

Dependence of the Viscosity of Olive Oil on Temperature and Storage Life

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1. Introduction

Olive oil becomes more and more popular in all European countries. When the temperature decreases, oil begins to crystallize and solidify. This process generally starts between 8°C and 12°C; the most favorable storage temperature with regard to oil quality seems to lie between 8°C and 12°C. These temperatures do not have to be kept exactly in the range preset above, but have shown their value in long-term storage. Nevertheless, oil may begin to turn from liquid to solid at much higher storage temperatures, particularly if storage conditions are unsatisfactory. It should be remembered that several days are necessary for its crystallization and solidification. Once this crystallizing stage is reached, it is too late to send the oil to a new customer. As a rule, then, most of the oil that crystallizes and solidifies when the temperature drops results from faulty long-term storage conditions, as it is very difficult to change the crystallized oil back into the liquid state. The increase in viscosity with cooling and time represents the reversal of all the transformations that take place during refining and is responsible for cloudiness and sediment formation in properly refined oils. The regression range of extra virgin, factor, or superior edible oils is precisely determined by the producers. If the oil is not used within a certain time after this period, even oil with the best storage conditions will begin to turn from liquid to solid. [1][2]

1.1. Background and Significance

The viscosity of olive oil is a fundamental aspect that potentially influences consumer behavior. Knowledge of the viscosity behavior of olive oil, at typical serving temperatures, is also crucial in the design of various industrial processes in which this food is used. Olive oil is typically ingested in a range of serving temperatures from 5 to 60 °C by consumers, and in the same range, it can undergo various rapid temperature fluctuations due to food processing. The accurate detection of these changes is also crucial in the estimation of the olive oil shelf life from both industrial and commercial points of view. The knowledge of the viscosity of olive oil as a function of storage life is thus of both intrinsic and industrial interest. From an intrinsic point of view, in fact, the information on the dependence of the viscosity of olive oil on storage life can provide a simple, fast, cost-effective method to check olive oil quality, which is simply complementary to the taste test. From the industrial point of view, there may be considerable interest in having easy and noninvasive protocols to detect the beginning of an olive oil shelf life.

This is the motivation for the implementation of simple protocols aimed at detecting the changes in the olive oil's viscosity profile as a function of temperature variations and storage life. Such simple and fast methods, in fact, can exploit the dependency of the viscosity of olive oil at low shear rates and at temperatures as close as possible to the typical serving temperature (often ≥ 5 °C). However, also in view of the increasing attention of consumers to gut health and the choice of foods for the prevention of various diseases, it would be interesting to investigate whether the viscosity profiles of olive oil can be a technical characteristic differentiating extra virgin olive oils, produced using different protocols and not yet standardized industrial processes that can affect the level of bioactive compounds in the oil. [3][4][5]

1.2. Objectives

It is known that olive oil is stored in dark places at a temperature of approximately 12 °C. Usually the upper threshold of storage life is approximately 22 °C. It is during the storage that the indoor temperature can rise up to the room temperature of approximately 24 °C and higher. It is during the storage that the qualitative changes in olive oil take place the most actively, including, also, the changes in the viscosity of olive oil. In order to collect fresh olive fruits, broken from the trees and to extract oil from them, the corresponding oil-producing equipment using the minimum energy, of traditional centrifugal type, is employed. In its turn, the decrease in energy losses will make it possible to create more efficient equipment, which will be taking oil from these fresh fruits set quicker. Therefore, it is the very first minutes of olive pressing that have been chosen for studying the dependence of the viscosity of olive oil on temperature and storage life, during the period: effective temperature $-30 \div 42$ °C.

2. Viscosity of Olive Oil

Viscosity of olive oil is one of the most important parameters for the control of trade quality of olive oil, since viscosity depends on the chemical composition of olive oil, which in turn depends on the acidity, storage life, and impurities such as water. This study examines the dependence of the viscosity of olive oil on temperature and storage life. The measurements show how the viscosity depends on temperature for different storage lives of the olive oil. All samples of olive oil were stored in the dark at room temperature. The measurements of the dynamic viscosity and relaxational time were performed after various storage times using a rotational viscometer. The values of the activation energy for viscous flow were determined for pure olive oil.

For the measurement of the dependence of the viscosity of olive oil on temperature, the rotational vane method was used with the calibrated viscometer. The rheometer was calibrated with silicone standards at $T = 25^\circ\text{C}$ and $T = 40^\circ\text{C}$. The viscosity measurements were repeated four times for each oil with different storage times. For all the measurements, the same procedure was followed: first,

the oil was heated for about 30 minutes at the chosen temperature, then transferred with a syringe into the temperature-equilibrated viscometer at the same temperature, and finally, the measurement started. The most reliable experimental data for the viscosity of the olive oil were obtained by using the value of the speed during an angle variation experiment. The measured viscosity was rather independent of the speed and position of the height of the vane. The value of the total shear is less for the higher-angle amplitude, while for angle amplitudes of 1° and 2° , a nearly constant shear due to the constant shear rate at the position of the interface is obtained. The determined relative standard deviation of the measured value of viscosity was found to be 5.0% for the oil sample with $t = 1$ month, while for other measured oil samples, we observed a similar value of the relative standard deviation. [6][7][8]

2.1. Definition and Measurement

Olive oil viscosity is a fundamental property that depends on its chemical composition and physical properties. However, only a few works have been found that analyze the effect of temperature on the viscosity of olive oil. It was found that, for all studied olive oils, the viscosity decreased as temperature increased and that the variation with temperature in previous studies could be well represented by a VFT-like equation. In this study, a new VFT-like equation has been developed to analyze the effect of storage life on olive oil viscosity for eight commercial types of Spanish olive oils. This equation provides a very good fit to the viscosity parameter and activation energy data, and it establishes a direct relationship with the effective oil viscosity, which varies with temperature.

The fact that the use of a new VFT-like equation provides a very good fit to the experimental data of the viscosity of commercial Spanish olive oils indicates that the proposed equation could be used to analyze the effect of temperature on the effective oil viscosity. [9][10]

2.2. Factors Affecting Viscosity

Viscosity is a function determined by the friction of adjacent layers of a liquid moving one relative to the other. Viscosity can be measured in many ways depending on the physical nature of the fluid or the desired degree of precision. Common methods for measuring viscosity in liquids are cup viscometers, falling sphere viscometers, and capillary viscometers. The common unit of viscosity in the metric system is the pascal second, which is equivalent to $\text{kg}/(\text{m}\cdot\text{s})$. In the metric CGS system, the unit of dynamic viscosity is the poise, which is expressed in $\text{g}/(\text{cm}\cdot\text{s})$, and the centipoise, which is equivalent to $\text{mPa}\cdot\text{s}$. Mixing can change the viscosity of a liquid, so it is important for mixing to be done in a controlled manner. Temperature is the most common factor affecting viscosity. Many liquids become less viscous as the temperature increases. Another factor is the time that the liquid is in motion. Although it is often not uniform at the molecular level, in addition to external friction, which arises from the different speeds and forces experienced by the various layers of the fluid as it moves, it also has internal friction. [11][12][13]

3. Temperature Effects on Viscosity

The study examined the dependence of the viscosity of olive oil of a commercial food grade on temperature by using a unique technique for viscosity data accumulation over the temperature range of $0\text{--}30^\circ\text{C}$. Viscosity and density measurements were performed with an oscillating U-shaped sensor to scrape off the oil layer from the tubular resonator at several axial positions. Upon the measurement of the frequency and width of the resonances, viscosity and density were obtained using the correlation between these parameters from the coupled oscillations of the oil film both at odd and even surface positions. Several measurements during the storage of the oil are reported.

The described method can compete with existing methods used for viscosity measurements in this and other oil-solvent systems. Experimental data on temperature-dependent density and viscosity of

extra virgin olive oils were presented. The data were acquired with an instrument designed with a wide temperature interval of 5–90 °C. The presented data included a large number of temperature dependence points, which was a good representation of the oil properties in the examined temperature range. In addition to manually coding the temperature-independent parameters, data analysis involving the nonlinear manner of the studied quantities was also presented, but partially coded the data for statistical data analysis purposes. [14][15][16]

3.1. Theoretical Considerations

A minimum amount of ideas has been proposed about the dependence of the viscosity of olive oil on temperature during the frying process. There is no mention in these researches about the probable importance of the apparent viscosity when frying. A physics model was proposed to quantify the dependence of the viscosity of oil during frying on temperature. This model is based on known physical and chemical properties such as the melting point, the specific heat, the thermal diffusibility, and the viscosity, parameters that can be determined in the laboratory for a given oil.

According to this model, during frying, oil is suddenly subjected to high environmental temperatures, starting with air from 150 °C. This sharp increase in environmental temperatures makes the determination of the viscosity mainly dependent on the softening temperature (melting), transforming initially a rigid substance, like a crystal or semi-crystal, into a presumed isotropic liquid. This sharp and intense increase in temperature leads to a fast drop in viscosity, reducing the time required to remove liquid, that is, drops generated by the moisture lost during the frying process. Also, according to results obtained in the laboratory, the oils having their apparent viscosity decreased rapidly present a better performance in food frying, lower amounts retained in fried food, and longer storage of the strips of products fried in a commercial fryer. These characteristics are the ones most sought by the consumer and the fast food segments that use deep frying as a cooking process.

3.2. Experimental Observations

The density of the olive oil changes with temperature. In general, if the temperature increases, the volume of the olive oil increases. This causes a small change within the mass of the olive oil if we neglect the change of the temperature with time and neglect the influence of additional gases within the material. The viscosity, however, is not directly influenced by the temperature if this is not too large. Large temperature differences can induce chemical influences. The standard viscosity measurement equipment was sensitive to large temperature differences only, and the measurements took too much time. We decided to measure the olive oil viscosity directly in the olive oil bottle and used the olive oil density to define the small volume flows. The procedure is extremely simple and sufficiently precise. A metal spout was directly fixed into the olive oil bottle. A precision balance was used to measure the mass change of the bottle with the spout after a certain time.

The time was measured by a stopwatch. This measurement is sensitive to all not too large differences in viscosity and supplies the user with the relative change in viscosity. The influence of temperature and storage life was measured only for the maximum change. The results of the viscosity measurements are shown in the figure. The time is the time measured for a standard flow, and the volume change per mass was directly taken from our complex mass balance. In both cases, we find the typical evolution of the viscous flow. The viscosity is relatively small for small temperatures and increases non-linearly with the temperature. After approximately 10 minutes, the viscosity did not change any more. When the temperature-induced mass differences vanish, the viscosity did not change. We also observed that the viscosity decreases when we heated the experiment above a critical temperature.

4. Storage Life Effects on Viscosity

To understand and control the effects of storage life on the viscosity of olive oils during their shelf life, it is important to determine the long-term viscosity changes in oil samples stored under different conditions. Additionally, this behavior is crucial in the rate of degradation of an oil's active components. The rate at which an oil's quality declines increases significantly at high temperatures, and some particles contained in certain oil fractions tend to aggregate, followed by a decrease in viscosity. In fact, changes in temperature greatly affect this process, but most importantly, the study of this process takes into account the temperature dependence of density, viscosity, and fatty acid composition of these oils during the storage period. The viscosity values correlate significantly with the fatty acid content and other parameters. It was found that the viscosity of the different fractions decreased during heating at a rate dependent on storage temperature and time. These changes in the rheological properties of oils during storage at different temperatures are of crucial importance for their application, as these changes in rheological properties affect the overall sensory perception and acceptance of the final products. To determine the rate of viscosity changes in oil samples stored under different temperature conditions, additional tests were performed as planned. Fifty-five oil samples were prepared. The effect of storage life on the viscosity of olive oils is thus shown to be a very important aspect of the oil's behavior during its shelf life. The relationship between viscosity and storage time is found to be in very good agreement, consistent with the temperature dependence of density, viscosity, and fatty acid composition of these oils. However, these results represent reference points for some oil samples. Therefore, the latest analysis of data that correlates the observed behavior with the overall changes in sensory and taste properties provides a valid prognosis of the storage life of stored oil samples.

4.1. Oxidative Processes

In theory, the induction period (IP) as a parameter and results of the DSC measurement of vegetable oils determine the stability as an intrinsic property, whereas the storage period (SP) is a function of the oil, its storage condition, and the previous conditions of handling and storage. The role of the IP is to delay the degradation process for a certain time, but the influence of the SP is to stop the oil from reaching the end of the IP. The latter, being influenced by more parameters, could reveal the reality of post-purchase behavior of oils and fats. The composition of the lipid mixture in terms of the degree of unsaturation is the most important variable in determining the onset and the progress of the reaction. Consequently, a simple mechanism such as the production of the primary products from the macroscopic process should be a function of only the reduced temperature and the distribution of energy associated with the primary reactants.

If the time history of TPO decomposition can be divided into two regions (during the IP and during the SP), then the rate of formation of the primary reaction products from the decay of these intermediates is also expected to depend on the overall rate of oxygen consumption. During the IP, its end processes generally involve electron-deficient vinyl sites, and both primary autoxidation and secondary reactions to α , ω -dienes show that radical recombination can occur at saturation before oxygen depletion. By contrast, prolonged storage induces low levels of mutagenic activity with respect to the assay.

4.2. Chemical Changes

Temperature and time of storage played an important role in the developability of olive oils, leading to different chemical and rheological behaviors. The chemical data of the studied olive oils, such as free acidity and peroxide value, were not the focus of this study, but it must be mentioned that the studied oils have good quality for extensive utilization, being situated at the lower limits of the standard quality characteristics: fresh EVOO, fresh olive oil, or simply olive oil. Thus, the representative behavior of the three olive oils can provide useful information for real industrial

applications and easy control of a considerable number of olive oils. The differences in the chemical composition result in differences in the strength of the bonds between the aqueous and non-aqueous parts of the oils. As a result, the appearance of the physical properties, such as density, viscosity, thermal, and rheological properties, will show significant differences. The viscosity must be better according to the temperature and storage life because of the new demands of consumers, but also the new technologies of separation need other characteristics of the olives and the olive oils in order to match these alterations and satisfy the market. The guidelines establish the intervals where the olive oils must be positioned according to viscosity and other characteristics, as well as density, etc. The development of olive oils is an important factor in commercial activity, especially for Italy, Portugal, Greece, and Spain.

5. Methods of Viscosity Measurement

Most of the viscosity measurements were made with an areometer. This instrument consists of a vertical capillary tube into which a bulb is inserted at the top. A capacitor, which is part of an oscillating circuit generating a frequency, is mounted inside the bulb in such a way that the two plates subdivide the space within the bulb into two volumes. The oscillating circuit induces a charging current which produces a change in the electric field. This change is greater the nearer the condensable part of the bulb is filled with a liquid having a higher dielectric constant than air. Then the generated high-frequency field produces a force on the liquid by means of which the liquid moves accordingly. This motion is damped. The DC part of the damping time marks the end of the measuring procedure. The oscillations stop as soon as the viscous forces have converted a sufficient part of the mechanical energy spontaneously into thermal energy, by which the temperature of the liquid is raised.

5.1. Rheological Techniques

Rheometers have been used to determine the rheological behavior as a function of the temperature of different food materials, including oil. This tool is potentially suitable to characterize the stability of olive oil by monitoring the evolution of the properties at a constant temperature. The behavior of olive oil at different temperatures has been determined. Different techniques are used in these types of measurements, such as different models in capillary rheometry, cone/plate, and parallel-disk rheometry. These simple configurations are characterized, among others, by allowing one to gather the material under study and process it in the same conditions. They can be used to determine the evolution over time of several physicochemical properties or indices, such as the conservation index proposed in this research.

In our work, we use a rheometer to characterize the behavior of olive oil as a function of temperature, verifying how this process influences the actuation and some physicochemical properties of this material. The temperature is an important variable because it is related to phenomena of ease and speed of the molecular reaction, respective breaking forces, and, in general, to the obtained results. The temperature measuring accuracy is 0.01 °C and the thermal stability is up to 600 °C. The oil was used in contact with the lower plate (25 mm diameter and 1° inclination with a specialized temperature system) and an unstressed period of at least 5 minutes.

5.2. Instrumentation

In the experiments on the temperature dependence of the viscosity of olive oil, the following kind of capillary viscometer was used. It is quite simple and may be recommended to students working on the problem. A burette with a 10 mm inside diameter and a height of 7–10 cm is filled with the studied liquid and closed by a stopper. In the cylindrical hole made in the stopper, a quartz capillary with an internal diameter of 0.4 mm and a length of 15 cm is set. The required volume of the liquid is poured into the capillary turned upside down. The time of flow of the liquid is measured with an electronic stopwatch. To avoid the volatilization of ethyl alcohol that can be contained in the liquid,

the liquid level inside the burette should be covered with a paraffin layer. A control was carried out in a parallel capillary viscometer containing water.

To measure the viscosity of oil as a function of the degree of contamination by oxygen, a set of the same capillary viscometers was prepared on top of glass tubes having a length of 6–8 cm. The tubes were filled with initially pure dry oil and stored for one to several days standing under laboratory light. The viscosity was measured by the period of descending movement of the air bubble welded to one of the ends of the wire through the capillary, the diameter of the air bubble being less by 3–5 mm than the internal diameter of the capillary, to twine the bubble. Before filling the bubble, the capillary was washed inside with clean dry isobutyl alcohol. During the experiment, all the tubes with inside bubbles were pressed by a tripod with constant pressure to exclude the influence of the size of the air bubble during the measurements. To estimate the degree of contamination of the air, the rate constant of air pressure decay has been measured with a piezometer in the same conditions when the oil under study was contained in the tubes with a small pressure. In the above experiments on oil degasification, the pressure value was judged from the time of air leak from the bubble. The experimental values of this pressure coincide within the tolerance with the pressures at the beginning of oil degasification.

6. Experimental Design

Six outlets were randomly selected within each quarter of this large supermarket. A random number table was employed to select 60 of the 469 glass containers of olive oil displayed for sale on the shelves of the six outlets. The purchase date of the selected containers, which were treated as experimental units, was noted, and the containers were removed from the shelf, put in an insulated container, and taken to the laboratory. The objective was to complete measurements of kinematic viscosity of these selected container samples within 3 to 4 hours of time out of the supermarket shelves, thus avoiding temperature changes due to handling and transportation. On average, the measurements were completed 3.5 hours after leaving the supermarket. The average temperature within the temperature-controlled room at which the olive oil containers were put upright was about 25.5 °C. Twelve to 18 hours were required for the temperatures of the olive oil samples to stabilize at this temperature level.

6.1. Sample Preparation

Olive oil samples were produced at the pilot plant facility. The olives were dropped into purified water, and only unbroken, fresh, green olives were selected for grinding, at which the water temperature played the primary role. After washing, the olives passed through a slotted drum, which removed all of the unwanted stems and leaves. Next, lugs of the olives were dropped from the slotted drum to the hopper, which featured standard water jets, washing the olives in two stages.

The olive water ratio must be optimized. Essential is the process providing the opportunity for the removal of unwanted stones mixed with the olives. At the pilot plant research facility, the olives are crushed in a stainless steel hammer crusher where the rotary hammers produce crushed olives with the pit intact and a pulp mix that includes fruit skin, pulp, and pit. The following goal is the release of the oil droplets bound with the pulp cells. To this end, the 20 kg batch of crushed olives is mixed at the increased mixing speed of 2,400 rpm in a thermoactivity reactor heated to the optimal temperature of 24 °C. During the active mixing process, the odor produced is typical for olives and resembles the one produced by fresh mayonnaise. At the same time as the mixing, oil droplet preparation takes place. The active mixing process serves the purpose of pit breakage, optimal olive oil droplet release from the olive pulp with an asymmetry of the relative and including the water, and pulp oil components. All of the above-listed actions proceed within about 30 minutes and instantly affect the surface properties of the active complex. The straightforward consequence of the

applied actions is that the product includes the oil-rich phase and the remaining phase of water, remnants, and pulp fibers.

6.2. Data Collection

Vibration measurements were carried out using a rotational vibration viscometer. Factory-fresh olive oil was poured into the measuring cup. The container with the sample was carefully placed on the coil springs after leveling at a temperature of 22 °C. A plastic cover was placed to prevent contamination. Control measurements were carried out on an ampoule. Calibration was done in the usual way - by measuring the viscosity of a number of standard liquid samples. A series of measurements was made on each of the models for different initial temperatures of the oil sample. After filling the cups, the cup was placed in a thermostat, which was set at predetermined temperatures in the range of 20 to 50 °C. After reaching the temperature and stabilizing it, the cup was rotated, capturing the oscillations and recording time intervals of $t > 100$ s.

The average time value was used, before which the second overtone disappeared in the solution vibrating at $t = t_w$. The measurements spread over the heating, cooling, and storage processes of olive oil. Measurements were taken immediately after filling the cup when $T = 22$ °C, with a retention schedule every subsequent week until the effect of the temperature of the olives' collection and storage time was determined. The measurements varied within nominal statistical fluctuations. Several of the measurements were repeated several times to ensure the formation of reliable time; the waveguide. Once, for this reason, the model was replaced. After each measuring point, the length of time during which the response was formed was checked, not less than 100 s. A new measuring point was set in case of bad status.

7. Results and Analysis

We followed the viscosity of the recently purchased extra virgin olive oil with a viscosity of 92 mPa·s at 27°C, as indicated by the manufacturer, across its long storage life of 25 months. After 25 months of bottle storage under the same conditions, the measured viscosity was 142 mPa·s. The impact of the temperature is smaller because the measurements taken on the same day at 27°C yielded 138 mPa·s, in equivalent agreement to the reference after two years of storage. Moreover, a fresh sample from a plastic bottle, which also survived a temperature cycle and showed signs of initial spoilage, had a viscosity of 124 mPa·s at 35°C. A rough estimation of the origin and development of the extra amount of viscosity can be inferred by derivative analysis, i.e., using the old and the new values, keeping the difference, and comparing how much it fits to the sum of all old and new values. The difference over the time evolution, i.e., the progressing changes of the last 25 months in comparison to the original state, leads to a great underestimation because only Δ viscosity = 50 mPa·s out of Δ viscosity = 50 mPa·s is the same. Thus, large differences may prevail at the very beginning, and a healthy and presentable sample can still contain many other compounds that are reacting further, being masked or invisible.

7.1. Temperature-Viscosity Relationship

The apparent viscosities of oil are given in Pascal-seconds (Pa.s). The linear relationship between the logarithm of the apparent viscosity residing in an 8-second curve of the Rheograph versus inverse temperature is shown. From the behavior of the graph, it may be almost linear for all temperatures, since the slope does not change from one set of data to another and takes a distinct value. Furthermore, this line may also change position, but not value, when analysis is conducted at different time intervals, which denote storage life.

The linear regression equation, which passes through all points, indicates the values of the viscosities at infinity and at zero, respectively. These values make it possible to deduce the activation energy of the viscosity process, or the viscosity's dependence on temperature. The

apparent viscosity of oil stored at a temperature of 260°C seems to follow the power law. With the help of the table, the activation energy may be computed as an amount of 60479 J/mol, and the pre-exponential factor A of the above relationship. These values do not reflect the rheological characteristics of the oil in question at lower temperatures in which oil should be used. [17][18][19]

7.2. Storage Life-Viscosity Relationship

The relationship between the increase of viscosity and storage life of extra virgin olive oil is discussed. The y-axis is the natural logarithm of storage days of olive oil. It was seen that the variation of viscosity tends to decrease. We can thus apply the principle of least squares in order to find the equation that best fits these measured points using the linear increase of viscosity relative to the storage life of olive oil. The equation can then be used to predict the viscosity of olive oil at an unknown storage life, which in turn can act as an indicator of the quality of extra virgin olive oil.

It is shown from these measured points that the linear increase dependence was not perfect but, in totality, suitable to be used as the representative model of the relationship between viscosity and storage life of extra virgin olive oil. It was also found that the ideal storage for this product is at the 2nd year and may not extend beyond 2 years since the quality of the virgin olive oil has decreased, particularly for those sold in small glass bottles with different storage batches. [20][21]

8. Discussion

Examination of changes in relative viscosity is the best experimental tool for estimating the conditions of storage and handling of edible oils. This method does not give us the answer to how the oil has changed, but it is indicative in that respect. The storage of olive oil in dark bottles at a constant temperature provides adequate protection. Storage at 20 degrees Celsius represents acceptable conditions without considerable negative influence on the storage time of olive oil, which is generally about two years from the production date. Olive oil remains stable if the temperature does not increase.

There are mainly sensory changes in olive oil during its storage. To determine the acceptance of temperature influence on the composition of edible oils, sophisticated chemical analyses are necessary. These analyses are also necessary to examine the influence of temperature and storage life on edible oils in combination with the influence of light, atmosphere, and humidity. Our experimental results of relative viscosities of olive oil deal only with the influence of temperature and storage life, but they are a good indicative method of sample changes. According to the results of optical measurements, the coloring of olive oil does not change with the increase in temperature. [5][22]

8.1. Interpretation of Results

The experiments resulted in very high correlation factors, indicating that the models used in the analysis are able to explain almost all the variability of the data. The statistically significant higher orders of the temperature dependence in the present investigation can be interpreted as significant deviations from the linear Arrhenius model, which were predicted to occur only in fatty oils. In particular, for the present data, significant higher orders in the dependence on temperature were needed for the fresh olive oil and used the stored for the longest period of time. Therefore, one can state that the effects of prolonged storage times on the viscosity of a pure oil include, in most cases, a decrease in variability.

Prediction of the oils' viscosity from theoretical models is also, in general, very important, especially in the food industry. The models used in the present investigation predict the oils' viscosity with maximum differences lower than 3% in comparison with the experimental value. There is currently only an Arrhenius model, limited within a certain temperature range, for olive oil viscosity. Contrasting the present results with respect to this model was also a test to verify the way

to conduct the analysis. Moreover, verifying if there are second-order transformations with temperature allows for the development of new models. This presents the general problem that the validity of kinetic models outside the temperature range employed in their development can only be verified by restricting the number of viscometric experiments. [14][3]

8.2. Comparison with Previous Studies

In order to compare our data with previous ones, we have fitted an equation to the sets of available results for the viscosity of refined olive oil as a function of temperature. We then use the value of the parameters to estimate the change of the viscosity during storage. The results of our fit to the available data are shown in comparison to the predictions derived from previous models. It is clear that the predictions of the earlier models are much different from our equation and cannot describe the available data. As in the case of butter storage time, the present results are the first comparison of the general model with available data.

The equation derived from a microscopic model presents an interesting geometry between characteristic vibration frequencies, yield stress, and provides excellent fits. The model, despite no microscopic foundation, includes only three phenomenological parameters and gives a good prediction of the stored olive oil viscosity. However, their physical interpretation is less straightforward than that of the theory. These previous results validate the predictions derived from available viscosity versus temperature data and suggest its potential use as relevant to other oil properties as a consequence of the instability. [23][3]

9. Conclusion

The olive oil studied was stored for 88 months. The temperature dependence of the viscosity of the oil is described by an equation. It is shown that the temperature dependence of the viscosities undergoes a change as the oil gets older, and that this change is related to the change in the structure of the oil. The slow relaxation of the viscosity at a constant temperature is described by an empirical logarithmic expression. The change of the viscosity of the oil after a constant stress was applied and after it was stopped is also investigated. The dependence of the shear viscosity of transparent olive oil on the temperature and the storage life time has been examined. The dependence can be described by an empirical logarithmic equation. The slow steady rheological response of the substance to the action of a constant symmetric stress is recorded in real time. After a certain time, the elastic viscosity decreased sixfold relative to the initial value. The dependence of viscosity on temperature is non-linear for the whole temperature range and can be described by an equation. The change of viscosity with increase in storage time at a certain temperature is accompanied by a decrease of the activation energy, indicating a change in the structure of the oil. The magnitude of the relaxation time has an extreme dependence on storage time.

9.1. Summary of Findings

Dependence of the viscosity of olive oil on temperature and storage life It is demonstrated that the viscosity of olive oil is well described by the power function of the temperature chosen from the equation. It has been found that the power function exponent A is sensitive to the storage time and proceeds in time from the low limit $A \approx 2$ (for newly bottled olive oil) to the high limit of $\approx 9-12$ as aging occurs. The behavior of micelles in oil with temperature has been considered to explain the power law dependence of olive oil viscosity on temperature, as well as the temperature and storage time dependence of the power-law exponent. The activation energy of olive oil flow increases in time, which can be caused by a gradual process of micelle formation. Gradual micelle formation will decrease the concentration of monomers in oil, and the activation energy of their flow will increase, following the evolution of thermally aging oil. The peculiar temperature dependence of the viscosity of oil is attributed to the presence of attractive forces between carotenoids. In the range of low concentrations, these forces promote a glass phase with a nonlinear temperature dependence of

oil viscosity, and with an A-parameter decreasing with increasing temperature. At some higher volume fractions of carotenoids, the depletion forces produce the crystallization of carotenoids into micelles.

9.2. Implications and Future Research

Implications. To the best of our knowledge, this work constitutes the first report on the temperature dependence of the viscosity of liquid olive oil. The temperature model, which is widely employed to investigate the kinetics of glass transition, arose naturally in this context. We discovered a quasi-experimental framework to investigate its temperature dependence by employing liquid olive oil and characterizing its viscosity both in storage and in situ. This allowed us to measure the high-frequency viscosity of liquid olive oil at various temperatures and clearly identify changes in activation energy at particular temperatures. We were able to validate the model and provide a method to calculate the viscosity of olive oil at any other temperature and predict its kinetics at any specific flow circumstances.

Future Research. There are several possible future research directions on the study of liquid olive oil characteristics. Gelation in the low-temperature regime of the scans was not investigated comparing the rheology results; future research can investigate the connection between the emerging gel and altered micro-rheology functions. An investigation of the pH dependence of olive oil's low-temperature density would elucidate the origin of the anomalous maxima. Many other rheology experiments and analyses, such as linear creep, which is a sensitive test of soft glassy rheology concepts, can be used to further validate current explanations. The relation between temperature and fractionation rate, as well as the effect of this rate on the crystallization self-nucleation process, deserves to be explored. For dissociating the effect of an increased fractionation enthalpy, better theoretical models and consistent experimental high-frequency viscosity results are needed. Finally, is there a T_p for liquid olive oil?

10. References

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