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Some physical changes in Bajo Aragón extra virgin olive oil during the frying process

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Abstract

Changes of viscosity, transmittance spectra and colour of Bajo Aragón extra virgin olive oil, during the frying process, were studied, comparing them to the changes that occur during the frying process of high oleic sunflower oil. The studied oil was obtained from Empeltre variety olives. These changes, due to the deterioration of the oil during this process, were monitored by polar compounds measurement. Polar compounds content increased linearly with the frying cycle in both types of oil; however, the increase was faster in high oleic sunflower oil. The olive oil's transmittance spectra, after the frying process, proved that, not only do the peaks corresponding to the carotenoids and the chlorophyll disappear but also that transformation of the chlorophyll occured. In high oleic sunflower oil spectra there were no changes. L^* and b^* colour parameters, measured on the CIELAB colour scale, showed the following behaviour: L^* values increased for olive oil after frying while the opposite happened for high oleic sunflower oil. In the case of the b^* parameter, the result was the same in both cases: when fried, more green and yellow colours appeared. The viscosity of both oils showed a non-linear increase with number of frying operations, which may correspond to a polynomial relationship. Despite their similar contents of oleic acid, olive oil was more stable to oxidation and there were some physical differences between the two types of oil.

Keywords: Bajo Aragón; Empeltre; Olive oil; Frying; Potatoes

1. Introduction

The deep fat frying method, that is, the process in which food is cooked by immersion in hot oil, is considered to be the oldest and most common unit operation used in food preparation, especially in the mediterranean area. The aim of deep fat frying is to seal the food by immersing it in hot oil so that all the flavours and juices are retained within the crispy crust. The quality of the products cooked using this method depends not only on the frying conditions, such as temperature of the heated oil, frying time, food weight and frying oil volume, but also on the types of oil and the kind of food used (Varela, 1994). The chemical composition of the frying oil and its physical and physicochemical properties also have an influence on the frying process. Usually many oils can be used for frying, e.g. palm oil, corn oil, cotton oil, soya oil and sunflower oil (Valenzuela, Sanhueza, Nieto, Petersen, & Tavella, 2003). Cottonseed, corn, peanut, and olive oils are used as a stable source of polyunsaturated fatty acids because of their low linolenic acid content (Boskou & Elmadfa, 1999). Since the most appropriate frying oil should be low in free fatty acids and polar compounds, extra virgin olive oil is a very interesting option when looking for a frying oil (Yaghmur, Aserrín, Mizrahi, Nerd, & Garti, 2001). There is a very notable production of olive oil in Spain and there are many different quality labels associated with the different olive varieties. In the region of Aragón, the quality label is "Bajo Aragón olive oil" and its source is the olives from the Empeltre variety.

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No studies have been reported about this extra virgin olive oil or its behaviour during the frying process.

During the frying process, there are many physicochemical changes in food as well as in oil (Valdés & García, 2006). The quality of frying oils worsens if it is used constantly. This is mainly due to three different factors: the moisture of food which may cause hydrolysis with free fatty acid formation; the atmospheric oxygen that enters the oil from the surface of the container (this factor increases the oxidative alteration) and the high temperature at which the operation takes place (a factor that results in thermal alteration). As a result of the deterioration, the oil sustains some physical changes: the colour darkens, the viscosity increases, and smoke appears (Paul & Mittal, 1997). Viscosity changes could be recorded by qualitative methods – *Viscofrit* – as well as by using viscometers and rheometers (Santos, Santos, & Souza, 2005). Colour changes could be tracked by spectrometric and colorimetric measurements.

The aim of this work is to determine how some physical parameters of extra virgin olive oil undergo changes during the frying process in comparison to high oleic sunflower oil. The variety of olive oil used for these experiments will be Empeltre. The frying process of this variety has not been studied. Research will mainly focus on the viscosity and colour.

2. Materials and methods

2.1. Materials

The following material was purchased at a local store: extra virgin Empeltre olive oil, high oleic sunflower oil and freezed potatoes.

2.2. Methods

2.2.1. GC analysis of the oils

Total fatty acids were transmethylated according to Frega and Bocci (2001). About two drops of olive oil were dissolved in six drops of a solution of 2 N KOH in methanol and then 2 ml of *n*-hexane were added. The mixture was vigorously shaken with a vortex for 2 min, sodium sulfate was added and the mixture was shaken again. The sample (0.4 µl) was injected 10 min later into a gas chromatograph (Hewlett–Packard 5890 CG) equipped with a split–splitless injector and a flame ionization detector. A DB-225, 30 × 0.25 mm ID and 0.15 µm column (J&W Scientific, Agilent) was used. The injector and detector temperatures were set at 250 °C. The oven temperature was kept at 190 °C for 1 min, then programmed from 190 °C to 210 °C at 4 °C/min, kept at 210 °C for 5 min, then heated from 210 °C to 215 °C at 3 °C/min and finally kept 18 min at the last temperature. Nitrogen was used as carrier gas at a flow rate of 1.0 ml/min.

The peak identification was carried out by comparing the peak retention time with those of the standard mixture. An internal standard was used for the quantification of fatty acids. The GC response factor of each fatty acid was calculated by using the internal standard. The results were expressed as *g* fatty acid/100 g total fatty acids (%).

2.2.2. Performance of the frying process

Frying was performed on a domestic fryer (DeLonghi Easy Clean) at 170 °C with the food/oil ratio being 200 g/4l over about 3 min. The frying temperature was controlled using a probe joined to the thermometer.

2.2.3. Polar compound measurements

Measurement of polar compounds (in percentage) was done with a rapid method, that is, using a Testo 265 based on dielectric constant measurement. This instrument allows measurement from 40 °C to 210 °C and there is an interpretation that corresponds to every temperature. A number of frying cycles was done until the sensitivity limit of the instrument (23–24% polar compounds) was reached.

2.2.4. Viscosity measurements

A Bohlin CS–ETO stress controlled rheometer was used to measure the different oil viscosities. By this procedure, a concentric cylinder system is submerged in the oil and the force necessary to overcome the resistance of the viscosity to the rotation is measured. The viscosity value, in mPas, is automatically calculated on the basis of the speed and the geometry of the probe. Temperature (20 °C) was controlled with a water bath connected to the rheometer. The experiment was carried out by putting 3 ml of sample in a concentric cylinder system using 100 s^{-1} as shear rate.

2.2.5. Spectroscopic analysis and instrumental colour

The spectral and instrumental measurements of colour were done in olive oil and high oleic sunflower oil samples after filtration. For transmission spectra, a spectrophotometer, Avantes Ava Spec 1024, was used with a wavelength range from 380 to 780 nm at intervals of 2 nm and in 1 cm width glass cuvettes, using hexane as a reference.

The CIELAB colour space (CIE, 1986) was studied after the spectra. Illuminant D65 was chosen as well as Observer CIE64. The following colour coordinates were determined: lightness (L^*), redness (a^*, red-green) and yellowness (b^*, yellow-blue). In addition, hue angle, which describes the hue or colour (h^*), was calculated ($h^* = \tan^{-1}(b^*/a^*)$) as was the saturation index or chroma (C^*) ($C^* = (a^{*2} + b^{*2})^{0.5}$) that describes the brightness or vividness of a colour.

3. Results and discussion

The Empeltre olive oil had a 69.8% oleic acid content and a 10.2% linoleic acid content in comparison to 57% for the oleic acid (usually 20–25% in normal sunflower oil) and 43% for the linoleic acid in high oleic sunflower oil (Table 1).

The aim was to establish a link between the fatty acid content and the oxidation stability during the frying pro-

Table 1
Principal fatty acid composition of the Empeltre olive oil and high oleic sunflower oil

Oil	Palmitic acid (%)	Stearic acid (%)	Oleic acid (%)	Linoleic acid (%)
Empeltre olive oil	16 ± 0.63	3.8 ± 0.3	69.8 ± 1.3	10.2 ± 0.6
High oleic sunflower oil	–	–	57 ± 0.9	43 ± 0.7

cess. In this sense, the rate of oxidation is proportional to the degree of insaturation (Paul & Mittal, 1997). Linoleic acid has two double bonds and for that reason, high oleic sunflower oil must be more susceptible to oxidation in the absence of antioxidants.

The polar compounds are a product of the oxidation and they are determined by a rapid method (Testo) in order to follow the life of the frying oil. Recently a good correlation of this method with the official one (by silica column chromatography) was established (Dobarganes, 2007). Fig. 1 shows the polar compounds content, depending on the frying number. In both oils there is a lineal behaviour with a very good correlation, although the degradation of high oleic sunflower oil occurs sooner, as expected, because of the fatty acid composition. Once the maximal sensitivity of the instrument was reached the experiments were stopped, that is, after the 60th frying process. Moreover, the limit established by the Spanish legislation for heated fats is 25% of polar compounds (Boletín Oficial del Estado, 1989).

There is a deterioration of the colour of oil during frying. According to Totani et al. (2006) one cause of this is the amino- carbonyl reaction between thermally oxidized oil and amino acids exuded by fried foods. Fig. 2 shows spectra of the frying oil at different numbers of frying operations. The shapes of the spectra in olive oil are very similar to those reported for other varieties of olive oil, Picual, Manzanilla, Lechín and Arbequina, submitted to an accelerated oxidation test (Ceballos, Moyano, Vicario, Alba, & Heredia, 2003). The first peak, at 450 nm, corresponds to a mixture of the chlorophylls and the carotenoids. The second peak, at 483 nm represents the carotenoids responsible for the yellow colour of the oil. After frying, both peaks disappear as a result of the oxidation. Ndjouenkeu and Ngassoum (2002) proved that heating during frying leads to bleaching of palm oils, caused by the destruction of carotenoids responsible for their colour.

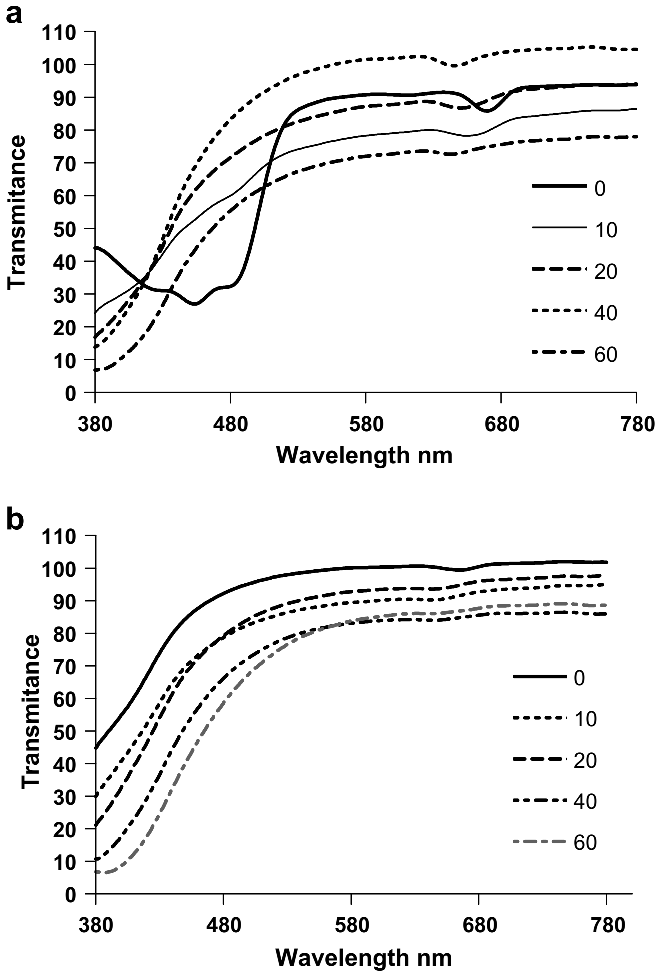

Fig. 2. Transmission spectra of olive oil (a) and high oleic sunflower oil (b) after the different frying cycles.

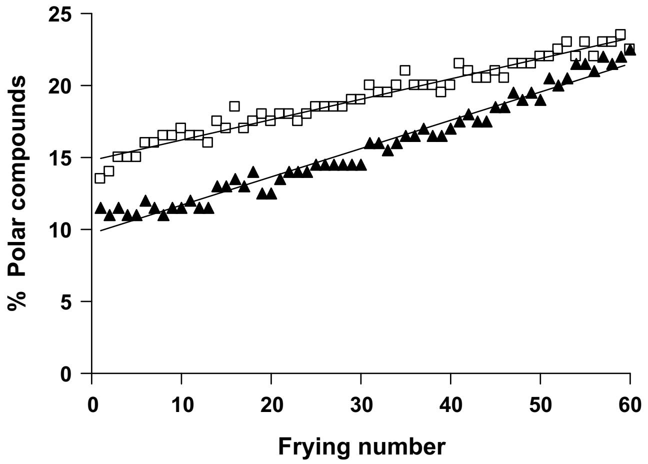

Fig. 1. Percentage of polar compounds depending on the frying number for olive oil (▲) and high oleic sunflower oil (□).

Another peak is seen at 666 nm, due to the chlorophyll. When the number of frying operations increases, the wavelength of this peak clearly changes. Such changes indicate the degradation of the pigment by loss of the magnesium of the molecule. The result of this degradation is a molecule of pheophytin (Guillén Sans, Yépez Pérez, Heredia Mira, & Guzmán Chozas, 1991). This last pigment provides a brown colour and it corresponds to the darker colour of the olive oil after frying. No maximal absorption appears for refined high oleic sunflower oil, but only a slight inflexion above 665 nm and a shoulder at 415 nm, probably because the industrial extraction process destroys the pigments. The spectrum of this oil does not change too much after oxidation. Figs. 3 and 4 show the L^* and b^* values of the oils after frying. Lightness in olive oil showed slight increases with frying already proved by other authors (Guillén Sans et al., 1991). Sunflower oil lightness decreased with the frying cycle. In both oils, b^* values are positive, showing more yellow colour.

On the other hand, during deep- fat frying processing operations, the viscosity of the oil changes considerably with frying time and oil temperature (Bensmira, Jiang, Nsabimana, & Jian, 2007; Tsaknis & Lalas, 2002).

The results for viscosity of both frying oils are showed in Fig. 5. A two-phase graph can be found. Viscosity increases faster in the first step than in the second step. Probably, this is due to dimer formation. This graph can be fitted by a polynomial type. The increase of oil viscosity was attributed to polymerisation and formation of high molecular weight compounds (Stevenson, Vaisey-Genser, & Eskin, 1984). Similar results are described by Besbes et al. (2005) in oil from Deglet Nour and Allig seeds after thermo-oxidation.

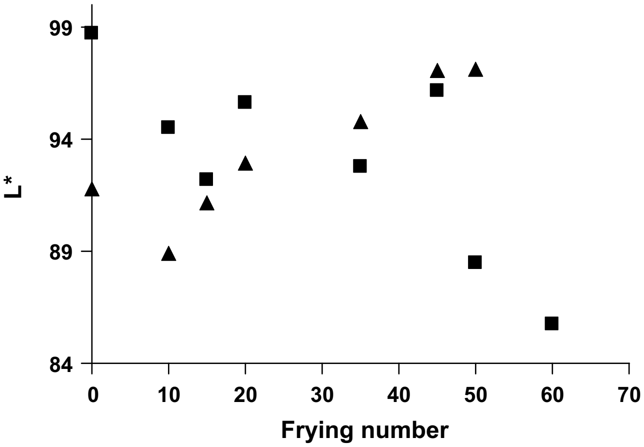

Fig. 3. L^* value depending on the frying cycle for olive oil (▲) and high oleic sunflower oil (■).

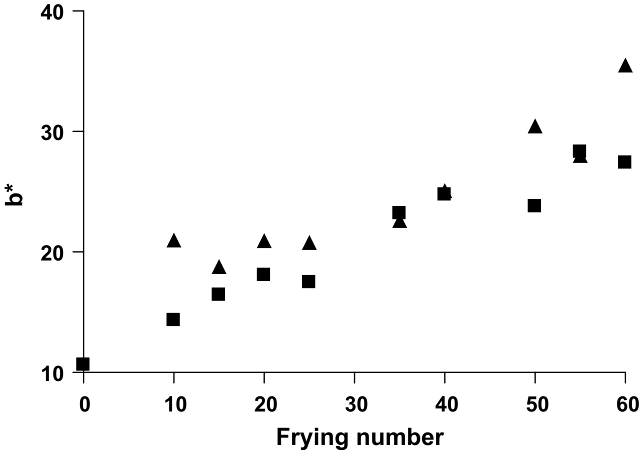

Fig. 4. b^* value depending on the frying cycle for olive oil (▲) and high oleic sunflower oil (■).

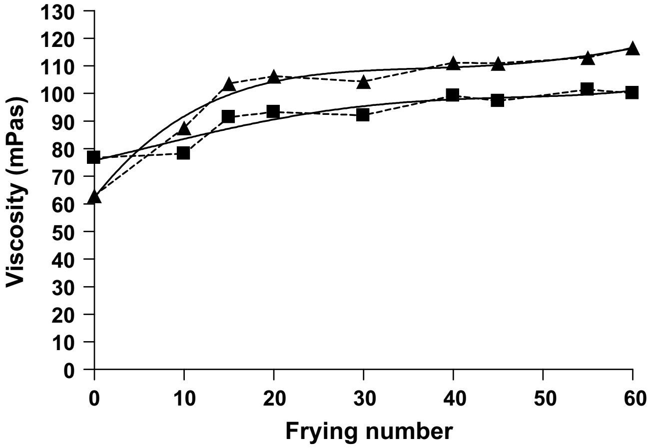

Fig. 5. Viscosity depending on the frying cycle for olive oil (▲) and high oleic sunflower oil (■).

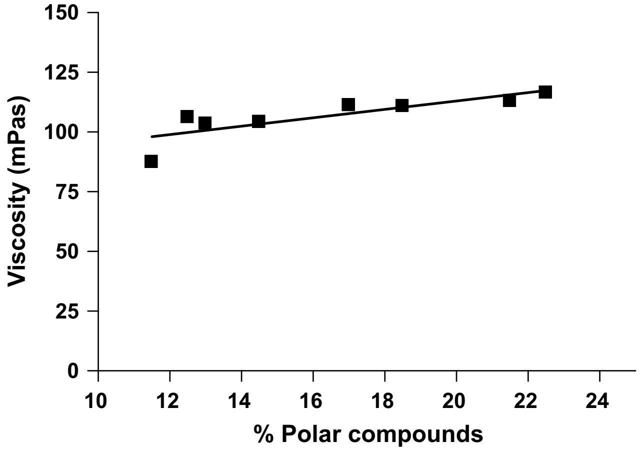

Fig. 6. Viscosity depending on the polar compounds for olive oil.

In addition, viscosity values were highly correlated to polar compounds (Fig. 6). For this reason, viscosity measurements are a good index of oil degradation (Benedito, Mulet, Velasco, & Dobarganes, 2002).

In previous works, with different oils, such as *Moringa stenopetala* seed oil (Lalas, Gortzi, & Tsaknis, 2006), soybean oil (Farag & El-Anany, 2006; Jorge et al., 2006), palm, cottonseed and sunflower oils (Farag & El-Anany, 2006) vegetable oil blends (Fawzy-Ramadan et al., 2006) and unconventional oils (Mariod et al., 2006), the influence on the polar compounds, the colour and the viscosity that result from the frying process were studied. However, such influence has not been studied in the Empeltre olive oil. Our results (polar compounds) show a higher stability for Empeltre olive oil than for high oleic sunflower oil, as other authors have already reported (Chatzilazarou et al., 2006).

4. Conclusions

Bajo Aragón olive oil is very interesting during the frying process due to its fatty acid composition (it is a product rich in oleic acid) and oxidation stability, despite physical changes it undergoes during this operation.

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