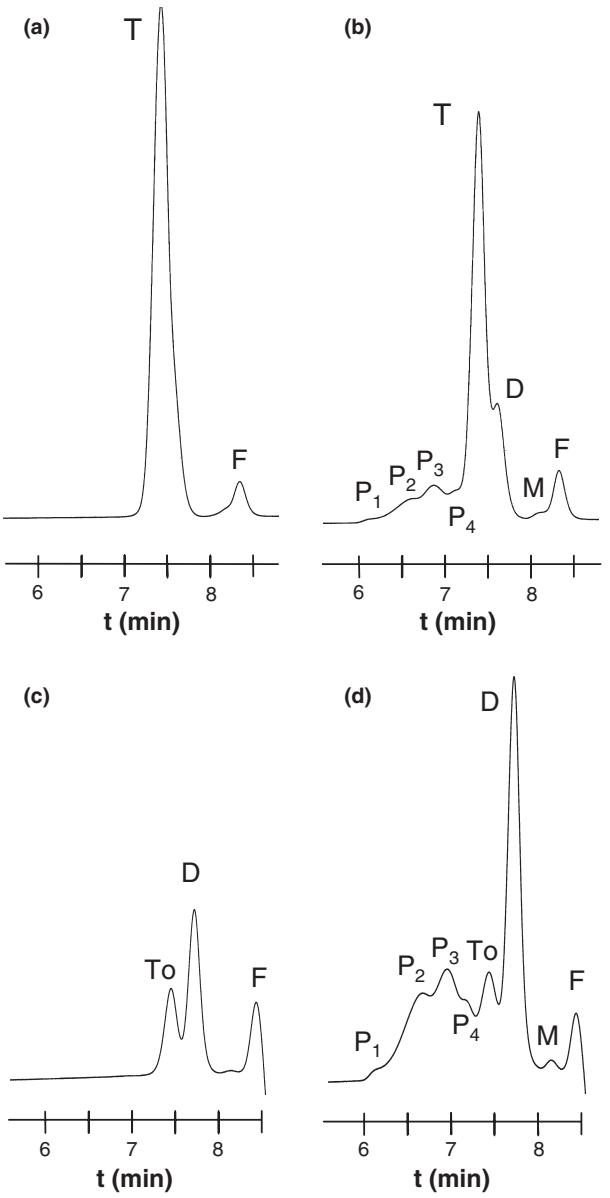

Figure 3 Chromatograms of whole extra virgin olive oil (a) and (b) and of its polar fraction (c) and (d). Chromatograms (a) and (c) correspond to fresh (unprocessed) extra virgin olive oil. (b) and (d) correspond to extra virgin olive oil with forty batches of frying at a high frying load. Peaks P_1, P_2, P_3 and P_4 stand for polymerisation products, T for triglycerides, To for oxidised triglycerides, D for diglycerides and M, F for compounds having lower molecular size than diglycerides. *t* denotes the retention time in HPSEC analysis.

large T peak. This was also the case in previous works (Dobarganes *et al*., 1988; Kalogianni *et al*., 2009). The F peak is also present in the chromatogram of the polar fraction of EVOO, indicating a group of polar compounds having lower molecular weight than diglycerides. Gomes (1992), analysing EVOO by HPSEC, obtained three peaks corresponding to triglycerides, diglycerides and free fatty acids, respectively. The D peak denotes that the unprocessed (fresh) oil has undergone hydrolysis. Hydrolysis can begin already in the olive fruit prior to extraction and is common to mature olives (Kiritsakis, 1990). Fresh EVOO is cold pressed and unrefined, so under these conditions polymerisation is absent. This is verified by the absence of any peak having lower retention time than triglycerides.

Figure 3b shows the chromatogram of whole oil at the end of the high frying load series. Apparently, the T peak decreases in area due to the transformation of triglycerides into products differing in molecular size. To start with, one can observe polymerisation products differing in molecular size (P_1–P_4). In the words of Wolff *et al*. (1991) such a peak pattern can be connected to 'complex degradation phenomena (hydrolysis)'. It should also be noted that the polymerisation products of different molecular sizes form progressively along the frying series starting from those having lower molecular sizes. The higher molecular sizes are detected at later stages of the frying series (results not shown). On the right-hand side of T peak, one can distinguish the D peak as well as the F peak. An additional peak has appeared corresponding to compounds of intermediate molecular size between diglycerides and compounds represented by the F peak. The D, M and F peaks are better resolved in the polar fraction chromatogram (Fig. 3d).

HPSEC chromatograms of EVOO samples obtained from the rest of frying and heating/quenching series exhibit the same qualitative characteristics as those presented in Fig. 3 and are not displayed due to space limitations.

The classes of compounds detected here have been also detected previously in EVOO, virgin olive oil and plain olive oil (Romero *et al*., 1995; Barrera-Arellano *et al*., 2002; Kalogeropoulos *et al*., 2007) and other oil types (Arroyo *et al*., 1992, 1995; Cuesta *et al*., 1993; Barrera-Arellano *et al*., 2002; Abidi & Rennick, 2003; Kalogianni *et al*., 2009) subjected to frying.

Results on whole EVOO

Figure 4a–c present the results obtained for frying at high load. Peaks are termed as in Fig. 3. Although four groups of polymerisation products have been detected (P_1–P_4 in Fig. 3), due to the low resolution of these peaks in the chromatograms (Fig. 3) the quantitative results are presented as total polymerisation products (TPP). TPP represent the concentration of all four groups of polymerisation products. Furthermore, as has been stated in Fig. 3 diglycerides exist in all EVOO samples but are not resolved in all chromatograms of whole oil.

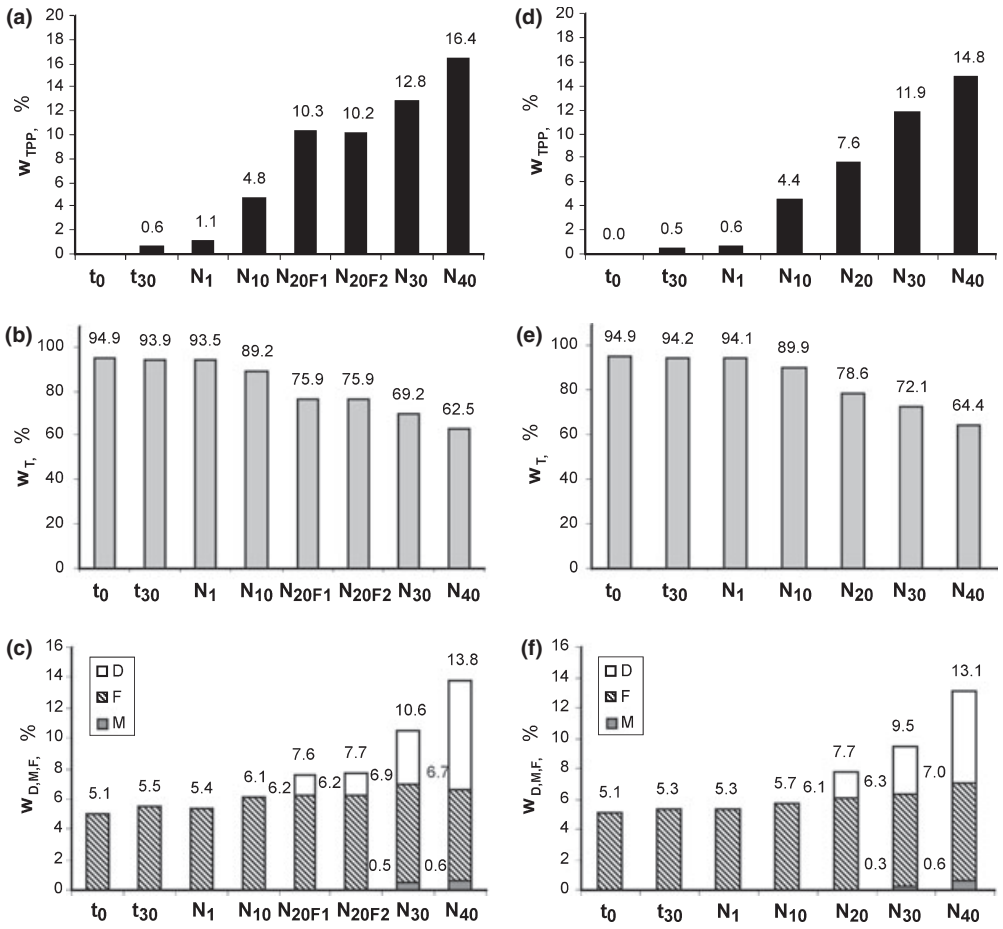

Figure 4 Changes in the composition of whole extra virgin olive oil induced by frying at high (a–c) and at low (d–f) frying load. t_0 and t_{30} denote the beginning of the frying series and the end of the initial 30-min heating period respectively and N_1 to N_{40} different numbers of frying batches. *w* denotes the weight percentage of each compound class. TPP stands for total polymerisation products. For T, D, M, F see Fig. 3. F_1 and F_2 denote results on the 1st fryer and on the 2nd fryer, respectively.

As stated in section 'Materials and methods' the experiments were carried out for four consecutive days. This was also the experimental approach followed by da Silva & Singh (1995) for frying in corn oil. Interestingly, these authors found that the oil degraded not only during the frying process but also in the waiting periods between frying days where the oil was left at ambient temperature. To check for this effect we compared the analysis of samples taken at the end of one intermediate frying day with that at the beginning of the next day. Virtually no differences are found (at most $\pm 0.2\%$). Therefore, it is assumed that conducting the experiments intermittently in 4 days and not continuously for 46 h did not affect our results.

EVOO composition changes considerably during the course of repeated frying at high potato-to-oil ratio (Fig 4a–c). TPP increase in concentration (Fig. 4a). This also holds for decomposition products (F, M and D in Fig. 4c) but at a smaller extent. The effect of repeated frying on the composition of EVOO agrees qualitatively with the results of previous studies that have used EVOO and virgin olive oil (Romero *et al.*, 1995; Kalogeropoulos *et al.*, 2007) or other oil types for repeated frying (Arroyo *et al.*, 1992, 1995; Cuesta *et al.*, 1993).

Figure 4d–f illustrate the composition of EVOO in a frying series conducted at low frying load (1/35 $kg_{potatoes}/L_{oil}$). Comparing data in Fig. 4d–f with those in Fig. 4a–c shows that the chemical changes induced at lower frying load were slightly less than at higher frying load, and mainly for TPP. This trend is rather expected if one takes into account that at higher potato-to-oil ratio more potatoes were processed in the fryer. However, the different potato-to-oil ratios had different time–temperature profiles; the low potato-to-oil ratio batches lasted less but were exposed to much higher

temperatures (Fig. 2). In general, a higher temperature can amplify the rate of chemical reactions during frying; this varies with the extent of temperature change and oil type (Tyagi & Vasishtha, 1996; Houhoula *et al*., 2003). Therefore, in order to separately assess the effects of potato-to-oil ratio from the frying time–temperature profile one has to contrast the results of the repeated frying experimental series against those of the repeated oil heating/quenching experiments with similar time-temperature profiles.

Figure 5a–f display results of the heating/quenching experiments where the temperature profiles of high and low load frying series were respectively simulated (Fig. 2). It should be noted that in the chromatographs of whole EVOO samples of the heating/quenching experiments the D peak could not be resolved because it was masked by the larger T peak. Therefore, results on diglycerides are not reported in Fig. 5. However, analysis of the polar fraction of a few samples subjected to heating/quenching showed that diglycerides do exist in heated/quenched samples. By comparing Fig. 5a–c with Fig. 4a–c and Fig. 5d–f with Fig. 4d–f, the effect of potato presence or absence in the fryer is clearly demonstrated. In the absence of potatoes in the fryer the M peak is absent and compounds corresponding to the F peak decrease in concentration. Besides, adding potatoes to the fryer results in an increase in concentration of compounds corresponding to the D, M and F peaks. This shows that frying induces the generation of compounds of lower molecular weight than the triglycerides (not generated during heating/quenching) and may imply hydrolysis in EVOO in the presence of potatoes. Previous studies performing frying with other oil types reported hydrolysis in the presence of potatoes (Dobarganes *et al*., 1988; Arroyo *et al*., 1992, 1995). On the contrary, there exist other studies (Cuesta *et al*., 1993; Romero *et al*., 1995; Abidi & Rennick, 2003; Kalogianni *et al*., 2009) that have not detected any increase of hydrolysis or other decomposition products during repeated frying. Amongst them, Kalogianni *et al*. (2009), who followed the same experimental procedure with the one used herein, reported for palm oil the absence on formation of compounds with lower molecular weight during repeated frying process under any of the applied experimental conditions. Those results contradict the present findings for EVOO and suggest a possible relation between the frying medium and the chemical compounds formed during frying and the corresponding chemical reactions in each case.

Regarding the nature of decomposition products, our analysis based on molecular size differences cannot provide proof on whether they originate from hydrolysis

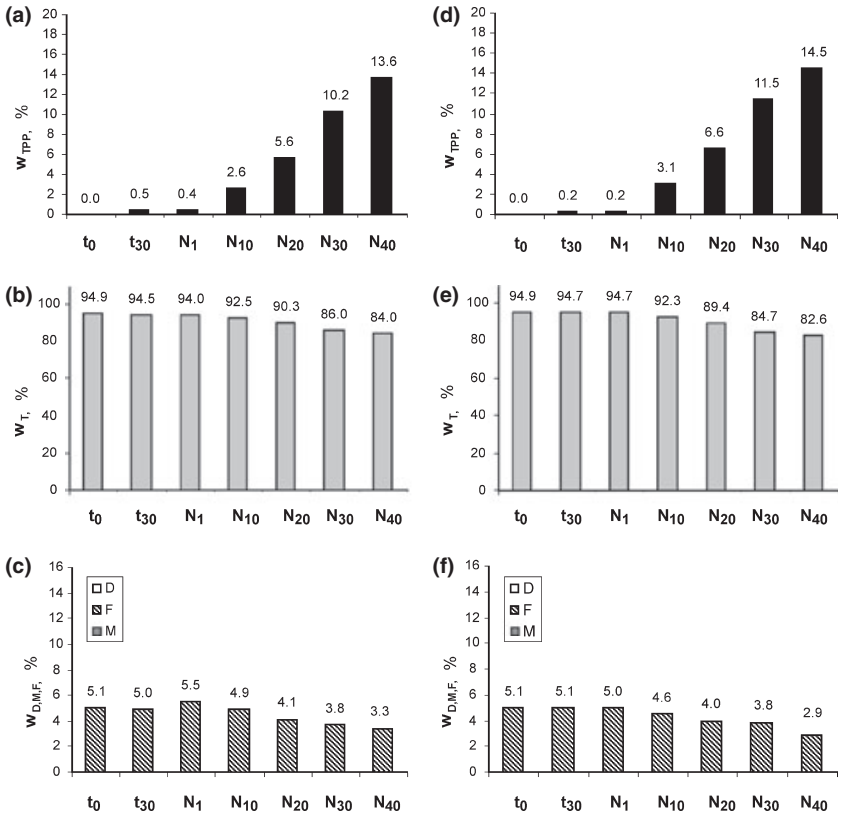

Figure 5 Changes in the composition of whole extra virgin olive oil induced by heating/quenching under temperature profiles simulating those of frying at high frying at high (a–c) and at low (d–f) frying load. t_0 and t_{30} denote the beginning of the frying series and the end of the initial 30-min heating period, respectively, and N_1 to N_{40} different numbers of heating/quenching batches. w denotes the weight percentage of each compound class. TPP stands for total polymerisation products. For T, D, M and F refer to Fig. 3.

or oxidation reactions. Therefore, the possibility cannot be excluded that decomposition products issuing from oxidation with similar molecular sizes as hydrolysis products are generated as well. In addition, during heating/quenching (Fig. 5) some of the compounds corresponding to the F peak were eliminated. Therefore, results on these compounds may not reflect the total amount formed, reflecting only the one remaining in the oil.

Results in Fig. 5a–c and d–f are similar. This manifests that the difference in time–temperature profile between the two potato-to-oil ratios did not affect significantly the generation of the examined compound classes. Consequently, the differences found between the two potato-to-oil ratios (Fig. 4) should be ascribed chiefly to the effect of the different potato amounts in the fryer. In our experiments different potato amounts in the fryer means different amounts of water released as steam bubbles from the potatoes. As the fried potatoes had similar water contents for both frying loads, the amount of water released from the potatoes was proportional to the amount of potatoes added in the fryer. Dana *et al*. (2003) showed that chemical changes in heated corn and canola oils are significantly affected by the amount of steam bubbles in contact with the oil. Furthermore, all potato sticks had the same size. Consequently, the surface area of potatoes in contact with the whole EVOO was proportional to their amount. This affects the area of interaction of potato constituents other than water with EVOO. Fedeli (1988) showed that starch and amino acids affect chemical changes in olive oil heated to frying temperatures. Finally, frying at high load involves a less intense mixing in the oil bulk due to bubble release (because the rate of bubble release is lower) but mixing lasts for a longer period of time and occurs at lower temperatures compared to frying at low frying load. The differences in the mixing intensity and time are expected to affect the oil contact with atmospheric oxygen and as a result oxidation in EVOO.

Figure 6 displays the mass percentage of TPP generated by frying or heating/quenching related to batch number (N) or series. In order to observe the net effect of frying or heating/quenching the values of TPP obtained during the preheating period were subtracted from the presented values. The generation of TPP in EVOO represented a linear equation ($w_{TPP} = r \times N$), being r (the slope of the equation) the rate of generation of TPP. N corresponds to batch number. This holds for repeated frying as well as for repeated heating/quenching. Table 1 shows linear regression analysis and analysis of variance for each frying series. All equations are significant at a confidence level of 95% ($P < 0.05$) and have high R^2 values. Bastida & Sanchez-Muniz (2002) reported that in deep frying with plain olive oil (40 repetitions), without replacement, frying different types of food and using domestic conditions (long intervals of cooling to ambient temperature between frying), the formation of TPP obeyed a power model ($w_{TPP} = k \times N^b$) in relation to frying batch number (N). In our case, a power model was inadequate to describe the data. This is possibly due to the significant differences in experimental conditions (replacement, time–temperature profile, food-type). Other models (e.g. logarithmic) were even worst in describing our data than the linear model and this was verified by the determined R^2 and P values as well as by plotting the residuals.

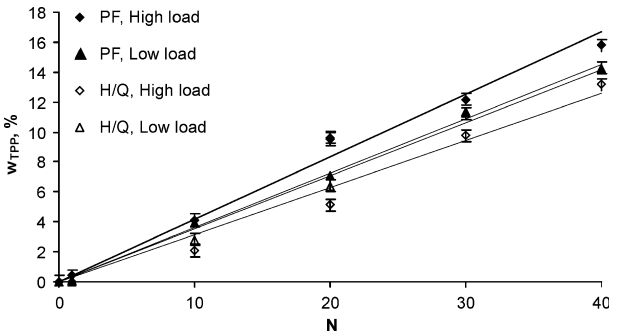

Figure 6 Weight percentage (w) of total polymerisation products (TPP) generated during repeated potato frying (PF) at high and low frying load or repeated heating/quenching (H/Q) simulating the time–temperature profile followed during frying at high and low load. TPP generated during the preheating procedure are subtracted from presented values. N represents the number of frying batches. The error bars stand for the standard deviation of repetitions.

Table 1 Rates (r) of total polymerisation products (TPP) generation as a function of frying batch number (N) during repeated frying (F) at high and low potato-to-oil ratio and during repeated heating/quenching (H/Q) at temperature profiles simulating the temperature obtained at high and low frying load. R is the coefficient of determination

Type of experiment	Frying load/ temperature profile	r (average ± standard error) (% oil mass/batch)	R^2 (–)	P-value of model
F	High load	0.42 ± 0.01[a]	0.98	0.000
F	Low load	0.36 ± 0.01[b]	1.00	0.000
H/Q	High load	0.31 ± 0.01[c]	0.98	0.000
H/Q	Low load	0.35 ± 0.01[b,c]	0.99	0.000

[a,b,c] when superscripts are the same they connote results equal at a level of significance $\alpha = 0.05$.

Multiple linear regression analysis with the aid of dummy variables and analysis of variance was applied in order to assess possible differences in the rate of generation of polymerisation products among frying series. The analysis showed that there is no statistically significant difference (at a level of significance $\alpha = 0.05$) in the rate of polymerisation between the heating/quenching series ($P = 0.080$) or between the frying series at low frying load and the heating/quenching

series following the same temperature profile ($P = 0.449$). However, frying at high potato-to-oil ratio proved to induce higher polymerisation compared to heating/quenching ($P = 0.002$) or frying at low potato-to-oil ratio. These results are connoted in the table with superscripts. As an outcome, the concentration of polymerisation products as a function of heating/quenching batch number or frying batch number for the low potato-to-oil ratio series could be described by the same linear equation ($r = 0.34 \pm 0.01$, $R^2 = 0.98$, $P = 0.000$).

In evaluating the effect of potato-to-oil ratio on the formation of polymerisation products in EVOO it is interesting to note that although there is a 5-fold increase in the potato-to-oil ratio between the two frying series the difference in the rate of generation of polymerisation compounds, although statistically significant, is not so remarkable (see Fig. 6 and Table 1). This result is different from what was obtained for palm oil where the same increase in potato-to-oil ratio had a marked effect on polymerisation rates (Kalogianni *et al*., 2009). This indicates that the effect of potato-to-oil ratio on polymerisation rate is oil type dependent.

The present results on the generation of polymerisation compounds in EVOO used for frying can be compared with those of Kalogeropoulos *et al*. (2007) and Romero *et al*. (1995). Kalogeropoulos *et al*. (2007) reported that frying potato sticks in virgin olive oil (8 batches) without oil replacement at a potato-to-oil ratio of 1/5 ($kg_{potatoes}/L_{oil}$) led to formation of 2.08% (w/w) TPP in the oil. In our case, although no measurement was conducted at the eighth frying batch, we would expect to have a slightly higher TPP concentration (under any of the examined conditions). This is not so surprising if one takes into account the small effects of frying load on TPP formation combined with the fact that Kalogeropoulos *et al*. (2007) followed a less abusive time–temperature profile compared to our study (they left the oil to cool down between frying batches).

Romero *et al*. (1995) reported that frying potato chips in extra virgin olive oil at a higher potato-to-oil ratio with oil replacement, less polymerisation and hydrolysis products appeared in olive oil. Comparing our results with Romero *et al*. (1995), higher polymerisation and hydrolysis products were obtained. It must be noted that frying of potato crisps releases higher amounts of water in the oil and involves a larger food surface area in contact with the oil compared to frying of potato sticks (chips). This is expected to intensify chemical reactions in the oil. On the other hand, potato crisps absorb significantly higher amounts of oil compared to chips, and this induces very high replacement rates. Apparently, the rates of replacement were high enough to still be able to use the oil after seventy-five frying batches.

The results obtained from the analysis of whole EVOO showed that potatoes presence in the fryer (separated from the effect of time and temperature) resulted in increasing the concentration of compounds differing in molecular weight from triglycerides. Dana *et al*. (2003) simulated frying experiments by injecting steam bubbles of different sizes and at different flow rates in corn and canola oil at 170 °C for 22 h. These authors observed that, although the presence of water bubbles increased the acid value of the oil, the quantity of conjugated dienes, the *p*-anisidine value and malonaldehyde concentration all decreased. The authors concluded that water release in the oil during frying can play a protective role by steaming out volatile compounds. It must be noted, however, that the decrease in conjugated dienes may also originate from cyclisation or polymerisation in the oil (Belitz *et al*., 2004) which would make an oil quality poorer rather than better but such products were not determined by Dana *et al*. (2003). Fedeli (1988) in his extensive experimental study showed that adding amino acids to oil played a protective role to various oil types heated at high temperatures whilst starch had an opposite effect. These two potato constituents surely play a role in the present results.

Results on the polar fraction of EVOO

Figure 7 presents the mass fraction of different compounds in the polar fraction of EVOO fried at high potato-to-oil ratio. In Fig. 7 comparisons can be made only among different components in the same frying batch but not for the same component among different frying batches. This limitation stems from the fact that these chromatograms display the relative concentration of each component in the polar fraction of the oil (whose mass changes considerably throughout the frying series) and not in the whole oil. As a consequence, in order to compare results among frying batches the mass of the polar fraction in every batch must be known (and is not known in our case).

Figure 7 shows the appearance of polar compounds generated in EVOO during repeated frying process. Results are similar to those reported by Dobarganes *et al*. (1988). The presence of diglycerides is predominant not only in the polar fraction of fresh oil but also throughout the frying series with exception for N_{40}. Furthermore, the relative concentration of polar TPP with respect to other polar compounds becomes more and more significant with the increase of frying batch number. Although the mass of the polar fraction is not known one could approximately estimate the total polar materials in the oil from the relevant quantities of diglycerides in the polar fraction and the whole oil which correspond to the same quantity. According to this, the total polar materials at N_{20}, N_{30} and N_{40} are approximately 21%, 26% and 35% (w/w) of the whole oil mass, respectively.

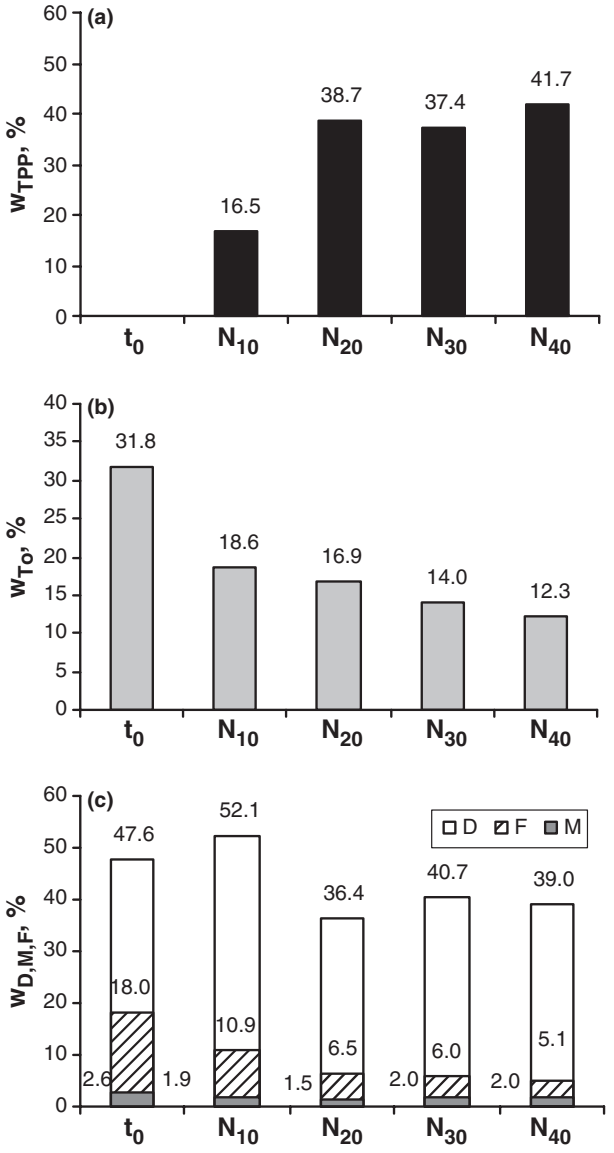

Figure 7 Changes in the composition of polar fractions of extra virgin olive oil in frying at high frying load corresponding to the beginning of the frying series (t_0) and different numbers of batches (N_{10}, N_{20}, N_{30} and N_{40}). *w* denotes the weight percentage of each compound class. TPP stands for total polymerisation products. For To, D, M and F refer to Fig. 3.

Conclusion

Results obtained showed that potato chips presence during frying process affects poorly the appearance of polymerisation products in extra virgin olive oil. On the other hand it accelerates the appearance of decomposition products. Although the concentration of decomposition products increased during the frying experiments, it decreased during the heating/quenching experiments, where potatoes were absent from the fryer. Furthermore, the effect of potato presence on the rate of generation of total polymerisation products was statistically insignificant when frying at low potato-to-oil ratio and became statistically significant, still not remarkable, at high potato-to-oil ratio. The difference in the temperature profile between experiments did not affect the concentration of either polymerisation or decomposition products. The concentration of polymerisation products as a function of batch number during frying and heating experiments could be adequately described by linear equations. The appreciable differences between the present results and results obtained with palm oil (Kalogianni *et al*., 2009) indicate that the rate of polymerisation as well as the generation (or not) of decomposition products during repeated frying depend on the employed oil type.

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