# Effects of Physical Refining on Contents of Waxes and Fatty Alcohols of Refined Olive Oil

**Rana M. Tubaileh, Antonio Garrido-Fernández, M. Victoria Ruiz-Méndez*, Manuel León-Camacho, and Enrique Graciani-Constante**

Instituto de la Grasa, CSIC, 41012 Sevilla, Spain

**ABSTRACT:** Changes in the contents of waxes and fatty alcohols during deodorization/physical refining of bleached olive oil were studied. Experiments were carried out with 1.85% acidity oil, which was physically refined in a discontinuous deodorizer of 250-kg maximum capacity using nitrogen as stripping gas instead of steam. The variables studied were load and temperature of oil in the deodorizer as well as $N_2$ flow. Analyses of waxes and alcohols were carried out at different operation times. The maximum content of wax was always observed when the oil reached the deodorization temperature. The variation in the wax content depended on temperature and $N_2$ flow. Wax decomposition started and continued during the operating time, and a progressive decrease, which was pronounced between 3 and 4 h, was observed. Small changes in waxes were observed between 4 and 5 h. Total content of fatty alcohols diminished throughout the operating time, and changes did not depend on the variables studied.

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**KEY WORDS:** Deodorization, fatty alcohols, olive oil, physical refining, waxes.

Virgin olive oil is obtained from olives only by mechanical or other physical means under conditions, particularly temperature, that do not lead to alterations in the oil. The only treatments olive oil undergoes are washing, decanting, centrifuging, and filtering. When the virgin olive oil has an off-flavor and/or its acidity is more than 3.3%, such oil is designated as *lampante virgin olive oil*. These oils do not meet the requirements for direct consumption and hence must be refined for edible applications (1). On the other hand, the olive residue (pomace) of the mechanical extraction may contain up to 8% oil and it is then extracted by solvent (usually hexane) and termed *crude pomace oil*. Refined olive–pomace oil is oil obtained from crude pomace olive oil by a refining process.

The International Olive Oil Council (IOOC) and European Economic Community (EEC) have developed an International Trading Norm or standard definitions for olive oil and olive–pomace oils. Because of its extraction with the solvent, olive–pomace oil contains higher levels of minor components than those found in virgin olive oils, for instance, waxes, total sterols, erythrodiol, etc. This provides the basis for designating pomace oil as a commercial product distinct from virgin oil or the blend "olive oil" (refined olive oil mixed with virgin oil) (2). Waxes are mixtures of monoesters of long-chain fatty acids and monohydric alcohols, and the esterification process occurring in crude olive oil is spontaneous. The rate of esterification is influenced by the storage conditions of temperature and time, and reagent concentration. A positive correlation has been observed between acidity and wax content, with $C_{46}$ showing the best fit among individual esters (3,4).

In physical refining, free fatty acids are eliminated by deodorization, a distillation at high temperature and under vacuum using stripping gas. The use of nitrogen ($N_2$) as stripping gas in deodorization instead of steam has been well established (5–10). The amount of stripping gas and the environmental pollution caused during the process due to the minimum oil losses are reduced. The main advantage of physical refining is that it reduces losses of neutral oil, minimizes pollution from soap water, and enables recovery of high-quality free fatty acids. Nevertheless, not all oils can be physically refined. In the case of olive oil, physical refining is not applied to oil with acidity above 2% because of the problems of interesterification produced at the high temperatures used (11). Lampante olive oil with a high content of free alcohols also presents problems when subjected to physical refining, since the refined oil becomes cloudy after deodorization owing to wax formation (12).

The wax ester content of olive oils is regulated even in the refined oil, but there are no studies concerning the influence of the physical refining process variables on the esterification reaction and on the wax content. The aim of this work was to study the effect of $N_2$ flow, temperature, oil load-layer thickness in the equipment, and time on changes in the fatty alcohol and wax contents of olive oil during physical refining.

## EXPERIMENTAL PROCEDURES

*Samples.* Olive oil from mechanical extraction, with 1.85% acidity, was bleached according to the technique described elsewhere (13). Briefly, conditions applied were: 0.5% clay (Type OD, Minas de Gador, Almería, Spain), temperature: 90 ± 1°C, and time: 30 min. Absolute pressure was lower than 30 mm Hg. The contents of waxes and fatty alcohols were $503 \pm 10$ and $312 \pm 6$ mg · kg$^{-1}$, respectively. Batches of 200 kg were taken from the homogeneous mixture of bleached oil.

Olive oil was physically refined in a batch deodorizer of 250-kg maximum capacity. The technique and the equipment for physically refining were already described (10), and the experimental design was one of centered cube "$2^3$" (complete factor design) with three central points in order to calculate the error and test the lack of fit (13). Variables were coded according to the following formula: $X = [X_i - (X_{max} + X_{min})/2]/[(X_{max} - X_{min})/2]$. The experiments were run in random order and the

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*To whom correspondence should be addressed at Instituto de la Grasa, CSIC, Avda. Padre García Tejero, 4, 41012 Sevilla, Spain. E-mail: mvruiz@cica.es

range of variables was selected according to the optimum values from a similar previous experiment. The $N_2$ flow was introduced when the temperature reached 100°C to protect the oil, and then refining began. The rate of $N_2$ flow (±0.04 $m^3/h$), the work temperature (±0.5°C), and the oil height in the deodorizer (measured by weight ± 0.5 kg) (10) were controlled according to the experimental design (Table 1). Time was measured from when the oil reached the working temperature. Each batch was sampled at 0, 1.5, 3, 4, and 5 h. After 5 h, the batch was cooled. The $N_2$ flow was stopped when oil reached 100°C. A sample of the cooled final oil was taken and stored in a freezer until analyzed.

*Analytical methods.* Oil samples were heated about 30 min at 40–50°C and rapidly stirred before analyzing. Wax content, fatty alcohols, and acidity were determined according the EEC regulations for olive oil and pomace olive oil, EEC no. 2568/91 changed by 183/93 for wax, 2568/91 for fatty alcohols and acidity (2). Analyses were performed in a Hewlett- Packard Model 5890-II gas chromatograph (GC) (Hewlett-Packard, Palo Alto, CA), and an IBM computer with software HPChem-Station v. A.05.01 (IBM Corporation, Armonk, NY) was used for quantification. The gas chromatographic conditions of the EEC regulations were slightly modified as follows:

*Waxes.* The GC was equipped with a cold on-column injector with oven-track system and a flame-ionization detector. A TRB-5 column (5% diphenyl/95% dimethyl polysiloxane, length 15 m, 0.32 mm i.d. and 0.1 µm film thickness; TRACER 120113) was used. Hydrogen (140 kPa inlet pressure) was used as carrier gas and nitrogen as makeup gas. The oven temperature was held at 70°C for 5 min and then increased at 45°C/min to 180°C and then at 5°C/min to 310°C where it was held for 7 min. The detector temperature was 350°C.

*Fatty alcohols.* The GC equipped with a split injector, on an HP-5 column (5% diphenyl/95% dimethyl polysiloxane, length 30 m × 0.32 mm i.d. and 0.25-µm film thickness; HP 19091J-413) was used. The carrier gas was $H_2$ with nitrogen as makeup gas. The oven temperature was held at 220°C and then increased at 3°C/min to 280°C where it was held for 30 min, the injector temperature was 280°C, and the detector temperature was 300°C.

All analyses were validated by calculating the uncertainty of the methodology used. Two samples of each batch were analyzed. Error was calculated, and its causes studied by means of analysis of variance (13) using 13 oils with different waxes and alcohols contents. Means of relative standard deviations (RSD) for various combinations of subsamples and chromatographic injections are shown in Table 2.

**TABLE 1**
**Relationship Between Original and Coded Variables**

| Assay | Oil load (kg) | $N_2$ flow ($m^3$/Tn · h) | Temperature (°C) | Coded variables $X_1$ | $X_2$ | $X_3$ |
|---|---|---|---|---|---|---|
| I | 125 | 1.5 | 240 | –1 | –1 | –1 |
| II | 175 | 1.5 | 240 | 1 | –1 | –1 |
| III | 125 | 2.5 | 240 | –1 | 1 | –1 |
| IV | 175 | 1.5 | 240 | 1 | 1 | –1 |
| V | 125 | 1.5 | 260 | –1 | –1 | 1 |
| VI | 175 | 1.5 | 260 | 1 | –1 | 1 |
| VII | 125 | 2.5 | 260 | –1 | 1 | 1 |
| VIII | 175 | 2.5 | 260 | 1 | 1 | 1 |
| IX | 150 | 2.0 | 250 | 0 | 0 | 0 |
| X | 150 | 2.0 | 250 | 0 | 0 | 0 |
| XI | 150 | 2.0 | 250 | 0 | 0 | 0 |

## RESULTS AND DISCUSSION

The physical refining conditions, such as oil load or $N_2$ flow, were fixed from the beginning. However, heating took time to reach the desired temperature of each assay. The physical refining processes under study started from that moment. The aim of the research was to study the influence of physical refining on the contents of fatty alcohols and waxes in the final product, but some information on the behavior throughout can be deduced from the analysis of samples taken at different time intervals.

Changes in the contents of total waxes and fatty alcohols for the different experimental runs at the end of the heating period and throughout physical refining are summarized in Figures 1 and 2. Analyses of samples taken at zero time may provide information on the changes produced during the previous heating period. Fatty alcohols have higher volatility than free fatty acids (14); hence, they are easier to remove during the heating period.

In general, the initial content of fatty alcohols (312 mg $kg^{-1}$) decreased during the heating period prior to the physical refining. This diminution was proportional to the operating temperature for each run and followed a consistent and parallel trend among temperatures; the lowest fatty alcohol content was found at the central $N_2$ flow. Concentrations ranged at that time from 260 to 292 mg · $kg^{-1}$ (Fig. 3). The high content of fatty alcohols at low $N_2$ flow could be explained by the low efficiency of stripping. On the contrary, the high content of fatty alcohols when high $N_2$ flow was used could be explained by the characteristics of the distillation equipment. These results may indicate that when $N_2$ was in excess, the vacuum system was not able to efficiently remove the gas and volatile compounds, such as fatty alcohols. This also occurs in the case of the free fatty acids (10). Vacuum, a noncontrolled variable in these experiments, may have had an influence. This fact stresses the importance of the deodorizer design.

Changes in fatty alcohol contents for the different runs during the physical refining period were also statistically analyzed. No significant effects on alcohol contents by the inde-

**TABLE 2**
**Means of Relative Standard Deviations (RSD) of Various Analytical Combinations of Subsamples and Chromatographic Injections**

| | Number of subsamples | | | |
|---|---|---|---|---|
| | 1 | 1 | 2 | 2 |
| | Number of injections | | | |
| | 1 | 2 | 1 | 2 |
| Waxes | ±6% | ±4% | ±4% | ±3% |
| Alcohols | ±10% | ±5% | ±5% | ±3% |
| Waxes | ±6% | ±4% | ±4% | ±1% |
| Alcohols | ±10% | ±7% | ±7% | ±5% |

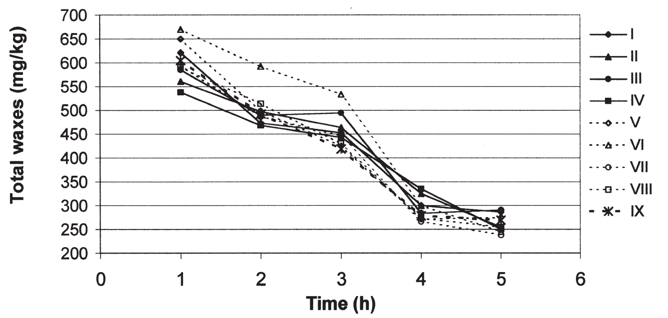

**FIG. 1.** Total fatty alcohols (mg · kg$^{-1}$) changes of the different runs during deodorization. Oil acidity: initial, 1.85%; final 0.12%. For run conditions see Table 1.

pendent variables (oil load, temperature, and $N_2$ flow) were observed (data not shown). The total contents varied with time (Fig. 2), with a general tendency to decrease. Final values in fatty alcohol contents ranged from 233 to 269 mg · kg $^{-1}$, being the runs with lowest $N_2$ flow and temperature that gave oils with high contents of fatty alcohols.

Changes in the wax content during the heating period for the bleached oil were also marked, and their concentrations increased according to the physical refining conditions. Statistical analysis of results at zero time showed significant effects of temperature and $N_2$ flow, as depicted in the Pareto chart for the standardized effects at 0 time (Fig. 4). The simultaneous effects of both variables on the wax content can be depicted for the highest oil load by the appropriate response surface, a plane because of the absence of significant interactions (Fig. 5). Wax content increased linearly with temperature and decreased linearly as the $N_2$ flow increased. Apparently, changes were slightly different for each level but not sufficient to be significant. This fact is in agreement with the normal kinetics of esterification. The esterification products (waxes) increased with temperature, but, the effect of stripping gas during the heating period reduced the content of one reactant (fatty alcohols) that prevents wax formation. Concentration of waxes at that moment ranged from 538 to 657 mg · kg$^{-1}$.

Changes in wax contents for the different runs during the physical refining period were also statistically analyzed at each other sampling time. Temperature exerted an important effect for a certain period of time and run VI, the one with the highest temperature and lowest nitrogen flow level, showed significantly higher wax contents at 3 h of deodorization. After 3 h, wax contents significantly decreased. In general, waxes progressively diminished with time, with only small differences among runs (except for run VI mentioned above). The sharpest decrease was observed between 3 and 4 h. No further improvements were observed after that time. As free alcohol contents decreased by distillation, a reverse predominant reaction of wax decomposition could have started. As in the wax contents, an important reduction was also observed in oil acidity after 3 h (10).

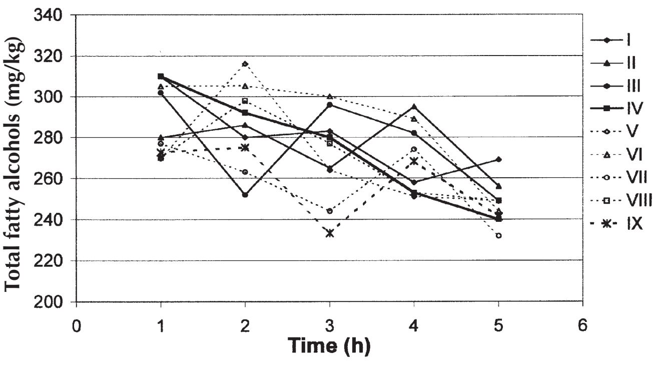

**FIG. 2.** Total wax (mg · kg$^{-1}$) changes of the different runs during deodorization. Oil acidity: initial, 1.85%; final 0.12%. For run conditions see Table 1.

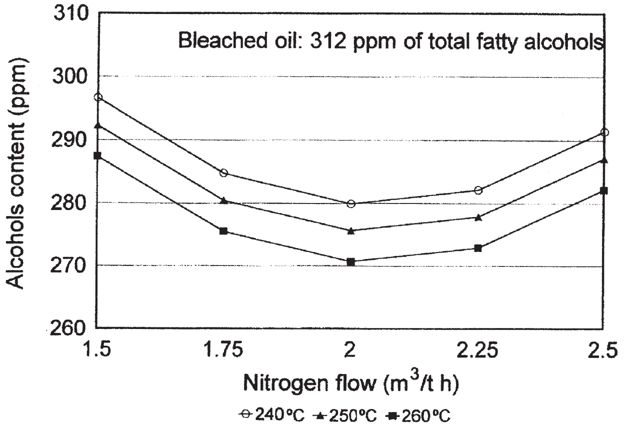

**FIG. 3.** Total fatty alcohol content (mg · kg$^{-1}$) as a function of temperature and nitrogen flow, at zero deodorization time.

The physical refining process could last about 5 h, and after that much time both fatty alcohols and waxes would have reached the minimum level. However, if only the wax content was considered, a period of only 4 h would be sufficient. In any case, physical refining is a complex process for which it is also important to consider acidity as a useful control measurement.

In order to provide some orientation to the industrial sector on possible operating times vs. working temperatures and stripping gas flow, we have made a simulation, considering the oil layer in our deodorizer (50 cm) and a bleached olive oil

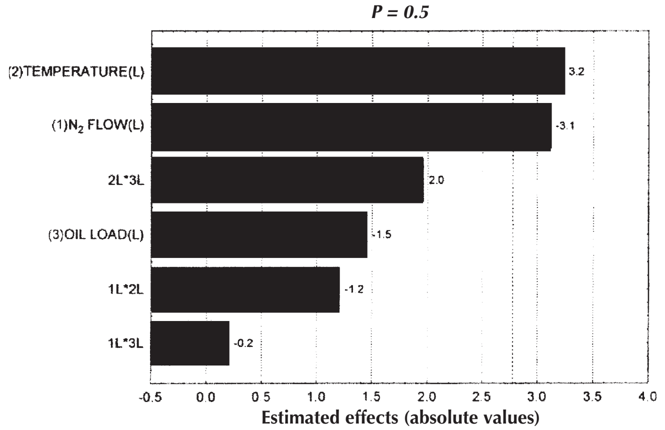

**FIG. 4.** Pareto chart for the standardized effects of the variables and interactions of total waxes to zero deodorization time.

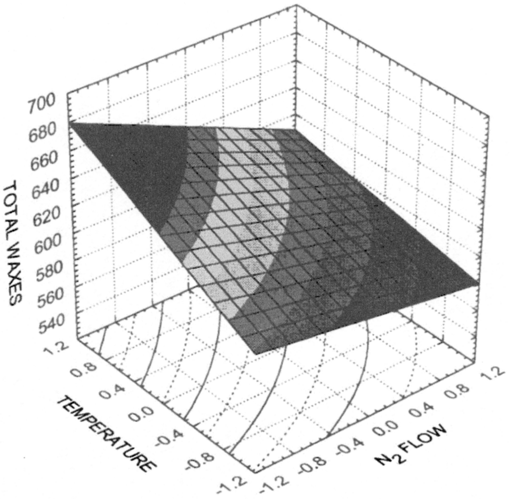

**FIG. 5.** Response surface of total waxes vs. temperature and $N_2$ flow at zero deodorization time.

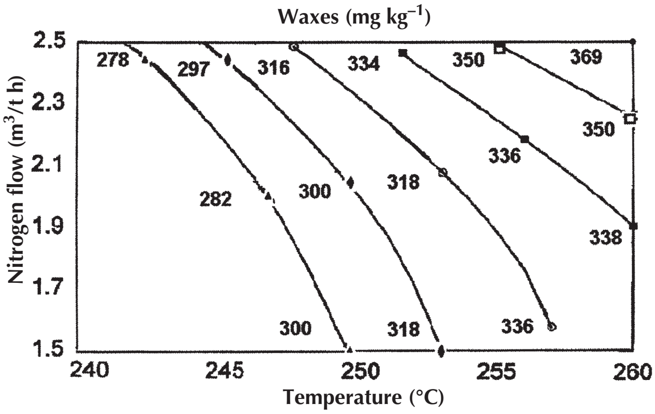

**FIG. 6.** Total wax content (mg · $kg^{-1}$) as function of the temperature and $N_2$ flow for a physical refining in a discontinuous deodorizer with layer thickness of 50 cm, for a bleached olive oil with 1.85% initial acidity that reached 0.12% of free fatty acids in the deodorized oil. (●) 3 h 15 min; (□) 3 h 30 min; (■) 3 h 45 min; (○) 4 h; (◆) 4 h 15 min; (▲) 4 h 30 min.

with initial acidity of 1.85%, with the aim of reducing acidity to 0.1–0.12% in the final product. The corresponding curves (Fig. 6) have been drawn by interpolating data from the different experimental runs. This will allow obtaining refined oils, which comply with the regulation about waxes and, at times, which preserve the best quality depending on the initial characteristics of the raw material. In order to reach minimum wax content in refined oil, it is advisable to work at a low temperature although it may require a longer operating time.

The present work suggests that during the oil heating process, precautions should be taken to optimize the physical refining of olive oil, thus minimizing the wax ester content. Wax ester formation could be attributed to an esterification reaction that takes place during the heating period, in which the free fatty acids react with fatty alcohols to form waxes. Hence, the final wax content depends on the amount of fatty alcohol present in free form in the crude oil. As these alcohols decrease by distillation, a reverse predominant reaction of wax decomposition is started during the deodorization process.

This heating period varies as a function of deodorizer design, the physical refining conditions, and the characteristics of the crude oils. It is possible to establish the operating time required to reach a final wax content under different conditions as a function of temperature and $N_2$ flow, considering a particular layer thickness. The curves could be obtained by interpolation between results of oil acidity and wax content.

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