Effect of repeated frying on the viscosity, density and dynamic interfacial tension of palm and olive oil

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ABSTRACT

The effect of deep-fat frying on the viscosity, density and dynamic interfacial tension (against air and water) of palm oil and olive oil was investigated. Repeated frying (up to 40 batches) at two different potato-to-oil ratios (1/7, 1/35 $kg_{potatoes}/L_{oil}$) was examined. Results were compared to those from simple heating the oils at the same temperatures. Viscosity increased during repeated frying for both oils. However, only palm oil viscosity was sensitive to potato-to-oil ratio. Due to the novelty of dynamic interfacial characterization of such systems a discussion was made about the appropriate timescales and deformation types for interfacial measurements. Significant effects of repeated frying on the dynamic interfacial tension at the oil/water interface were observed. Contrarily, changes in density were not significant. Results were assessed with respect to the evolving chemical profile of the oils determined in previous works. Possible implications of the determined properties on the frying process were discussed.

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1. Introduction

Frying is an intense process inducing a multitude of chemical reactions in the frying medium and generating a plethora of chemical compounds (Belitz et al., 2004). Most of these compounds are non-volatile, so they remain in the frying medium and affect its physical properties (Tyagi and Vasishtha, 1996; Gertz, 2000). Furthermore, the physical–chemical properties of fried oils and fats are also affected by frying (Gil and Handel, 1995; Dana and Saguy, 2006) due to the generation of surface-active substances. Changes in the physical properties of oils and fats during frying have been used for a long time as indicators of the chemical deterioration of frying media (Gutiérrez et al., 1988; Stier, 2004). As an outcome, rapid methods based on the measurement of physical properties have been proposed in order to assess frying oil quality (Garziano, 1979; Kress-Rogers et al., 1990; Innawang et al., 2004; Benedito et al., 2007). In the following years it is expected that rapid tests will continue to be applied and developed (Stier, 2004) so the determination of changes in physical properties of oils and fats during frying remains in the limelight.

Changes in certain physical properties and physicochemical properties of oils and fats during frying have been blamed for changes in the food that undergoes frying. In particular, the increase in viscosity during repeated frying has been identified by some authors as the factor responsible for an increase in oil uptake of fried foods (Guillaumin, 1988; Moreira et al., 1997). Furthermore, changes in the viscosity and density of the frying medium during repeated frying can be expected to affect buoyant bubble removal from the food surface and, consequently, the convective heat transfer from the oil to the food that undergoes frying.

It has been suggested long ago that interfacial phenomena may influence the characteristics of fried foods (Stern and Roth, 1959). Blumenthal (1991) proposed the "surfactant theory of frying" according to which the generation of surfactants in the frying oil is responsible for the surface and internal changes in fried foods induced by ageing oils. Unfortunately, these authors did not test their theories by means of interfacial tension measurements in the fried oil. Later, Gil and Handel (1995) proposed that the increase in oil uptake of doughnuts due to repeated frying was related to the decrease in the frying fat/water interfacial tension. Recently, Rossi et al. (2009) found a significant correlation between the oil uptake of French-fries and the contact angle of sunflower oil on a glass substrate. All the above underline the need to examine in-depth the changes of these properties in the course of repeated

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frying. At the moment, only limited information exists in the literature regarding interfacial properties of fried fats and oils which indeed show some effect of the frying process. Moreover, up to now the literature has addressed only the equilibrium (or quasi equilibrium) properties whereas the intense (in terms of interfacial dilation) and fast phenomena occurring at the food/oil/steam interface would suggest the measurement of dynamic interfacial properties. Nevertheless, we were not able to locate any published work presenting measurements of dynamic interfacial properties.

This work focuses on determining changes in viscosity, density and dynamic interfacial tension at the oil/air and oil/water interface caused by repeated batch potato frying. Two specific oil types were examined due to their different attributes: palm oil and extra virgin olive oil. The first is a highly saturated oil commonly used in the food industry for producing French fries and the second is an oil rich in monounsaturated fatty acids with high nutritional value customarily used in the Mediterranean Sea countries for food preparation and frying. Regarding viscosity, possible deviations from the Newtonian rheological behavior were examined first. Then the effect of oil type, frying load (potato-to-oil ratio in the fryer: 1/7 and 1/35 $kg_{potatoes}/L_{oil}$) and frying batch number (up to 40 batches) were examined. Results are compared to changes in viscosity induced by simply heating the oil (potato-to-oil ratio in the fryer: 0 $kg_{potatoes}/L_{oil}$) under the same time-temperature profile as the one used for frying. This allows evaluation of the contribution of potato presence to the increase in viscosity during frying. Finally, the effect of compounds generated during frying and differing in molecular size form triacylglycerols is assessed and an equation is proposed for relating some of these products to the measured viscosity. Changes in density and dynamic interfacial tension are monitored during frying at high potato-to-oil ratio (1/7 $kg_{potatoes}/L_{oil}$) because under these conditions the oils undergo higher degradation (Kalogianni et al., 2009, 2010). Before presenting the results of dynamic interfacial tension a discussion is made about the selection of the appropriate time-scales and types of deformation for dynamic interfacial tension measurements so that the measured properties can be related to the dynamic phenomena occurring during the frying operation. An attempt is also made to explain the results of dynamic interfacial tension based on the chemical changes induced in palm and olive oil during repeated frying that were recently presented elsewhere (Kalogianni et al., 2009, 2010). Finally, possible implications of the changes of the measured properties on heat/mass transfer and interfacial phenomena occurring during frying are discussed.

2. Materials and methods

2.1. Materials

Refined palm oil was supplied by Elais S.A. (Piraeus, Greece). Fresh, cold-pressed virgin olive oil was purchased from a local producer at the time of production. Both palm and olive oil were stored at −18 °C in sealed 5 L containers. Angria variety potatoes were bought at the local market and conditioned according to Lisińska and Lesczyński (1989). Potatoes having a specific gravity between 1.07 and 1.10 were selected for frying.

2.2. Frying and heating experiments

Four series of experiments were performed with each oil type: two series of repeated frying experiments of potatoes (potato-to-oil ratio: 1/7 $kg_{potatoes}/L_{oil}$ or high frying load and potato-to-oil ratio: 1/35 $kg_{potatoes}/L_{oil}$ or low frying load) and two series of heating experiments of the frying medium in the absence of food. The selection of potato-to-oil ratios (or frying loads) was based upon values used in the industry (high frying load) and in the catering/resatuation sector (low frying load). Frying was conducted in temperature-controlled fryers (Fig. 1a) using raw potato sticks (1 cm × 1 cm × 8 cm) equally spaced in the oil volume (4 L). This assured temperature homogeneity in the oil bulk (Kalogianni, 2007). Each repeated frying experimental series consisted of 40 frying batches conducted in four consecutive days. Two days before the experiments palm or olive oil were removed from the freezer and put in a fridge (6–8 °C) then the day before the experiments they were left in ambient conditions to reach room temperature. This was enough to melt olive oil but not palm oil. The olive oil container was then rolled in order to homogenize its content and poured into the fryer. In the case of palm oil the whole quantity of 5 L was added in the fryer in solid pieces (this procedure is followed also in the industry) and melted. Residual oil (>4 L) was discarded. Initially the oil was heated up to 182 ± 2 °C and was kept at this temperature for 30 additional minutes before the potatoes were added. 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. The oil was not replenished during the repeated frying process; on the contrary, the potato-to-oil ratio was kept constant through frying batches. At high potato-to-oil ratio each frying batch lasted 12 min whereas at low potato-to-oil ratio each batch lasted 3 min. This was because the oil temperature profile was significantly different between the two frying loads (Fig. 2a). The dura-
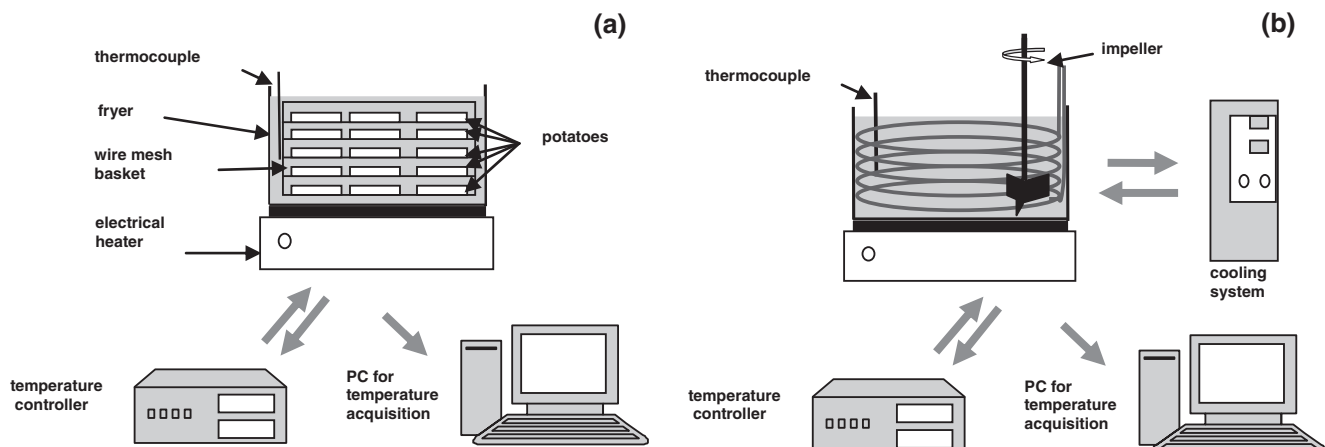

Fig. 1. Experimental set-up used during the repeated frying (a) and heating (b) experiments.
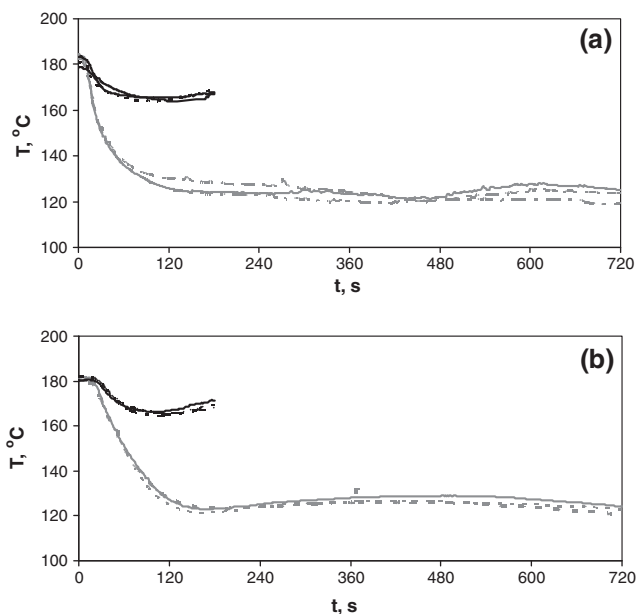
Fig. 2. Indicative temperature profiles during one batch obtained during (a) the frying and (b) heating experiments at high (in gray) and low (in black) frying load.

tion of frying was decided in preliminary tests (Kalogianni, 2007). In order to make meaningful comparisons between the heating and frying experiments the temperature profile of the oil during the frying experiments was replicated in the absence of potatoes by employing a custom made cooling system which can remove high amounts of heat in short time (Fig. 1b). The repeatability of experimental conditions was checked by monitoring the temperature profile in the oil bulk (results not shown). The experimental procedure is described in further detail in Kalogianni et al. (2009) and Kalogianni (2007).

2.3. Sampling and storage

Oil and fat samples were collected at the beginning (unused or fresh oil) and after 1, 5, 10, 15, 20, 25, 30, 35 and 40 batches. Samples were kept at −26 °C, under a nitrogen atmosphere, in airtight closed, dark-colored glass bottles.

2.4. Measurements of physical and physicochemical properties

All measurements were conducted at 50 ± 1 °C; at this temperature both olive and palm oil are in the liquid state. Differential Scanning Calorimetry (DSC) measurements have shown that few crystals still exist at 47.5 °C in palm oil even at very low temperature scanning velocities (Tan and Che Man, 2002).

2.5. Samples preparation for measurements

The day of the measurements the samples were put in a fridge (2–4 °C) and progressively transferred from the fridge to a small convection oven held at 50 °C and after having melted they were taken out of it. Due to the small size of the bottles this procedure lasted only a few minutes. The bottles were shaken before opening for homogenization of their content and then put in the thermostated instruments.

2.6. Density measurements

Oil or fat density was determined by a special accessory of TD1 tensiometer (LAUDA).

2.7. Rheology and viscosity measurements

The presence of pseudoplastic-dilatant rheological behavior of the oil and fat samples was investigated using a cone and plate viscometer (CVOR-150, Bohlin, Malvern Instruments Ltd., Worcestershire) by measuring shear stress at variable shear rates between 50 and $1500 \, s^{-1}$. In addition, a possible time-dependent rheological behavior (thixotropic or rheopectic) was examined by recording viscosity continuously for 5 min at a shear rate of $200 \, s^{-1}$. A cone and plate viscometer (RVTDV-II, Brookfield, Massachusetts) was used in this case. The latter viscometer and shear rate was employed to measure the viscosity of the samples.

2.8. Dynamic interfacial tension measurements

Dynamic interfacial tension measurements were conducted both at the oil/air and at the oil/water interface. Measurements at the oil/air interface spanned surface ages from 0.01 to 50 s and were conducted by the maximum bubble pressure method (MBP) using BPT-1 tensiometer (Gammalab, Germany). Before each measurement, all parts of the instrument in contact with the liquid (capillary, sample holder) had been cleaned by immersion in dense sulfuric acid (MERK) for 1 h. Subsequently, they were rinsed with copious amounts of filtered water (Milli-Q, Millipore; resistivity at 25 °C: 18 MΩ cm). The cleanliness and dryness of the capillary were automatically tested by the tensiometer. Results by this method are presented as a function of the so called effective adsorption time (t_{eff}) which is calculated automatically by the apparatus. The definition of t_{eff} has been discussed in more detail elsewhere (Fainerman and Miller, 1988).

Measurements at the oil/water interface spanned interface ages between 2 s and 1 h and were conducted by the drop profile analysis method using PAT-1 (Sinterface, Berlin). A schematic representation of the set-up is shown in Fig. 3. As can be seen in the figure, the geometry of the capillary used in such measurements depends on the densities of the drop and the surrounding medium. In the system under study it was preferable to form an oil drop in water
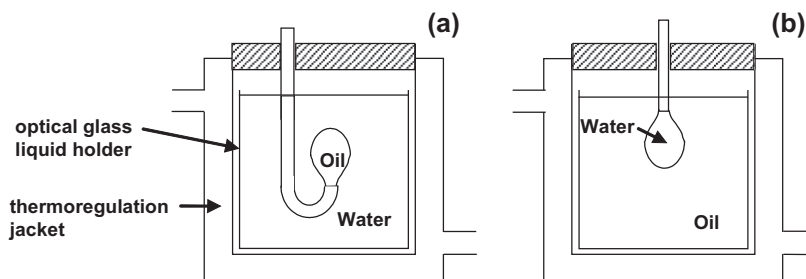

Fig. 3. Experimental assembly for interfacial tension measurements at the oil/water interface.

(Fig. 3a) because palm and olive oil are not fully transparent, particularly after successive frying batches. However, in the fried olive oil/water system the droplet was unstable. Droplet instability when performing measurements with the pendant drop technique at liquid/liquid interfaces is not uncommon and several reasons can lead to it. Such reasons can be (a) the small density difference between phases tensions compared to liquid/air systems, which, combined with the smaller interfacial tension make systems more susceptible to ambient vibrations, (b) the transfer of surfactants across the interface which can produce hydrodynamic instabilities and macroscopic oscillations (Hennenberg et al., 1980) and (c) the changes in the pinning of the drop at the capillary due to changes in interfacial tension. In our case, however, there is yet another possibility for droplet instability when an oil drop is formed in water. "Clouding" (see Section 3) around the droplet caused blurring of the droplet contour in the image registered by the instrument and deceived the control of the droplet size which is done automatically by operating a miniature syringe. Moreover, "clouding" could have potentially interfered with the accurate determination of interfacial tension (again via affecting the captured image). Therefore, forming an oil drop into water (Fig. 3a) was abandoned. Instead, the set-up shown in Fig. 3b was chosen. For all measurements with PAT Teflon capillaries were used. Teflon had the appropriate wetting properties for the formation of stable droplets in the oil/water system. The capillary was cleaned with distilled hexane, subsequently with distilled ethanol and finally with filtered water (the same as for MBP measurements). The cleanliness of the capillary was verified by measuring filtered water surface tension. The optical glass liquid container was cleaned as described for the MBP measurements.

Before the formation of the actual measurement drop, a few drops were produced and removed from the tip in order to create a fresh interface with the least possible impurities. Measurements were conducted at least in duplicate.

2.9. Statistical analysis

Analysis of variance (ANOVA) following the General Linear Model (GLM) was applied in order to compare results on density, viscosity and interfacial tension. According to the results of ANOVA and wherever the effect of examined variables was significant ($\alpha = 0.05$) the data were further compared using the Tuckey's test. The above analysis was used also for the results on interfacial tension. In this case comparisons were made only after the change of interfacial tension as a function of time had reached a plateau (changes in interfacial tension less than 0.1 mN/m).

Results on viscosity were related to the frying or heating batch number using regression analysis. The significance of the regression equation terms was assessed using sequential analysis of variance.

Results on viscosity were related to results on the chemical profile of the frying media using linear regression analysis and assessed by analysis of variance. In order to choose which variables (predictors) were statistically significant, linear regression tests were conducted by the conventional regression method (making all possible combinations of all possible predictors), by the stepwise regression method (by forward selection and backward elimination methods) and by the best subsets method. Statistical analysis was performed using Minitab 14 (Minitab Inc.).

3. Results and discussion

3.1. Changes in palm oil and olive oil density

Fig. 4 shows the change in the density of palm and olive oil as a function of the frying batch number during frying at high
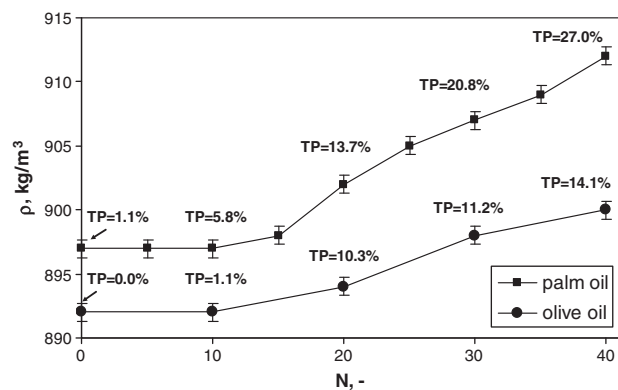

Fig. 4. Density (ρ) (at 50 °C) of palm oil and olive oil as a function of frying batch number (N) for a frying series conducted at high frying load. $N = 0$ denotes the fresh oil/fat. The error bars represent the standard deviation of measurements. In the plot TP denotes the polymers concentration of each sample as measured by HPSEC (Kalogianni et al., 2009, 2010).

potato-to-oil ratio. As one can see, the densities of the fresh frying media ($N = 0$) differ slightly between the two oil types. Such differences are common between different oil types and are due to differences in composition (Formo et al., 1979). As repeated frying proceeds (increase of batch number (N)) the density of both oil types increases significantly. An increase in density and specific gravity due to repeated frying has been reported in the past (Paul and Mittal, 1996; Tyagi and Vasishtha, 1996; Tseng et al., 1996) but to the best of our knowledge not for palm or olive oil. During frying and heating, oxidation, polymerization, isomerization (in both frying and heating) and hydrolysis (only during frying) occur in the oil generating a multitude of products (Belitz et al., 2004). Among these products, higher molecular weight products compared to triacylglycerols are generated originating from polymerization and oxidation reactions (Dobarganes and Márquez-Ruiz, 1996; Kalogianni et al., 2009, 2010). In the present work and for the sake of simplicity all these compounds will be called polymers, a term customarily used in the literature as a generic term to define these compounds. Polymers have been linked in the past to the increase of oils density (Paul and Mittal, 1996).

Changes in palm oil density are more significant. This is expected, due to the higher polymer generation when frying with palm oil (see the total polymers (TP) values noted on Fig. 4). Results on polymer generation in palm and olive oil have been presented in more detail elsewhere (Kalogianni et al., 2009, 2010). ANOVA showed that the frying batch number is a significant ($\alpha = 0.05$) variable affecting the density of the oil. Comparisons of results between different frying batches for both oil types (Tuckey's Test, confidence intervals (CI) of 95%) showed that changes in density become significant from the 20th frying batch and on. Paul and Mittal (1996) proposed a power law relationship between the total polymer content of canola oil and its specific gravity ($S = 0.50 + 0.41 * TP^{0.003}$). Our results for either of the two oil types examined do not follow a power law equation but rather a second degree polynomial equation (fitting not shown).

Density is an important property affecting the heat transfer by natural convection and the buoyant movement of gas bubbles in a liquid (in our case steam bubbles in the oil). Changes in density may therefore be responsible for changes in heat transfer from the fryer to the oil bulk as well as from the oil to the potatoes. In our case however, the changes observed in the density of palm and olive oil are small and are least expected to affect the above phenomena.

3.2. Changes in viscosity

Edible oils are Newtonian liquids (Formo et al., 1979). The only exception found in literature is linseed oil which showed a thixotropic behavior mainly at high shear rates (Weltman, 1943). This is most likely because linseed oil is prone to intense oxidation (inducing also the generation of oligopolymers) even at low temperatures. Due to the high degree of polymerization in the samples (see TP in Fig. 4 and also Kalogianni et al., 2009, 2010), it was decided, to check the rheological behavior of the palm and olive oil samples with the highest polymer content. Shear stress measurements as a function of shear rate for selected palm and olive oil samples are shown in Fig. 5. The results demonstrate the linear dependence of shear stress on shear rate. Furthermore, there was no variation of viscosity at a shear rate of $200\,s^{-1}$ (results not shown). The above results show that even the most polymerized oil and fat samples present a Newtonian behavior under the conditions of measurement. Therefore, it was assumed that the rest of the oil and fat samples behave as Newtonian liquids under the conditions used for viscosity measurements. Tseng et al. (1996) and Santos et al. (2005) observed that heating (190 °C) for several hours had not changed the Newtonian behavior of several oil types including olive oil. However, we are not aware of any previous study examining the rheological behavior of an oil or fat used for frying.

Fig. 6a displays palm oil viscosity as affected by repeated frying at different potato-to-oil ratios as well as by heating under the same time-temperature profile as the one used for the frying experiments. As can one can see there is a marked increase in palm oil viscosity during repeated frying as well as during simple oil heating. This has been observed previously for several oil types under different experimental conditions (Miller et al., 1994; da Silva and Singh, 1995; Tyagi and Vasishtha, 1996; Tseng et al., 1996; Saguy et al., 1996; Aggelousis and Lalas, 1997; Jaswir et al., 1999; Jaswir and Che Man, 2000; Yaghmur et al., 2001; Che Man et al., 2003; Santos et al., 2005; Chatzilazarou et al., 2006; Sánchez-Gimeno et al., 2008; Tekin et al., 2009). Regression analysis was performed in order to examine the dependence of viscosity on the number of frying batches. In the model we did not include results arising from the effect of preheating period on viscosity but only these of actual frying. The analysis showed that, for the high frying load viscosity was related to the frying batch number following a second order polynomial equation (Fig. 6a). According to sequential ANOVA both terms (linear and quadratic) were statistically significant ($\alpha = 0.05$). The equation and the coefficient of
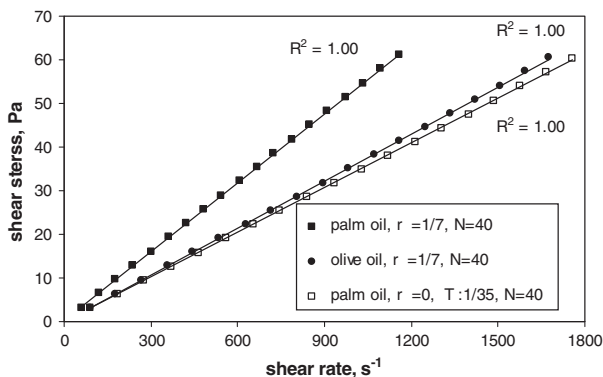

Fig. 6. Palm oil (a) and olive oil (b) viscosity (η) (at 50 °C) as a function of frying batch number (N). $N =$ F represents the viscosity of fresh fat, $N =$ P represents the viscosity of preheated fat. Also, r is the potato-to-oil ratio in $kg_{potatoes}/L_{fat}$, T is the temperature profile followed (simulating that of high (T:1/7) or low (T:1/35) frying load) during heating. Error bars representing the standard deviation of repeatability are always smaller than the data markers. Regression equations and their coefficient of determination (R) are displayed for each group of data.

determination (R) are displayed in Fig. 6a. For the low frying load, regression analysis showed that viscosity was linearly dependent on N. The addition of a quadratic term in the equation was not statistically significant ($a = 0.05$). The linear equation and the coefficient of determination is displayed in Fig. 6a.

The viscosity of heated palm oil in the absence of potatoes is identical (as verified by ANOVA at an $\alpha = 0.05$) for both applied temperature profiles ($r = 0$, T:1/7, 1/35). This was expected as long as one compares previous results on polymerization products generated under the same two temperature profiles and notes that this temperature difference between profiles did not significantly affect polymer generation in the fat (Kalogianni et al., 2009). According to the above, a linear equation, common for both heating series, was used to express the dependence of viscosity on batch number using linear regression analysis (Fig. 6a).

The results in Fig. 6a show that adding potatoes in the fryer increases the rate of viscosity increase, this being more dramatic at high potato-to-oil ratio. The same effect of potato-to-oil ratio was also reported by da Silva and Singh (1995) during repeated deep frying of potatoes in corn oil. Nevertheless, at the beginning of the frying series (up to the tenth frying batch, $N = 10$) palm oil undergoes practically the same viscosity changes for both potato-to-oil ratios. Only for $N > 10$, differences do become significant. This is in line with the observed changes in the generation of polymers in palm oil (Kalogianni et al., 2009). Since, the different temperature profiles between the two heating series had practically no

Fig. 5. Shear stress as a function of shear rate for selected palm oil and olive oil samples (at 50 °C). In the plot r is the potato-to-oil ratio in $kg_{potatoes}/L_{oil/fat}$, N the frying batch number and R the linear regression coefficient. T:1/35 denotes that the temperature profile during heating was similar to that for r = 1/35.
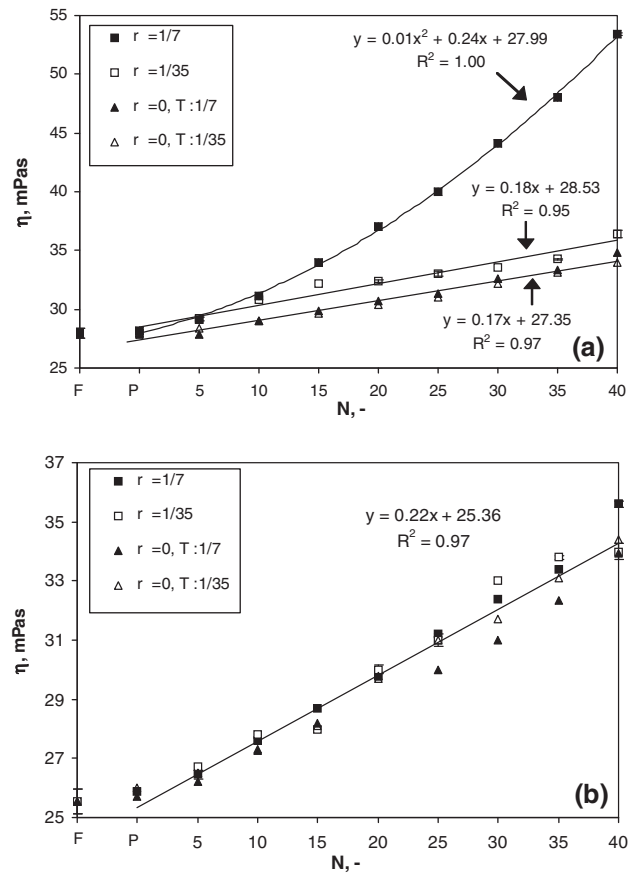
effect on viscosity, the changes in viscosity observed for the different potato-to-oil ratios can be ascribed to the higher potato quantities added to the fryer. Increasing the potato-to-oil ratio in the fryer (i.e. the frying load) leads to increased agitation in the oil due to more intense bubbling (and therefore increased contact with atmospheric oxygen and oxidation) as a higher amount of steam bubbles leave the food. Furthermore, a higher potato-to-oil ratio involves a larger food surface area interacting with the oil.

Fig. 6b displays the changes in the viscosity of olive oil during repeated frying and during heating under different conditions. As expected, olive oil viscosity increases appreciably during the frying or heating procedure. Interestingly enough, hardly any effect of potato presence is observed even at high potato-to-oil ratio. This was also verified by ANOVA (GLM) at $\alpha = 0.05$. Therefore a common linear equation was used to describe changes in viscosity under all examined conditions (Fig. 6b). The overall changes in viscosity are comparable to those observed for palm oil in the absence of potatoes (the Y scales in Fig. 6a and b are different). Previous studies (Aggelousis and Lalas, 1997; Yaghmur et al., 2001; Santos et al., 2005; Chatzilazarou et al., 2006) have shown that olive oil undergoes a lower increase in viscosity than many other oil types during frying except sunflower oil (Sánchez-Gimeno et al., 2008). Yet, no study has been previously conducted, to the best of our knowledge, comparing their performance in the absence or presence of foods or between palm oil and olive oil.

The observed viscosity rise, particularly that of palm oil at high potato-to-oil ratio where the viscosity almost doubles its value after 40 repeated frying batches is expected to affect momentum, heat and mass transfer in the oil bulk (bubble buoyant motion in the fryer, convective heat transfer within the oil bulk and from the oil to the food surface). Furthermore, such significant changes can play also a role to bubble formation growth and detachment from the food being fried.

The changes in the viscosity of an oil or fat during repeated frying and heating can be expected to depend on products generated during frying and differing in molecular size from triacylglycerols (i.e. oxidation, polymerization, hydrolysis and fission products). In addition, it is known that the viscosity of natural oils depends highly on their degree of saturation (Formo et al., 1979). During food frying or simple heating many reactions result in increasing saturation (Belitz et al., 2004); these reactions may also affect viscosity changes. Nevertheless, it is apparent that viscosity changes due to molecular size changes induced by frying are much more significant than the changes induced due to the saturation of double bonds of triacylglycerols.

On this account, an attempt was made to relate the measured viscosity to the various products generated during frying and differing in molecular size from triacylglycerols. Fig. 7 displays indicative chromatograms of both palm and olive oil (Kalogianni, 2007). In the chromatograms the analysis of the oils as a function of molecular size is clearly observed. Linear regression analysis was applied in order to relate the measured viscosity to the chromatographic analysis results (chromatographic analysis results can be found in Kalogianni (2007) and Kalogianni et al. (2009, 2010)). The measured viscosity was the response parameter and the concentrations of the newly formed products were used as predictors. For palm oil, among the detected compounds differing in molecular size from triacylglycerols only the polymers increased in concentration in the course of each experimental series (Kalogianni et al., 2009). As an outcome, the concentrations p_1, p_2 and p_3 (% w/w) of P_1, P_2 and P_3 polymer compound classes (Fig. 7a) were used as predictors in the linear regression analysis. The analysis of variance showed that the viscosity was linearly dependent on the presupposed predictors at a level of significance $\alpha = 0.05$ ($p = 0.000$) with a very high multiple regression coefficient ($R^2 = 1.00$). All variables (predictors) considered in the model were
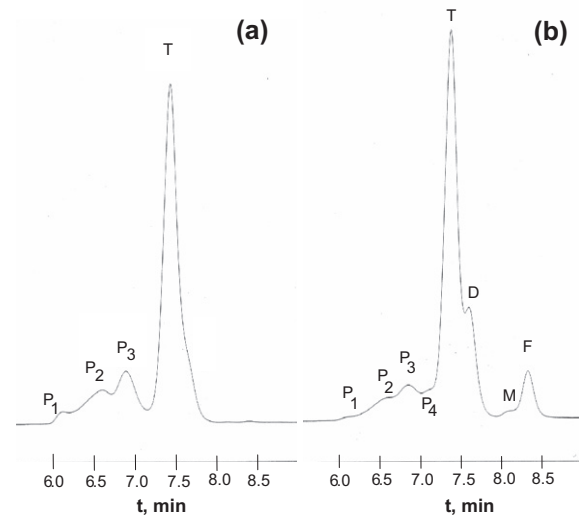

Fig. 7. Typical palm (a) and olive (b) oil chromatograms used for frying (from Kalogianni, 2007). Where P_1, P_2, P_3 and P_4 the four polymerization products peaks, T and D the triglyceride and diglyceride peak respectively, M the monoglyceride peak and F the free fatty acid peak. t denotes the retention time.

statistically significant at an $\alpha = 0.05$ ($p = 0.000$ for p_1 and p_2 while $p = 0.012$ for p_3). The resulting equation was:

$$\eta_p = 27.6 + 3.31p_1 + 1.42p_2 + 0.288p_3 \tag{1}$$

where η_p is the palm oil viscosity in Pa s $\times 10^{-3}$. As might be expected, the constant of the equation was very close to the measured viscosity of fresh fat (see Fig. 6a) whilst the coefficients differ according to the size of the polymer they refer to (the coefficient of p_1 is greater than those of p_2 and p_3). This is normal as higher molecular weight polymers are expected to contribute more to the increase in viscosity.

In the case of olive oil, more groups of products differing in molecular size from triacylglycerols are generated during repeated frying compared to palm oil including polymers and partial acylglycerols (Fig. 7b). The linear regression analysis showed that the only statistically significant predictors for describing viscosity at $\alpha = 0.05$ were the concentrations p_2 and p_3 (expressed here also in % w/w) of P_2 and P_3 polymer compound classes. In this case $p = 0.000$ for p_2 and $p = 0.039$ for p_3. This was verified by all the applied linear regression methods (see Section 2). The contribution of only p_2 and p_3 in the model is justified because these compound classes are the ones presenting the most significant concentration changes during frying and heating whereas in the same time they have a marked difference in molecular size compared to triacylglycerols (Kalogianni, 2007). Again the analysis of variance verified the linear dependence of viscosity on p_2 and p_3 ($p = 0.000$).The resulting regression equation for olive oil viscosity is:

$$\eta_o = 25.7 + 1.47p_2 + 0.235p_3 \tag{2}$$

where η_o is olive oil viscosity in Pa s $\times 10^{-3}$. In this case $R^2 = 0.99$. As with palm oil, the constant takes a value very close to the fresh olive oil viscosity (Fig. 6b) value whilst the coefficient of each variable (once again differing according to the size of molecule) is similar to that found for palm oil (Eq. (1)). The coefficients computed for Eqs. (1) and (2) in the two equations can be considered equal if one takes into account the standard error of each coefficient (results not shown). This is not surprising since the two polymer groups have the same retention times in the chromatograms for both oil types (Kalogianni, 2007).

As an outcome one could propose an approximate unified equation for both oil types. This equation takes the form:

$$\eta = \eta_u + 3.31p_1 + 1.47p_2 + 0.235p_3 \qquad (3)$$

where η is the fried olive or palm oil viscosity and η_u is the unused (or fresh) palm or olive oil viscosity both in Pa s $\times 10^{-3}$ and p_1, p_2 and p_3 the concentrations (in % w/w) of P_1, P_2 and P_3 compound classes. In this case $R^2 = 0.99$ and $p < 0.05$ for all p_1–p_3.

3.3. Considerations on the measurement of interfacial properties related to the frying process

There are a few measurements in the literature regarding the surface and interfacial properties of edible oils and fats including very limited measurements on oils and fats used for frying (Fisher et al., 1985; Gaonkar, 1989; Gil and Handel, 1995; da Silva and Singh, 1995; Paul and Mittal, 1996; Rossi et al., 2009). Different interfacial properties have been measured applying several methods. However, the selection of property and measurement method is very important. Here, we would like to focus on properties relevant to the process of frying. Therefore, before presenting and discussing our results we consider important to stress a few points on the selection of appropriate properties and methods. When interfacial properties are used as means of characterizing and understanding a certain process, a critical question is whether dynamic or equilibrium properties should be measured; the answer depends on the application of interest and whether surface-active substances are present in the system. When the interest lies in industrial processing and unit operations (e.g. frying) where surfactants are present, then the measurement of dynamic properties is often more appropriate. This is because (a) in most industrial applications the characteristic timescale (e.g. the rate of formation of a steam bubble during frying) is much shorter than the time required for the interface to reach equilibrium and (b) the presence of surface-active substances causes a strong time-dependence of interfacial tension. As a result, the properties affecting the related phenomena are not the equilibrium but the dynamic ones corresponding to the rate of interfacial deformation and to the adsorption time of surfactants to the interface.

In order to select the appropriate method, the type of deformation is also important; some processes are characterized by surface dilation (e.g. radial growth of a gas bubble during boiling or liquid degassing) and others by shear deformations (e.g. liquid drainage in foams, phases separation in emulsions).

In the case of frying, we will examine the case of a hydrophilic food item (e.g. a potato piece). In this case two sub-processes may be affected by interfacial phenomena: wetting of the hydrophilic raw food surface with hot hydrophobic oil, and bubble release from the food piece. It must be noted that oil uptake takes place mainly after frying (Ufheil and Escher, 1996; Moreira et al., 1997) and this involves the study of the characteristics of the porous crust and the crust/oil wetting properties (interfacial tension, contact angle etc.) (Kalogianni et al., 2004). In this work, however, we are interested in phenomena occurring during frying when the food piece is totally immersed in the hot oil so post-frying wetting effects are irrelevant.

Regarding bubble release from the food surface during frying, we have macroscopically observed that it happens at a rate of the order of 10 Hz at the beginning of frying but slows down to less than 1 Hz at the end of frying. This of course depends on the oil temperature and on the food type. Although bubbles may be released during frying of a food piece at rates in the order of a few Hz, their surface expansion rate is larger involving surface lifetimes well below 100 ms (Kalogianni et al., 2006). Therefore, for the timescales of interest to frying and taking into account that bubble formation is a dilatational process, an appropriate technique for studying dynamic oil/air interfacial tension is the maximum bubble pressure technique. The surface ages that can be attained by the technique range from 1 ms to 100 s (Fainerman et al., 1994).

Considering now the wetting of the hydrophilic food surface with hot oil during frying it is necessary to measure the oil/food contact angle and its variation with time (dynamic contact angle). This is a very difficult task not only because the food surface is relatively rough for this type of measurements but also and more important, because the food surface looses moisture during the course of the measurement and this affects it's wetting behavior.

In order to understand the behavior of an oil or fat against a hydrophilic medium one could, as a first approach, measure the oil/water interfacial tension. This was also the approach used by Gil and Handel (1995) who measured equilibrium interfacial tension. The timescale of interest for such a measurement is from ∼1 s up to ∼10–20 s, this being the time that a potato takes to heat-up and form the first bubbles and depends on the oil temperature (Kalogianni, 2007). During this period (the first 1 to 10–20 s of frying) it is valid to assume that there is no dilation or important shear and therefore a static method is adequate as long as it covers the appropriate timescale. Such a method is the pendant drop technique. The technique is adequate for liquid/liquid systems and it can cover surface lifetimes between few seconds and few hours or more (Joos, 1999). Details on the method can be found in Chen et al. (1998) and Loglio et al. (2001).

To sum up, the measurement of dynamic interfacial tension using the maximum bubble pressure method and the pendant drop method were considered adequate to provide an insight on interfacial phenomena relevant to the food frying operation.

3.4. Changes in dynamic interfacial tension at the oil/air interface

Fig. 8 presents the results of dynamic interfacial tension of palm oil and olive oil against air. In the plots, effective adsorption times up to 3 s are displayed because, for higher effective adsorption times, no significant changes of interfacial tension as a function of time were observed (a drop less than 0.1 mN/m). First of all, one can observe a slight decrease of interfacial tension as a
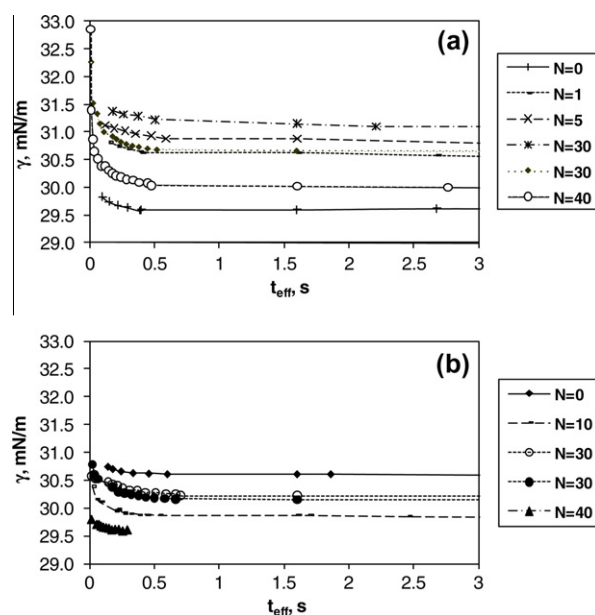
Fig. 8. Interfacial tension (γ) between palm oil and air (a) and between olive oil and air (b) (at 50 °C) as a function of effective adsorption time (t_{eff}) and frying batch number (N). $N = 0$ denotes measurements in the fresh fat. Frying was conducted at high potato-to-oil ratio ($r = 1/7$ $kg_{potatoes}/L_{fat}$).

function of effective adsorption time. However, this decrease is due to hydrodynamic effects on the value of interfacial tension determined from pressure measurements by the technique rather than an effect of surfactants adsorption at the interface. Hydrodynamic effects may increase the measured value of interfacial tension up to several mN/m at short adsorption lifetimes and are larger with increasing viscosity (Fainerman et al., 2004). The results of interfacial tension corresponding to different frying batches and for the values after the stabilization of γ as a function of t_{eff} (changes in γ less than 0.1 mN/m) were compared using the GLM of ANOVA. The analysis showed that there are statistically significant differences between samples ($\alpha = 0.05$). However, differences wherever detected (Tuckey's test, CI = 95%), were very small (<1 mN/m and in most cases <0.5 mN/m) and no persistent trend was observed. Paul and Mittal (1996) and da Silva and Singh (1995) measured the equilibrium oil/air interfacial tension for a canola based shortening and corn oil respectively and did not find any significant effect of frying on equilibrium values as well.

3.5. Changes in dynamic interfacial tension at the oil/water interface

As mentioned previously the timescale of interest for this type of measurements spans from ~1 s (time for potato to be fully immersed in the oil) up to ~10–20 s (time for boiling onset at the potato surface). With the drop profile analysis apparatus employed for our measurements it was possible to measure in a time range from 2–3 s up to a few hours. Although measurements at periods longer than 10–20 s are not directly related to frying they still give information on the interfacial activity of the studied systems. Such information is valuable as it appears for the first time in the literature. Furthermore, in order to assess whether it is necessary to conduct dynamic interfacial tension measurements or equilibrium measurements suffice to characterize frying it is important to know if there are differences between values obtained at long and short adsorption times. So, when this was technically feasible, it was attempted to let the interface reach equilibrium. The equilibrium (or quasi equilibrium) oil/water interfacial tension values can serve as reference values for the studied systems, and allow comparisons with literature where only equilibrium measurements have been reported for fried oils and fats.

Fig. 9 presents the palm (a) and olive (b) oil/water interfacial tension (at 50 °C) as a function of time (interface lifetime) for unused oils ($N = 0$) and oils fried for 20 and 40 batches at high potato-to-oil ratio ($r_{po} = 1/7$ kg$_{potatoes}$/L$_{oil}$). Focusing first on palm oil (Fig. 9a) at "0" time (which corresponds to about 2 s of actual interface lifetime) unused palm oil exhibits the highest measured interfacial tension. This is followed by palm oil fried for 20 and 40 times. As the lifetime of the interface increases, the interfacial tension decreases, for the unused as well as for the fat used for frying. This is indicative of the presence of surface-active substances in fresh as well as fried palm oil. The interfacial tension of the unused fat is higher and reaches an equilibrium value of 15.2 ± 0.1 whereas this of the fried fat 13.6 ± 0.1 mN/m after 20 frying batches and 13.4 ± 0.2 mN/m after 40 frying batches. ANOVA (GLM) on quasi-equilibrium values showed that repeated frying affects significantly ($\alpha = 0.05$) the interfacial tension of palm oil at the oil/water interface. Comparisons (Tuckey's test, CI = 95%) between results from different samples showed that differences were statistically significant only between fresh and fried samples and not between samples fried for $N = 20$ and $N = 40$. However, the differences in dynamic interfacial tension (Fig. 9a) are more pronounced at short times which are more significant for the frying process than long times reaching equilibrium.

In a previous study (Kalogianni et al., 2009) we determined the chemical profile changes in palm oil using size exclusion chromatography as a function of frying batch number for the same experi-
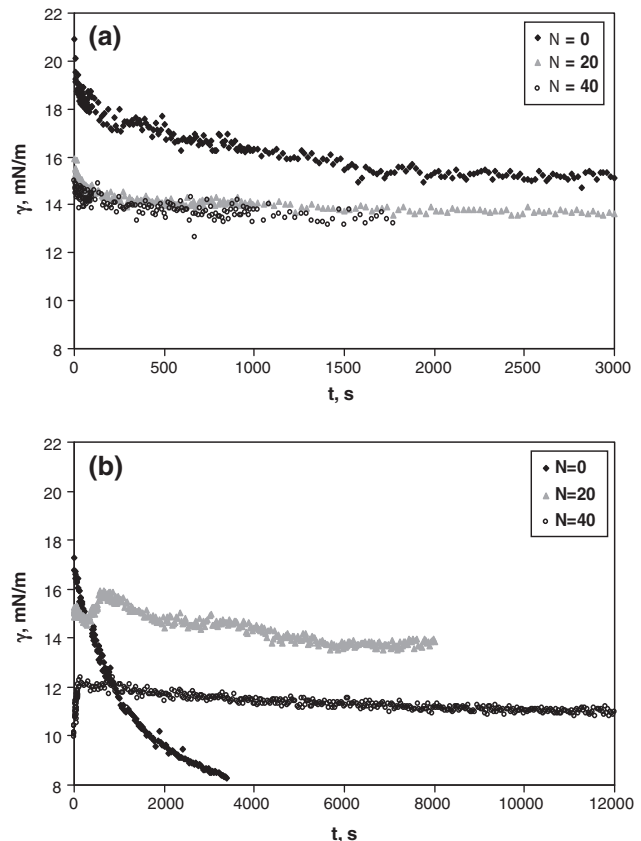

Fig. 9. Palm oil (a) and olive oil (b) interfacial tension (γ) against water as a function of time (t) and frying batch number (N). $N = 0$ denotes measurements in the fresh frying medium. Frying was conducted at high potato-to-oil ratio ($r = 1/7$ kg$_{potatoes}$/L$_{oil}$).

iments. According to those measurements, the only detected known surface-active compounds were diacylglycerols. Diacylglycerol addition in oils/fats in smaller quantities (up to 1% w/w, Gil and Handel, 1995 and at 0.075% w/w, Gaonkar, 1989) did not affect the equilibrium (Gil and Handel, 1995) or dynamic (Gaonkar, 1989) value of the interfacial tension of the oil or fat against pure water. On the other hand, Reis et al. (2008) found significant effects of diacylglycerols addition at higher concentrations on the interfacial tension at a phosphate buffer/decane interface. Therefore, the high concentration of diacylglycerols present in all examined palm oil samples (around 7% w/w) could be responsible for the observed decrease in the water/oil interfacial tension. On the other hand, the fact that the interfacial tension at "0" time decreases as a function of frying batch number indicates the increase of surfactant concentration in the system. This combined with the fact that equilibrium surface tension seems practically unaffected between 20 and 40 frying batches indicates that the CMC (Critical Micelle Concentration) value of the surfactant(s) is reached or even surpassed at 20 frying batches. According to the above, the oil/water interfacial tension measurements cannot be explained by only the presence of diacylglycerols in the system. Among the compounds, which, according to literature, could have caused such an effect, are monoacylglycerols and ACM (alkaline contaminant materials). However, monoacylglycerols are surface active at concentrations detectable by our chromatographic analysis (Gil and Handel, 1995); so the effect of monoacylglycerols must be excluded. On the other hand, it was found that ACM exhibit a marked surface activity at concentrations around 100 ppm (Gil and Handel, 1995) which are beyond the detection capacity of our analysis (Kalogianni et al., 2009). Therefore, a possible effect of ACM could

not be excluded. During frying in palm oil it is not possible for ACM to be produced since hydrolysis was absent (Kalogianni et al., 2009). However, they could have been generated in palm oil prior its use for frying and remain in the fat after the refining process. Other compounds, not examined previously, might have affected the dynamic interfacial tension of palm oil against water. These compounds are oxidized triacylglycerols (which are more polar than those originally present in the oil) and polar as well as non-polar polymerization products. The effect of these polar compounds is expected to be inferior compared to this of compounds such as diacylglycerols. In the case of polymerization products (dimers and oligopolymers of triacylglycerols, for details see Kalogianni et al., 2009) the effect is expected to be mainly indirect via their effect on bulk viscosity and, consequently on the diffusion of surface-active substances. However, in order to elucidate the above issues further research is needed.

Regarding olive oil (Fig. 9b) measurements for the fresh oil/water system present a continuous and rapid decrease with time for a period of ~1 h. For longer periods of time and so for lower interfacial tension it was not possible to keep the drop stable at a constant surface area and therefore it was impossible to conduct measurements. Thus, the value of equilibrium interfacial tension is not known. Nevertheless, the equilibrium interfacial tension is expected (according to the evolution of the interfacial tension curve with time) to be considerably different from that concerning the time period of interest for frying. This underlines the need of dynamic measurements for studying interfacial phenomena in frying. Comparing the value of interfacial tension of olive and palm oil at "0" time, olive oil has a slightly lower value attributable not only to the different triglyceride composition but also to the presence of more surface-active compounds than in palm oil. Interestingly, the rate of decrease in interfacial tension for the first 100 s, is almost the same for both systems (fresh palm oil/water and fresh olive oil/water). This may indicate similar diffusion coefficients of surface-active compounds in both oil types if a diffusion controlled adsorption is considered.

The curves obtained for fried olive oil are completely different from those of fried palm oil (compare $N = 20$ and $N = 40$ between Fig. 9a and b). This difference may not be only due to the different chemical profiles of the oils but also to the different set-up of the measurement (a water drop is formed into the oil phase rather than the inverse). Olive oil fried for 20 times presents initially a small drop of interfacial tension, subsequently a small increase and finally a drop of interfacial tension approaching equilibrium values at about 8000 s (the measurement was repeated in quadruplicate in order to verify the repeatability of this behavior). The overall changes of interfacial tension span within a very small range (2 mN/m). When olive oil fried for 40 times is measured against water the initial first drop of interfacial tension is absent (at least for a time period from 2 to 3 s and on). The interfacial tension increases sharply and then drops in a very slow rate (equilibrium has not been reached even after 4 h). The quasi-equilibrium values of interfacial tension of olive oil for $N = 20$ and $N = 40$ were compared using the GLM of ANOVA, the results showed statistical significant differences at $\alpha = 0.05$.

Ferrari et al. (1997) studying the adsorption kinetics of an alkyl-phosphine oxide and performing pendant drop measurements reports a similar pattern when a pendant drop of pure hexane was formed in the water phase where the oxide was dissolved "the measured interfacial tensions exhibit a steep initial decrease, pass through a minimum and then level off at a value which depends on the initial surfactant concentration". In their case the oxide although initially dissolved in water it was also soluble in hexane. The time-dependence of interfacial tension was explained by an adsorption and subsequent transfer of the surfactant into the second bulk phase. Interestingly, when the measurement was conducted by placing the water droplet containing the oxide in a bulk of pure hexane the time-dependence of interfacial tension was also similar to that measured for fresh olive oil. Hansen and Fagerheim (1998) also observed a similar time-dependence of interfacial tension with ours when certain nonylpolyphenol-poly(oxyethylene) surfactants were dissolved into water and came in contact with a pure chlorobenzene phase where transfer of the surfactant between the phases occurred. We believe that there is an analogy between these measurements and ours.

What is also interesting to note is that when a fried olive oil drop was formed into pure water phase a thin white cloud surrounded the oil drop. By stirring the water, this moved and dispersed into the water bulk. It seems as if, together with the transfer of some water soluble substances, some water insoluble substances were transferred as well, and that this resulted in forming microscopic droplets. The same effect was also described by Hansen and Fagerheim (1998) in the chlorobenzene/water nonylpolyphenol-poly(oxyethylene) system. These authors linked the peculiar time-dependence of interfacial tension with the same phenomenon (called "clouding") and explained as probable solvation of chlorobenzene in the nonylpolyphenol-poly(oxyethylene) micelles.

Chromatographic analysis of the fried olive oil samples (Kalogianni et al., 2010), showed that fried olive oil is a very complex system containing a high percentage of polar compounds as well as different types of surface-active compounds (di-, mono-acylglycerols, free fatty acids) generated by hydrolysis during frying. Some of these hydrolysis products participate in the polymerization process (Dobarganes et al., 2000) but the effect of these products on interfacial tension has not been studied yet. Until this moment it is known that free fatty acids initially present in the oil phase are also soluble in water, and, thus mass transfer from the oil to the water phase is expected to occur (Joos, 1999). The olive oil/water system is far more complex than this of palm oil. Therefore, the time-dependence of interfacial tension is the result of adsorption of different surfactants and adsorption and transfer of the free fatty acids and possibly other water soluble surface active molecules. Overall, it can be said that frying affected significantly the wetting properties of palm and olive oil. Olive oil due to its higher content of surface-active compounds (fresh as well as fried) presented lower interfacial tension which would suggest better wetting on hydrophilic surfaces compared to palm oil.

4. Conclusions

Repeated frying and heating led to a significant increase in the viscosity of both oil types under all examined conditions. The two oil types behaved differently: the increase in the viscosity of palm oil was greater than this of olive oil. Moreover, the gradual change of viscosity throughout a frying series was influenced by the presence of potatoes in the fryer and the particular potato-to-oil ratio. The significant changes in palm oil viscosity when frying at high potato-to-oil ratio would suggest possible effects on heat and mass transfer during frying. In contrast to what was observed about palm oil, olive oil viscosity remained practically uninfluenced by the presence of potatoes even at a high frying load. Linear regression analysis for both oil types showed that oil viscosity during frying and heating is a function of fresh oil viscosity and the concentration of different polymer compound classes generated during the frying and heating process. It might be possible that this equation is valid also for other oil types provided that the same compound classes are generated during frying and heating.

The changes observed in the density of both oil types due to repeated frying, although statistically significant, were not very intense despite the high level of polymerization in some samples.

Such changes would not suggest any effect on the heat and mass transfer during frying.

Dynamic interfacial tension measurements have revealed an effect of repeated frying on the dynamic interfacial tension of both palm and olive oil. It is interesting that the time-dependence of interfacial tension is different in the two oil types when they are fried. Such a difference was related to the different degradation compounds formed in each oil type during frying. Furthermore, the peculiar change of interfacial tension as a function of interface lifetime in the fried olive oil samples was attributed to possible transfer to the water phase of substances initially dissolved in the oil phase. Overall, the values of dynamic interfacial tension at the oil/water interface were different than those measured at equilibrium or quasi equilibrium, underlining the need of dynamic interfacial tension measurements when phenomena occurring during the frying process are addressed.

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