

# A study of the evolution of the physicochemical and structural characteristics of olive and sunflower oils after heating at frying temperatures

Adolfo F. Valdés, Ana B. Garcia \*

*Instituto Nacional del Carbón (CSIC), Francisco Pintado Fé 26, 33011-Oviedo, Spain*

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## Abstract

The evolution of the density, viscosity, oil/water interfacial tension and structure of vegetable oils after heating at frying temperatures was studied to explore the possibility of reusing waste vegetable oils as solid agglomerants for different purposes. Commercial olive and sunflower oils were heated at 150 and 225 °C in the time interval of 1–15 days to achieve a wide range of alteration degrees. Structural changes in the oils were monitored by FT-IR and <sup>1</sup>H NMR. Significant variations occur in the physicochemical and structural characteristics of these oils, which may affect their agglomeration capability, when they were heated at frying temperatures for periods above two days. Under these conditions, the viscosity of the oils increased very quickly, whereas their unsaturation degree decreased noticeably. Decreases in the relative intensities of the NMR spectra signals of the unsaturation-related protons were observed, those corresponding to the diallyl protons occurring much faster. Of the two vegetable oils studied, sunflower oil was found to be more sensitive to thermal treatment, undergoing greater changes in its properties, especially in viscosity, which may show a marked increase.

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## 1. Introduction

Vegetable oils with negligible sulfur, nitrogen and metal contents are renewable, available and non-polluting energy resources. Because of these important characteristics, they are suitable candidates for purposes other than food. For example, alternative uses, such as biodiesel production, are being investigated (Ahn, Koncar, Mittelbach, & Marr, 1995; Ergeneman, Ozaktas, Karasmanoglu, & Arslan, 1997; Karaosmanoglu & Kurt, 1998; Özaktas, Cigizoglu, & Karaosmanoglu, 1997; Poitrat, 1999; Staat & Vallet, 1994). However, at present, vegetable oils are mainly employed in nutrition. In Spain, large

quantities are used for frying food, which in turn leads to the production of waste oils that must be biologically degraded before disposal. Consequently, the reuse of these waste oils would be profitable from both environmental and economic points of view. In this context, the production of hydrocarbon fuels from waste vegetable oils by means of catalytic pyrolysis has already been reported (Dandik & Aksoy, 1998; Dandik, Aksoy, & Erdem-Senatalar, 1998). Recently, they have been successfully employed as flotation collectors of coals and coal wastes (Alonso, Castaño, & Garcia, 2000).

Sunflower, soyabean and colza oils have been previously used in our research group as agglomerants to clean coal fines (Garcia, Martínez-Tarazona, & Vega, 1996; Garcia, Martínez-Tarazona, Vega, & Wheelock, 1998) and to recover coal from coal fines wastes

\* Corresponding author. Tel.: +34 985 118954; fax: +34 985 297662.  
E-mail address: [anabgs@incar.csic.es](mailto:anabgs@incar.csic.es) (A.B. Garcia).

(Alonso, Valdés, Martínez-Tarazona, & Garcia, 1999; Alonso, Valdés, Martínez-Tarazona, & Garcia, 2002). Oil agglomeration belongs to a group of agglomeration processes in which those fine particles of greater oleophilicity are separated from an agitated aqueous suspension because they are preferentially wetted (agglomerated) by the oil. Because of the relatively large amount of oil used in this process, the commercial implementation of the agglomeration, as a method to recover coal from products, such as coal wastes, will depend on finding a suitable low-cost oil. Based on the above mentioned experiments, in which original vegetable oils were employed as agglomerants, the use of waste vegetable oils for this purpose appears as an alternative that should be taken into account. Prior to exploring this possibility, it was considered that a study of the evolution, after heating, of certain oil characteristics, such as density, viscosity, oil–water interfacial tension and structure, which are known to determine the oil agglomeration capability (Capes & Germain, 1982), should be carried out. In the work described below, commercial olive and sunflower oils were heated at two different frying temperatures in the time interval of 1–15 days to achieve a wide range of alteration degrees. Structural changes in the oils were monitored by FTIR and  $^1\text{H}$  NMR. To complete this work, two vegetable oils of household origin, which had been employed for frying different types of food, were selected and characterized. Although the characteristics of a particular waste vegetable oil may differ considerably, depending on previous uses, it was found interesting to compare them to those of the vegetable oils heated under controlled conditions.

## 2. Materials and methods

### 2.1. Oils selection and designation

- *Original oils*: an olive (ABO), a sunflower (GIRO) and an olive: sunflower 1:1 v:v mixture (JSO) oils. All of them are commercial oils.
- *Original heat-treated oils*: samples of the original olive and sunflower oils were heated at 150 °C and 225 °C for 1–15 days.
- *Waste oils*: an olive (AB) and an olive/sunflower 1:1 v:v mixture (JS) oils which had been employed several times for frying vegetables, fish and meat. These oils were filtered to remove pieces of food.

### 2.2. Density, viscosity and interfacial tension against water

The densities of the oils were determined in a picnometer. A HAAKE rotational Viscotester VT5 R was used to measure the oil viscosities. By this proce-

dure, a disk/spindle is submerged in the oil and the force which is 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 spindle. According to previous vegetable oil viscosity values, which were determined following the ASTM method D445-86, a spindle speed of 60 rpm was chosen in this work to carry out the measurements. The interfacial tensions of the oils against water were measured by the drop volume method, using a Lauda tensiometer, model TVT 2. The principle of this technique consists in accurately determining the volume of a drop formed at the tip of a given capillary. Due to the force balance, the critical drop volume  $V$  (volume at moment of detachment) correlates directly with the interfacial tension  $\gamma_{w/o}$  (Shaw, 1992) through the following equation, where  $\Delta\rho$  is the difference in density of the two adjacent phases,  $g$  the acceleration due to gravity,  $r_{\text{cap}}$  the radius of the capillary and  $F$  a correction factor:

$$\gamma_{w/o} = Vg\Delta\rho F/2\pi r_{\text{cap}}$$

The measurements of these physical properties, of the original, original heat-treated and waste vegetable oils, were carried out at 20 °C.

### 2.3. $^1\text{H}$ NMR

The oil samples were dissolved in chloroform-*d* and placed in 5 mm diameter NMR tubes for the analysis. A sample concentration of 20 wt% was used. TMS was then added as a chemical shift reference (1/1000 v/v). The spectra were obtained in a Bruker AC-300 MHz spectrometer at a resolution of 0.44 Hz by using an acquisition time of 2.294 s and 64 scans. Both the phase and the baseline corrections of the spectra were manually performed. To eliminate errors in these corrections, three integrations were performed in each spectrum and the relative intensity of each signal was calculated from the average value. The chemical shifts and the assignment of the main resonances in the  $^1\text{H}$  NMR spectra of vegetable oils previously reported by Sacchi, Addeo, and Paolillo (1997) were used in this work.

### 2.4. FTIR

Infrared spectra were recorded in a Nicolet Magna IR-560 interfaced to a personal computer operating with Windows-based Nicolet Omnic software (version 3.1). A film of the oil sample was deposited between two disks of NaCl. The spectra were recorded from 4000 to 400  $\text{cm}^{-1}$ , the number of scans being 256 at a resolution of 4  $\text{cm}^{-1}$ .

### 3. Results and discussion

#### 3.1. Physicochemical properties

As can be seen in Figs. 1 and 2, the density and viscosity of the original vegetable oils, heated at 150 and 250 °C, tend to increase with the time of treatment. For a given oil, the magnitude of these increases is both time- and temperature-dependent, the influence of temperature being more important. Oil viscosities increase very quickly with the time of heating. This effect is particularly noticeable in the case of sunflower oil, where the viscosity grows to 8400 mPas after 10 days at 150 °C. Under the same conditions, the heat-treated olive oil exhibits a viscosity value of 500 mPas (Fig. 2). Considering that, among other factors, strong attractive intermolecular interactions in a liquid lead to a greater viscosity, the presence in the heat-treated sunflower oils of a higher number of functionalities, which are known to cause long-range dipole–dipole attractions, may explain the differences in the viscosity values between the

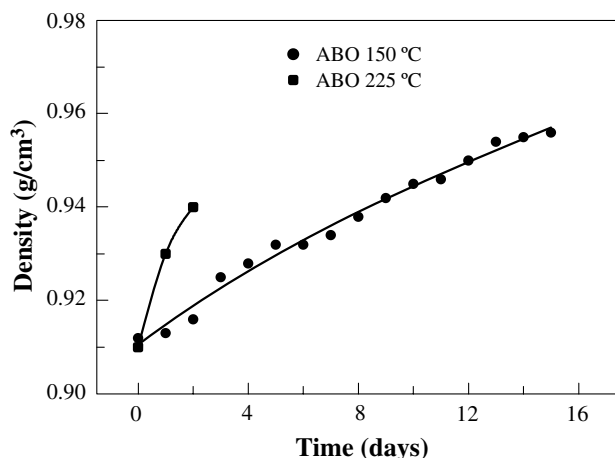


Fig. 1. Evolution of the density of ABO oil after heating.

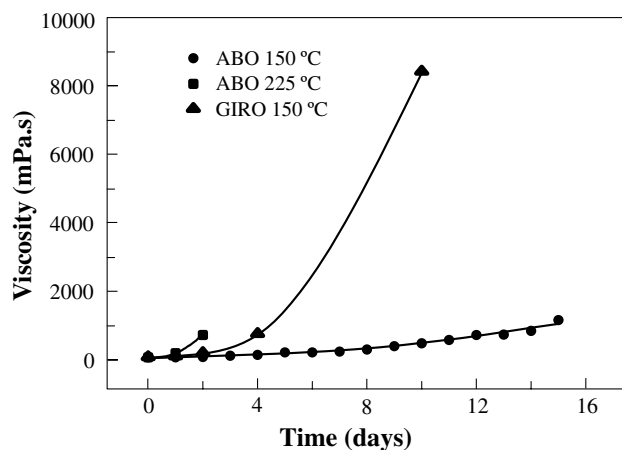


Fig. 2. Evolution of the viscosity of ABO and GIRO oils after heating.

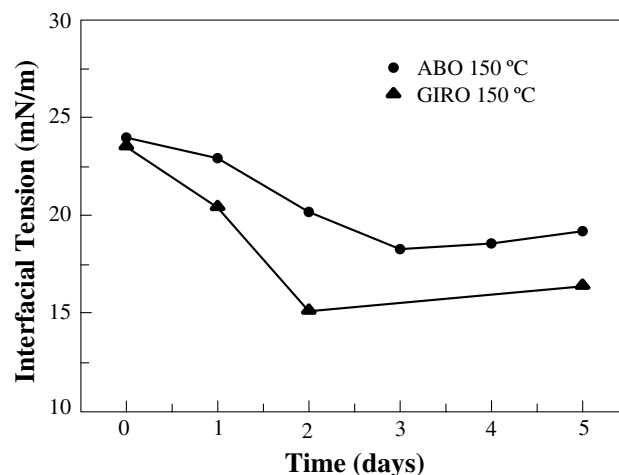


Fig. 3. Evolution of the oil/water interfacial tension of ABO and GIRO oils after heating.

two heated vegetable oils. As can be seen in Fig. 3, the oil/water interfacial tensions of the oils decrease when the heating time is increased to 2–3 days. The extent of this decrease, which is a consequence of the formation of the polar groups, is higher in GIRO, thus confirming the previous explanation. No significant variation in this oil property was found at times above those mentioned. In fact, a value of 19 mN/m was determined for ABO oil after 15 days at 150 °C. Since oil viscosity increases monotonically with the heating time (Fig. 2), these results suggest that factors other than oil functionalities must also be responsible for this effect. According to the work of Fountain, Jennings, Mckie, Oakman, and Fetterolf (1997), oil viscosity is not only related to intermolecular forces but also to structural interactions. As reported by these authors, larger triglycerides have more ability to form long-range structural interactions than lower ones, which result in a more viscous oil. Based on these findings, an increase in the amount of larger triglycerides, as a consequence of polymerization (Jorge, Ap. Guaraldo Goncalves, & Dobarganes, 1997), in ABO and GIRO oils by heating at 150 °C, can be inferred. From the results in Table 1, it can be seen that the density, viscosity and oil/water interfacial tension of the AB and JS waste vegetable oils are comparable with those of the corresponding original ABO and JSO oils, thus indicating the relatively low degree of alteration of these waste vegetable oils.

#### 3.2. Structural analysis

The degree of unsaturation of the original vegetable oils was observed to decrease after thermal treatment. Following the work reported by Arnold and Hartung (1971), this degree was determined from the ratio between the absorbances of the infrared spectra bands at 3005  $\text{cm}^{-1}$  ( $A_{3005}$ ) and at 2850  $\text{cm}^{-1}$  ( $A_{2850}$ ) which are assigned to the stretching vibration of the *cis* double

Table 1  
Density, viscosity and interfacial tension against water of the original (ABO, JSO, GIRO) and waste (AB, JS) vegetable oils

Vegetable oil	Density (g cm <sup>-3</sup> )	Viscosity (mPa s)	Oil–water interfacial tension (mN m <sup>-1</sup> )
ABO	0.91	79	23.99
JSO	0.92	67	22.06
GIRO	0.92	69	23.54
AB	0.91	83	21.28
JS	0.92	73	22.11

bonds and to the symmetric stretching vibration of the aliphatic C–H bonds in methylene, respectively (Guillén & Cabo, 1997). By this method, values of 0.118, 0.172 and 0.241 were calculated for the unsaturation degrees of the original ABO, JSO and GIRO oils, respectively. The decrease of the unsaturation degree of ABO and GIRO (expressed as a percentage) is plotted versus the time of heat treatment in Fig. 4. This degree decreases remarkably with the heating time. For example, a fall in the unsaturation value of 33% for the ABO oil was produced after 6 days of heating at 150 °C; this percentage reached a maximum of 56% when the time was raised to 12 days. A comparison between the FT-IR results and those of the oil/water interfacial tensions in Fig. 3 suggests that, in addition to an oxidation process, other oil transformations occurring during heating, may contribute to the decrease in the number of oil double bonds. In this context, the formation of small amounts of complex mixtures of monocyclic fatty acids in heat-treated vegetable oils, at temperatures between 140 and 200 °C, leading in turn to a decrease in the unsaturation degree value of the oil, has been previously reported (Dobson, Christi, & Sebedio, 1996). A much larger fall in the unsaturation level of ABO oil was obtained by increasing the temperature to 225 °C. Thus, after two days at this higher temperature, the oil unsaturation

degree decreased by more than one half (57%). A comparative analysis of the structural evolution (loss of unsaturation degree) after the thermal treatment of the two original ABO and GIRO oils in Fig. 4, shows that double bonds with a higher reactivity are present in sunflower oil, which agrees with the presence in this type of vegetable oil of a larger proportion of linoleic acid (Gunstone, 2004). Although the physicochemical properties of the waste vegetable oils are comparable with those of the original ones, as discussed previously (see Table 1), slightly lower unsaturation degrees were determined for the waste JS and AB oils. Thus, losses of the order of 9% were calculated for AB oil, this value being similar to that exhibited by ABO oil after 1 day of heating at 150 °C. These results indicate that small structural variations, as a consequence of heating, do not affect the physicochemical properties of the oils.

As might be expected from the discussion of the FT-IR data, decreases in the relative intensities of the NMR spectra signals corresponding to vinyl (A), diallyl (D) and allyl (F) protons, all of which are related to the degree of unsaturation, were observed after the vegetable oils were heated and/or used in food processing (Table 2). Parallely, increases in the  $\alpha$ - (E) and  $\beta$ -carboxyl (G) proton signals occur. For a given type of proton, the extent of these variations tends to increase with temperature and heating time. In general terms, they are of small significance in the selected waste AB and JS oils, the signal intensities for these protons being comparable to those measured for the original oils after 1 or 2 days of heating at 150 °C. For example, while the value of the vinyl proton signal of the ABO oil is reduced from 5.08 to 2.29 after 15 days of heating at 150 °C and to 2.95 after only 2 days at 225 °C; values of 4.55 and 4.76 were calculated for this proton signal in the AB oil (waste) and in the ABO oil heated for 2 days at 150 °C, respectively.

To compare the evolution of the different types of oil protons during heating, the percentages of loss or increase of signal intensities for the above-mentioned vinyl (A), diallyl (D), allyl (F),  $\alpha$ - (E) and  $\beta$ -carboxyl (G) protons were calculated. Some of these percentages are shown in Fig. 5. As can be seen in the graph, an increase in the time of heating from 10 to 15 days at 150 °C, for the ABO oil, leads to greater loss percentages for the A, D and F protons. This fall in the signal intensities is much more significant when the temperature is increased to 225 °C. In this case, a loss of 91% for the diallyl proton signal occurs after only 2 days of treatment, this value being comparable to that obtained at 150 °C and 15 days. For a given time of heat treatment at 150 °C, the decrease in the signal intensity of the unsaturation-related protons follows the sequence: diallyl (D) > vinyl (A) > allyl (F). By increasing the temperature to 225 °C, the difference between the A and F protons practically disappears (Table 2, Fig. 5). The appearance of a band

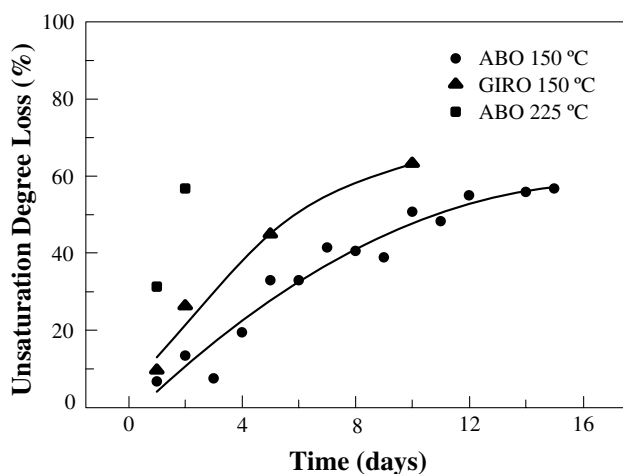


Fig. 4. Loss percentage of the unsaturation degree of ABO and GIRO oils after heating.

Table 2

Relative intensities of the different  $^1\text{H}$  NMR spectra signals of the original (ABO, GIRO, JSO), waste (AB, JS) and original heat-treated vegetable oils

Oil	Temperature ( $^{\circ}\text{C}$ )/time (days)	A	B	C	D	E	F	G	H	I	J
ABO	–	5.08	1.12	3.91	0.46	5.98	10.28	6.32	58.35	0.07	8.43
AB	Waste	4.55	1.67	4.09	0.43	5.65	10.33	6.53	58.20	0.72	7.83
ABO	150/1	4.79	1.31	3.94	0.46	5.76	10.05	6.80	58.41	0.45	8.03
ABO	150/2	4.76	1.35	3.99	0.42	5.83	9.65	6.94	58.73	0.37	7.98
ABO	150/5	3.13	1.97	4.23	0.22	6.30	8.42	7.40	59.53	0.31	8.50
ABO	150/10	2.85	0.95	4.27	0.17	6.78	7.94	9.19	58.75	0.73	8.37
ABO	150/15	2.29	1.81	4.41	0.04	6.65	6.81	7.96	60.78	0.43	8.82
ABO	225/1	3.72	1.32	4.18	0.16	6.11	8.38	7.30	59.75	0.52	8.56
ABO	225/2	2.95	1.42	4.49	0.04	6.37	5.93	7.39	61.93	0.75	8.73
GIRO	–	7.88	1.59	4.00	3.04	6.05	10.64	6.62	51.37	0.75	8.05
GIRO	150/1	7.11	2.02	4.17	2.73	6.17	9.70	6.68	52.67	0.62	8.12
GIRO	150/2	5.66	2.20	4.17	2.04	6.61	9.85	7.82	52.95	0.73	7.97
GIRO	150/5	4.92	2.04	4.31	1.60	6.89	8.46	8.01	54.64	0.65	8.48
GIRO	150/10	4.16	1.53	4.59	1.16	7.54	7.67	9.57	54.64	0.80	8.34
JSO	–	6.54	1.21	3.91	1.99	6.11	10.50	6.45	54.50	0.15	8.61
JS	Waste	6.44	1.23	3.95	1.60	5.98	10.20	6.62	55.29	0.70	7.99

A,  $\text{CH}=\text{CH}$ ; B,  $\text{CHOCOR}$ ; C,  $\text{CH}_2\text{OCOR}$ ; D,  $\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}$ ; E,  $\text{CH}_2\text{COOH}$ ; F,  $\text{CH}_2\text{CH}=\text{CH}$ ; G,  $\text{CH}_2\text{CH}_2\text{COOH}$ ; H,  $(\text{CH}_2)_n$ ; I,  $\text{CH}=\text{CHCH}_2\text{CH}_3$ ; J,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ .

at  $\sim 967\text{ cm}^{-1}$ , corresponding to the *trans*  $=\text{C}-\text{H}$  bonds (Guillén & Cabo, 1997), in the FT-IR spectra of the heated samples of ABO (particularly in those prepared over periods longer than 10 days and/or  $225\text{ }^{\circ}\text{C}$ ), confirms that the much faster loss of the D protons signal is due to the ability of the diallyl radicals formed during heating to stabilize by chemical transposition. This leads to conjugated double bonds with *cis-trans* isomerization (Cengarle, Carta, & Pranzetti, 1990). Whereas slightly higher losses of the vinyl (A) and allyl (F) protons signal intensities were calculated for the GIRO oil, those corresponding to the more reactive diallyl (D) protons were comparable in both the ABO and GIRO oils (Fig. 5). Based on this, more reactive double bonds in the vinyl and allyl groups might be expected in the GIRO oil, which would explain the larger loss percentage of the unsaturation degree of GIRO during heating (Fig. 4).

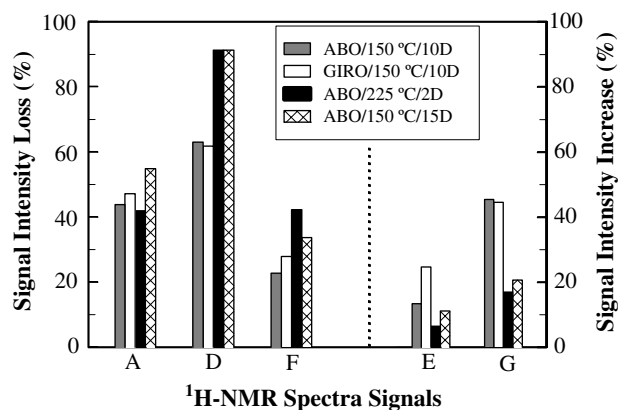


Fig. 5. Changes in the relative intensity of vinyl (A), diallyl (D), allyl (F),  $\alpha$ -carboxyl (E) and  $\beta$ -carboxyl (G) NMR protons signals of ABO and GIRO oils after heating.

Fig. 5 shows that, for a given heating time, a higher growth of the intensity signal of the protons in the  $\beta$ -position (G) with respect to those in the  $\alpha$ -position (E) of the carboxyl groups was obtained in the ABO and GIRO oils. These growth percentages were reduced when the time of heating was extended to beyond 10 days, particularly that of the  $\beta$ -carboxyl (G) protons. Thus, increases in the G signal intensity of 45% and 21% were calculated for the ABO oil after 10 and 15 days of heating at  $150\text{ }^{\circ}\text{C}$ , respectively. Considering that the increase in the E and G proton populations is mainly due to the oxidation of the oil unsaturations during heating, their reduction with time can only be explained as due to oil polymerization. Finally, while similar increased percentages for the G proton signal intensities were achieved by heating the two original oils studied, a higher increase was calculated for the E protons in GIRO.

#### 4. Conclusions

Significant variations occur in the physicochemical and structural (unsaturation degree) characteristics of the vegetable oils, which may affect their agglomeration capability, when they are heated at frying temperatures for periods of times above two days. Under these conditions, the viscosities of the oils increase very quickly whereas their unsaturation degrees show a marked decrease. Decreases in the relative intensities of the NMR spectra signals of the unsaturation-related protons were observed, those corresponding to diallyl protons occurring much faster. Of the two original vegetable oils studied, sunflower oil was found to be



more sensitive to thermal treatment, undergoing greater changes in its properties, especially in viscosity, which may increase considerably. As a consequence of the low degree of alteration in the selected waste vegetable oils, practically no changes in their physicochemical properties were found. Even so, slightly lower unsaturation degrees were determined for these waste oils as compared to those of the corresponding original vegetable oils. The results indicate that small structural variations, as a consequence of heating, do not affect the physicochemical properties of the vegetable oils.

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