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Faculty of Graduate Studies

Temperature and Storage Age-Dependence of Olive Oil Viscosity in Different Locations in Palestine

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Dedication

This thesis is dedicated to my father and mother, as well as,

to my brothers and sisters.

With respect and love.

This thesis is also dedicated to Mr. Sameeh Abed Al – Azeez for his support.

Acknowledgement

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الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحمل العنوان:

Temperature and Storage Age-Dependence of Olive Oil Viscosity in Different Locations in Palestine

اعتماد لزوجة زيت الزيتون على درجة الحرارة وعلى عمر التخزين في أماكن مختلفة في فلسطين

اقر بان ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص ، باستثناء مـــا تمـــت الإشارة إليه حيثما ورد، وان هذه الرسالة ككل من أو جزء منها لم يقدم من قبل لنيل أية درجة أو بحث علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى .

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's name:	**اسم الطالبة:**
Signature:	**التوقيع:**
Date:	**التاريخ:**

List of Abbreviations

AAD%	percentage of average absolute deviation
ANOVA	Analysis of Variance
CGS	Centimeter-Gram-Second
cP	Centipoise
cSt	Centistokes
E_a	Activation Energy
Eq.	Equation
EVOO	Extra Virgin Olive Oil
FFA	Free Fatty Acids
Fig.	Figure
IOOC	International Olive Oil Council
N	Newton
P	poise
Pa	Pascal
P-value	Probability
R	Gas Constant
R^2	Coefficient of Determination
rpm	Revolution Per Minute
SD	Standard Deviation
SI	Système International d'Unités
SMC	Spindle Multiplier Constant
SP	Spindle
T	Temperature in Kelvin
VOO	Virgin Olive Oil
L_1	Jeet
L_2	saida
L_3	Alyamun
L_4	Beita
L_5	jenin
L_6	Arraba
L_7	Meithaloon
L_8	Asira Al-Shamaliyeh
ρ	Density
η	Dynamic Viscosity
ν	Kinematic Viscosity
η_{cal}	Calculated Dynamic Viscosity
η_{exp}	Measured Dynamic Viscosity

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Abstract

The dynamic viscosity of olive oil samples of different storage ages in yearly and weekly basis from different locations was measured as a function of temperature. In this study, the overall results of the effect of dynamic viscosity as a function of storage age in yearly and weekly basis indicate a decrease of dynamic viscosity. This study, shows that Abramovic's and Andrade's formulas that describe the dynamic viscosity of olive oil as a function of temperature don't fit our experimental data. Accordingly, our experimental data have been fitted to our proposed two-constant formula. As a result the best coefficient of determination (R^2) has been found to be 0.999. The P-value of dynamic viscosity for all olive oil samples is ≤ 0.05. This work, also propose three and multi-constant formulas to obtain more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples from different location in Palestine. The best AAD% (percentage of average absolute deviation) was calculated using our proposed formulas to be 0%.

The acidity of olive oil samples of different locations and different storage ages in yearly and weekly basis was measured.

In this work, the overall results of the effect of acidity as a function of storage age in yearly basis indicate a deterioration of oil quality. The acidity results for some olive oil samples suggest that the oil can be stored for a period not more than 12 years without deterioration.

The overall results of weekly basis of this study indicate that the acidity increased incrementally as a function of storage age.

The relationships between the viscosity of olive oil samples with temperature and storage age, and the acidity with storage age, have been found by fitting equations.

Chapter One
Introduction

1.1 Olive Oil

Olive originated in the countries of South Asia and was carried by birds to the Mediterranean via the Middle East. The most ancient oleaster traces in Greece are fossilized leaves found in the caldera on the island of Santorini dating back some 50,000 – 60,000 years ago (Boskou D., 2006).

Olive oil is used throughout the world, especially in the Mediterranean, it is a staple food in the warmer regions around the Mediterranean Sea. It is now becoming popular throughout Europe, the United States, Canada and other countries. This is due to its highly characteristic flavor in addition to the promotion of the health benefits of Mediterranean dietary patterns. Olive oil has a remarkable stability and can be stored for 18 months or more (Boskou D., 2006). It is commonly used in cooking, cosmetics, pharmaceuticals, soaps and as a fuel for traditional oil lamps.

1.2 Previous Studies

1.2.1 Viscosity as Quality Factor

Viscosity is a fundamental characteristic property of all liquids and it is one of the most important parameters required in the design of technological processes. Additionally, viscosity is an important factor that determines the overall quality and stability of food systems. Viscosity is influenced by different factors such as catalyst, temperature, shear rate, storage age, molecular weight, pressure and concentration.

There were numerous researchers who worked to propose alternative equations to describe the effect of temperature on dynamic viscosity. An equation to replace the well-known Arrhenius-type relationship was derived by Giap. Giap tested his model using six vegetable oils and proved its accuracy (Giap S. G. E., 2010). Barnett proposed a functional form for the variation of liquid viscosity (η) in cP with temperature (t) in ºC (Barnett R. *et al*, 1897). De Guzman proposed three-constant form to represent liquid viscosity as a function of temperature (de Guzman J., 1913). Vogel also proposed a three-constant representation (Vogel H., 1921). Goletz then applied the temperature dependence proposed by Vogel over the full range from the normal boiling temperature to the freezing point and developed a generalized form (Goletz E. *et al*, 1977). Poling presented power law form of liquid viscosity as a function of temperature (Poling B. *et al*, 1987). Poling also represented liquid viscosity in the polynomial form (Poling B. *et al*, 1987). Bu then presented Reid form in logarithm equation to the base 10 instead of the natural logarithm for liquid viscosity between the melting and critical points (Bu L. *et al*, 1994). Danner utilized a new formula to represent the dynamic viscosity data as a function of temperature for a large number of substances (Danner R. *et al*, 1994). Natarajan utilized a similar form for both absolute and kinematic viscosities and the constants of their equations are presented (Natarajan G. *et al*, 1989). Dutt in his study obtained the constants of Natarajan form for 100 liquids substances (Dutt N. *et al*, 2004).

Qun-Fang proposed a two-parameter formula (Qun-Fang L. *et al*, 1997). Abramovic described the effect of temperature on dynamic viscosities for a number of vegetable oils by using modified versions of the Andrade equation (Andrade E. N. C., 1930). In addition, Abramovic suggested a new form to describe the effect of temperature on viscosity which has been also used by several investigators (Clements L. D. *et al*, 1992; Abramovic H. *et al*, 1998; Hsieh F.H. *et al*, 1999; Rao M. A., 1999; Calligaris S. *et al*, 2005).

Viscosity of liquid is influenced by the storage age of the liquid. For instance, in a study by El-hefian measurements of acidity and viscosity of some samples of virgin olive oil as a function of storage age were carried out at room temperature (20^{o}C). El-hefian determined viscosity of pure virgin olive oil and virgin olive oil in the presence of chitosan at temperatures from 15^{o}C to 40^{o}C. The relationships between acidity-age, viscosity-age as a function of temperature were plotted. Results showed that there was an increase in acidity and a decrease in viscosity with increasing period of storage age. In addition, the samples of oil containing a small amount of chitosan showed an increase in viscosity above that of the pure olive oil samples at each temperature of interest in the above-mentioned temperature range. This increase in viscosity strongly indicates that chitosan could be a suitable aid in extending the commercial life of olive oil (El-hefian E. *et al*, 2007).

The effect of accelerated ageing on the emulsions rheological properties of olive oil was investigated by Tan Hsiao Wei. He used oscillatory measurements and a viscometer test at the interval of one day, one week and one month of storage age (Tan Hsiao Wei, 2009).

Some researchers studied the viscosity of different materials (oils, organic compounds and water) as a function of temperature, storage age, intensity of light, pressure, molecular weight and density. For instance, Bridgman has developed a method by which the relative viscosity of liquids may be determined over a wide range of pressures at various temperatures. The method has been applied to 43 liquids in the pressure range between atmospheric and 12,000 kg /cm at 30°C and 75°C (Bridgman P. W., 1925). Another study by Bakshi, gives an empirical relation between velocity of sound in a liquid and viscosity (Bakshi N *et al*, 1953).

Studies on vegetable oils determined the relationship between viscosity and average molecular weight by Bayrak (Bayrak Y. *et al*, 1997). Hsieh predicted viscosity of vegetable oils from density data (Hsieh F.H. *et al*, 1999). In his studies, Ahmad evaluated the viscosity changes of vegetable oils, and fitted the viscosity with well-known rheological equations. They identified model limitation through graphical and numerical observations. Vegetable oils were subjected to viscometer measurements of viscosity at shear rate (3-100 rpm) and temperature (40-100°C) (Ahmad M. F. *et al*, 2009).

The variation of vegetable oils quality as a result of thermal treatment was evaluated by Dumitru (Dumitru A. *et al*; 2010). The evaluation is based on the measurement of some important phisyco-chemical properties of vegetable oils, before and after thermal treatment including: density, viscosity, refractive index and acid number (Dumitru A. *et al*; 2010). The results of these researches gave some empirical relations that describe the dependence of viscosity on different parameters.

1.2.2 Acidity as Quality Factor

The acidity is the oldest parameter used for evaluating the olive oil quality since it is tightly related to the quality of raw material and represents the extent of hydrolytic activities.

The excellent quality of virgin olive oil is the culmination of a process that begins with the tree and ends in the bottle. Thus, it is necessary to care for each step of the process and of the factors that can affect its commercial life (oxygen, light, temperature and metals) leading to a deterioration in quality as a consequence of oxidative and hydrolytic degradations. Similar to other products that are produced in a limited period of time, but that are consumed throughout the year, it must be stored, and these storage and packing conditions are going to determine the commercial life of the olive oil. Moreover, during storage of olive oil, hydrolysis, especially a partial loss in the minor constituents, considered primarily responsible for its beneficial health effects (Buszewski B., 2008). To assess the role of the different modes of storage on the quality of olive oil, literature results concerning the analytical definition of the quality and composition of oils stored were critically reviewed

There have been some data published on the effect of olive storage before oil extraction. For instance, in his study, Bechir two tunisian cultivars of olive oil, Chemlali and Chetoui olive fruits were stored for different periods before oil extraction. Results showed that fruit storage led to the deterioration of the oil parameter qualities such as acidity which was more rapid in Chemlali oils than that of Chetoui cultivar (Bechir B. *et al*, 2012). The effect of machinery groups, packing materials and light intensities was studied on the extra virgin olive oil quality indexes, extra virgin olive oil for one season of olive harvesting was stored for sixth months. The acidity was affected by the type of machinery and packing material (Kiritsakis A. *et al*, 2007). In addition, the influence of olive storage period on oil quality was studied by Bento. The results confirm that storage of fruits produces losses in the olive oil quality. Acidity indicates a progressive deterioration of oil quality as fruit is stored (Bento A. *et al*, 2002).

The effect of some storage conditions and packaging material on olive oil quality and on extra-virgin olive oil quality was studied by several authors. The changes in oil quality are also reflected in the standardized quality indices. A study by Brahmi showed that the effect of packaging materials on the quality of extra virgin olive oil (EVOO) as a function of storage time (0 to 12 months) were studied (Brahmi F. et al, 2011). The results show that quality indexes were strongly influenced by the type of packaging material and the time of storage. Free fatty acids increased with storage time (Brahmi F. et al, 2011). Another study by Falque agreed with Brahmi study. In Falque study, four commercial samples of extra-virgin olive oil were analyzed in order to evaluate the influence of storage time on quality. The quality parameters were determined after 3 and 6 months of storage acidity. The results showed a gradual loss of quality during storage that included increase in acidity (Falque E. *et al*, 2007).

In his study, Ayadi has analyzed olive oil samples in order to evaluate the influence of storage time on their quality. Six months storage at 50 ºC in the dark revealed a loss in oil stability. This finding was reflected by the greater increase in peroxide value and a decrease of sterol content. During oil storage, in Ayadi study there was no significant variation in fatty acid composition (Ayadi M. et al, 2008).

Chemical analyses (acidity, peroxide value, specific extinction coefficient at 232 and 270 nm, fatty acid composition, pigments, total phenols, oxidative stability, etc) were carried out by numerous researchers in order to evaluate the effect of storage age on oil quality. The results of researchers showed that quality indexes were strongly influenced by the time of storage (Bechir B. *et al*, 2012; Brahmi F. *et al*, 2011; Ayadi M. *et al*, 2008; Falque E. *et al*, 2007; Kiritsakis A. *et al*, 2007; Bento A. *et al*, 2002).

It has been known that olive oil quality and behavior can be influenced by the cultivars, the degree of ripeness, and the industrial processes employed for oil extraction, as well as environmental conditions (mineral nutrition, room temperature, light and availability of water) and cultural practices (Bechir B. *et al*, 2012; Bento A. *et al*, 2002).

1.3 Objectives of the Study

The main goal of this work is to study the dependence of dynamic viscosity of olive oil samples from different location in Palestine on temperature and compare our results with the standard values. In addition, the dependence of the dynamic viscosity and the acidity of olive oil on storage age will be studied. The relationship between the viscosity of olive oil with temperature and storage age, and the acidity with storage age will be found by fitting equations using SPSS (Statistical Package for Social Sciences) program.

Chapter Two
Theory of Viscosity

Viscosity is a measure of the resistance to flow or shear. Viscosity can also be termed as a drag force and is a measurement of the frictional properties of the fluid. It can be expressed in two distinct forms:

a. Dynamic viscosity (η)

b. Kinematic viscosity (ν)

Dynamic viscosity is defined as the ratio of shear stress (force over cross section area) to the rate of deformation (the difference of velocity over a sheared distance), and it is presented as:

$$\eta = \frac{\tau}{\frac{\partial u}{\partial x}} \qquad (2.1)$$

Where, η is the dynamic viscosity in Pascal-second (Pa.s); τ is shear stress (N/m^2); and, $\frac{\partial u}{\partial x} = \gamma$ is rate of deformation or velocity gradient or better known as shear rate (1/s) (Dutt N. *et al*, 2007).

The Kinematic viscosity requires knowledge of mass density of the liquid (ρ) at that temperature and pressure. It is defined as:

$$\nu = \frac{\eta}{\rho} \qquad (2.2)$$

Where, ν is kinematic viscosity in centistokes (cSt), ρ is in g/cm^3 (Dutt N. *et al*, 2007).

The flow characteristics of liquids are mainly dependent on viscosity and are broadly divided into two categories:

1. Newtonian fluids:

These fluids have the same viscosity at different shear rates (different revolution per minute) (rpm). These fluids are called Newtonian over the shear rate range they are measured. Water is an example of these fluids (James F., 1996).

2. Non-Newtonian fluids:

These fluids have different viscosity at different shear rates (different rpm). They fall into two groups:

a) Time Independent

Time Independent means that the viscosity behavior does not change as a function of time when it is measuring at a specific shear rate. Pseudoplastic materials are an example of that fluid which displays a decrease in viscosity with an increase in shear rate. It is also known as "shear thinning". If viscometer readings for a material are taken from a low to a high rpm and then back to the low rpm, and the readings fall upon themselves, the material is time independent pseudoplastic and shear thinning (James F., 1996). Olive oil is classified to be pseudoplastic materials (Ahmad M. *et al*, 2009; Adnan Q. *at al*, 2009).

b) Time Dependent

Time Dependent means that the viscosity behavior changes as a function of time when measuring at a specific shear rate (the duration for which the fluid has been subjected to shearing as well as their previous kinematic history). A thixotropic material is an example of that fluid which has decreasing viscosity under constant shear rate. Many gels are classified to be thixotropic material. If a viscometer is set at a constant speed and the viscosity values are found to decrease with time, the material is thixotropic (James F., 1996).

2.1 Viscosity Units

The unit for dynamic viscosity is used to be CentiPoise (cP) which is the most convenient unit to report dynamic viscosity of liquids. cP is 10^{-2} of Poise.

In the SI System (*Système International d'Unités*) the dynamic viscosity units are $N \cdot s/m^2 \equiv Pa \cdot s$, where N is Newton and Pa is Pascal. The dynamic viscosity is often expressed in the centimeter-gram-second system (CGS) as $g/cm \cdot s$, $dyne \cdot s/cm^2$ or poise (P) where, 1 poise = $dyne \cdot s/cm^2$ = $g/cm \cdot s = 10^{-1}$ $Pa \cdot s$ (Dutt N. *et al*, 2007).

2.2 Pure-Liquid Viscosity Theories

The effect of temperature on dynamic viscosity is normally fitted with the Arrhenius-type relationship (Clements C. *et al*., 2006). Which has the form given by:

$$\eta = \eta_{\infty,T} e^{\frac{E_a}{RT}} \qquad (2.3)$$

Where η is the dynamic viscosity in Pa.s, $\eta_{\infty,T}$ is the viscosity at infinite-temperature in Pa.s, E_a is the exponential constant that is known as activation energy (J/mol); R is the gas constant (J/mol.K) and T is the absolute temperature Kelvin (Clements C. et al.; 2006, Ahmad M. F.; 2009, Giap S. G. E.; 2010).

Equation (2.3) has failed to provide a good representation of real phenomena for all fluids. It indicates the presence of scientific gap for which new equation is needed.

There has been no comprehensive theory of viscosity for liquids because of its complex nature. Theoretical methods of calculating liquid viscosities give results in large deviations from the measured viscosity data. Empirical methods are used to find relationships between viscosity and other properties, by means of mathematical expressions that provide the best fit of the experimental data. The variation of liquid viscosity with temperature will be discussed. For practical purposes, it is often sufficient to know the viscosity of liquids at atmospheric pressure as a function of temperature. Available experimental data reveal that the viscosity of liquids generally decreases with temperature in a rapid and non-linear fashion and is not significantly dependent on pressures up to several atmospheres (Dutt N. *et al*, 2007).

Simple as well as complex expressions have been proposed for the representation of liquid viscosity as a function of temperature with the main objective of representing the available experimental data. Some of the different forms of temperature dependence of viscosity proposed under correlation methods are given. There were numerous researchers who responded to propose alternative equations.

2.2.1 Two-Constant Equations

Among several proposed relations, De Guzman proposed the simplest form of representation of liquid dynamic viscosity as a function of temperature, which is:

$$\eta = A\, e^{\frac{B}{T}} \tag{2.4}$$

Where η is the dynamic viscosity in cP, T is the temperature in Kelvin, A and B are positive constants, and are characteristics of each substance. The equation is popularly known as the Andrade equation (De Guzman J., 1913; Andrade E.; 1930).

Duhne in his research used equation 2.4 in the logarithmic form which is given by:

$$Ln\eta = A + \frac{B}{T} \tag{2.5}$$

Where η is the dynamic viscosity in cP and T is the temperature in Kelvin. Duhne evaluated the constants A and B for a number of substances (Duhne C.; 1979). The constants of equation (2.5) were also obtained by Dutt N. for 100 substances (Dutt N. *et al*; 2004). In addition, Viswanath and Natarajan in their Databook on Viscosity of Liquids tabulated the constants of equation (2.5). They also tabulated the constants of the following equation which is given by Natrajan (Natarajan G. *et al*, 1989):

$$\eta = CT^{D} \tag{2.6}$$

Where η is the dynamic viscosity in cP, T is the temperature in Kelvin, C and D are constants.

Abramovic described the effect of temperature on dynamic viscosity by using the following equations:

$$Log\,\eta = \frac{A}{T} - B \tag{2.7}$$

$$\eta = A - BLogt \tag{2.8}$$

Where η is the dynamic viscosity in cP, T is the temperature in Kelvin, t is the temperature in degrees Celsius. A and B in both equations are constants. The constants of equations (2.7) and (2.8) of olive oil and other oils are presented in Table 2.1 (Abramovic H. *et al*; 1998).

Table (2.1): Constants of equations 2.7 and 2.8, with temperature range from 298.15 K to 328.15 K.

The substances	Equation (2.7)			Equation (2.8)		
	A	**B**	**η (cP) at 298.15 K**	**A**	**B**	**η (cP) at 25.15 ˚C**
Olive oil	1558.2	3.433	62.12	235.4	124.1	61.59
Refined Corn oil	1464.1	3.207	50.54	186.6	97.4	50.19
Salad oil	1442.5	3.141	49.79	183.2	95.4	49.59
Refined Sunflower oil	1443.3	3.157	48.29	177.2	92.3	47.93

2.2.2 Three Constant Equations

A three-constant representation proposed originally by Vogel of the form

$$Ln\eta = A + \frac{B}{t + C} \tag{2.9}$$

Wher η is the dynamic viscosity in cP, t is the temperature in °C. A, B and C are constants. This form of the equation is more accurate than the two-constant form. It is often preferred for engineering design purposes (Vogel H., 1921).

In addition, Abramovic used the Andrade equations that are represented in the following equations:

$$Ln\eta = A + \frac{B}{T} + \frac{C}{T^2} \tag{2.10}$$

$$Ln\eta = A + \frac{B}{T} + CT \tag{2.11}$$

Where η is the dynamic viscosity in cP, T is the temperature in Kelvin. A, B and C are constants. The constants of Andrade equations of olive oil and other oils are presented by Abramovic as shown in Table (2.2) (Andrade E.; 1930, Abramovic H. *et al*; 1998).

Table (2.2): Constants of Andrade equations given by Abramovic.

The substances	Equation (2.10)				Equation (2.11)			
	A	B×10^{-3}	C×10^{-5}	η (cP) at 298.15 K	A	B	C	η (cP) at 298.15 K
Olive oil	4.3806	4.0938	11.9926	79.89	-32.72	7462.27	0.04	69.03
Refined Corn oil	2.7691	2.9769	9.9107	15.94	-27.89	6572.41	0.03	22.16
Salad oil	4.8140	4.2094	11.7573	123.23	-31.56	7120.03	0.04	69.87
Refined Sunflower oil	3.0044	3.1068	10.0457	20.17	-28.09	6575.60	0.03	18.34

Another study by Natarajan utilized the Antoine type equation given by:

$$Log\,\eta = \frac{B}{C - T} + A \tag{2.12}$$

Where η is the dynamic viscosity in cP, T is the temperature in Kelvin. A, B and C are constants. The constants of equation (2.12) for dynamic viscosity (η) of olive oil and some liquids are presented in Table (2.3) (Natarajan *et al*; 1989).

Table (2.3): Constants of the Antoine type equation given by equation (2.12).

The substances	A	B	C	Temp. Range (K)
Olive oil	– 4.9110	– 699.70	110.30	290 to 340
Water	– 4.5318	– 220.57	149.39	270 to 380
Mercury	– 3.1105	– 51.209	124.04	290 to 380
Ethanol	– 5.5972	– 846.95	24.124	210 to 350
Soya bean oil	– 4.4977	– 581.28	115.28	290 to 340

2.2.3 Multi-Constant Equations

Some equations with more than three constants have been proposed to improve upon the accuracy of representation, particularly over wider ranges of temperature. A study by Poling represented liquid dynamic viscosity in the polynomial form:

$$Ln\,\eta = A + \frac{B}{T} + CT + DT^2 \tag{2.14}$$

Where η is the dynamic viscosity in cP and T is the temperature in Kelvin. A, B, C and D are constants. Poling in his work estimated the constants of equation (2.14) for several substances. Table 2.4 shows the constants of equation (2.14) for different substances (Poling B. *et al*, 1987).

Table (2.4): Constants of equation 2.14 were given by Poling.

The substances	A	B	C	D x 10^{-5}	η (cP) at (25°C)
Water (H_2O)	-24.71	4209.0	4.527×10^{-2}	-3.376	0.90
Hydrochloric acid (HCL)	-3.488	481.0	7.062 x 10^{-3}	-3.168	0.068
Ethanol (C_2H_6O)	-6.210	1614.0	6.18 x 10^{-3}	-1.132	1.04
Benzene (C_6H_6)	4.612	148.9	-2.544 x 10^{-2}	2.222	0.61

Clements in his study used the formula of the form:

$$Ln\eta = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \ldots \qquad (2.15)$$

Where, η is the dynamic viscosity in cP and T is the temperature in Kelvin. A, B, C and D are constants (Clements L. *et al*; 1992).

Chapter Three
Methodology

The samples of extra virgin olive oil and virgin olive oil were used from different regions in Palestine. They were collected from 1997 to 2010, from different locations. The olive oil samples were obtained from a Palestinian quality assured industrial oil mill, from the crop of 1997 until the crop of 2010. These samples were kept under the same conditions (in closed glass bottles were placed in dark place at room temperature). The viscosity of olive oil samples of different ages and different locations was measured. The experimental data were fitted and the correlation constants of the best fits were estimated.

The viscosity of olive oil samples of crop 2010 from two different locations (AL yamun (L_3) and Beta (L_4)) at different temperature was measured weekly during the period from June 2011 till August 2011.

The viscosity of olive oil samples of crop 2010 from Jenin (L_5) was measured as a function of temperature.

The acidity of olive oil samples of different location and different storage ages were measured by using the titration method. The acidity of olive oil samples (2010) from three locations (meithaloon (L_7), AL yamun (L_3) and Beita (L_4)) were measured weekly during the period from June 2011 till January 2012. The experimental data were fitted and the correlation constants of the best fit were estimated.

3.1 Experimental Apparatus

3.1.1 Viscosity Apparatus

Two models of viscometer of different ranges were used to measure the range of viscosity of olive oils samples:

1. A Brookfield Viscometer Model DV-I+ with set of seven spindles (RV SPINDLE SET) and UL-ADAPTER with accuracy ±1%. The rotational speeds of the spindles are two set. The first set: 0.0, 0.5, 1, 2, 2.5, 4, 5, 10, 20, 50 and 100 rpm. The second set: 0.0, 0.3, 0.6, 1.5, 3, 6, 12, 30 and 60 rpm. The spindles measure viscosity range from 100 up to 13300000 cP.

2. Digital Viscometer Model NDJ-8S with a set of four spindles with accuracy ±1%. The rotational speeds of the spindles are: 0.3, 0.6, 1.5, 3, 6, 12, 30 and 60 rpm. The spindles measure viscosity range from 1 up to 2000000 (mPa.s). This model was used to measure low viscosity readings.

3.1.1 I Calibration of Brookfield Viscometer Model DV-I+

When the calibration of the Brookfield Viscometer Model DV-I+ was verified, the instrument and viscosity standard fluid error were combined to calculate the total allowable error. The instrument is accurate to ±1% of any full scale spindle/speed (a spindle at specific speed) viscosity range. Brookfield Viscosity Standards Fluids are accurate to ± 1% of their stated value.

The accuracy of the instrument was verified with Brookfield Viscosity standard fluid with a viscosity of 4840 cP at room temperature and RV-3 Spindle at 2 rpm was used. Viscometer Model DV-I+ was used to measure the viscosity of standard fluid and the result was 5150 cP.

The maximum viscosity (Full scale viscosity range) was calculated using the following equation:

$$\text{Full Scale Viscosity Range (cP)} = \frac{TK \times SMC \times 10000}{RPM}$$

Where TK is the torque constant for viscometer model = 1, SMC is the spindle multiplier constant = 10, rpm is the revolution per minute.

$$\text{Full Scale Range} = \frac{1 \times 10 \times 10000}{2} = 50000\,\text{cP}.$$

The viscosity is accurate to ± 500 cP (which is 1% of 50,000). The viscosity standard fluid is 4840 cP and it is accuracy is $\pm 1\%$ of 4840 or ± 48.40 cP. The total allowable error is (48.4 + 500) cP = $\pm$ 548.4 cP.

The measured viscosity (5150 cP) shows that the viscometer is operating correctly. Any viscosity reading between 5388.4 cP and 4291.6 cP indicates that the viscometer is operating correctly. Any reading outside these limits may indicate a viscometer problem (Brookfield, 1999).

3.1.1 II Determination of Viscosity

Low viscosity readings of olive oil samples were measured using the Digital Viscometer Model NDJ-8S. The SP-1 spindle was operated at 60 rpm. The Digital Viscometer Model NDJ-8S gives indications for out-of-range operations when % (Torque) readings are ≤ 20% or ≥ 90%. Therefore the temperature ranges, which were measured, were different according to the viscosity range of the olive oil sample. A Brookfield Viscometer Model DV-I+ also was used to measure the viscosity of olive oil samples. The SP-1 spindle was operated at 60 rpm. A Brookfield Viscometer Model DV-I+ gives indications for out-of-range operations when % (Torque) readings ≤10% or ≥100 % (Brookfield, 1999).

3.1.2 Temperature Apparatus

Temperature was measured using Digital Prima Long Thermometer with accuracy $\pm 1\%$ which measures temperature ranges from –20°C up to +100°C.

The Fried Electric model WB-23 was used to increase the temperature of the oil samples to a specific temperature.

3.1.3 Determination of Acid Value of Olive Oil (Titrimetric Method)

The acid value of oil was determined using the recommended official method (AOAC 1997).

Definition:

Acid value of oil = mg KOH required to neutralize 1 g oil dissolved in ethanol-ether mixture, and titrated with standard KOH solution.

Procedure:

A) Preparation and standardization of 0.1 M ethanolic KOH solution:

1- Transfer about 0.56 g of solid KOH into a 100-mL volumetric flask and dissolve in absolute ethanol.

2- Weigh out accurately 0.204 g of dry primary standard KHP (Molar mass = 204.23 g/mol) into a 250 mL conical flask and dissolve in ~ 50 mL of distilled water.

3- Add 3 drops of phenolphthalein and titrate drop wise in the vicinity of the end point with KOH until the color change from colorless to pink color and persists for 30 seconds.

4- Repeat steps 2 and 3 three times.

5- Calculate the average molar concentration of KOH solution.

$$KHP + KOH \rightarrow K_2P + H_2O$$

$$\text{molarity of KOH} = \frac{\text{weight of KHP (g)} \times 1000}{204.23 \times \text{mL of KOH}}$$

B) Preparation of ethanol-ether mixture:

1- Mix 50 mL absolute ethanol and 50 mL ether in a conical flask.

2- Add 3 drops of phenolphthalein solution, and add ethanolic KOH solution, (A), to faint pink color.

C) Determination of acid value of oil:

1- Weigh, to nearest mg, 5-10 g oil, into 250- mL conical flask.

2- Add 50 mL ethanol-ether mixture and 3 drops of phenolphthalein solution.

3- Titrate with the standard ethanolic KOH solution (A) until permanent faint pink appears and persists for 30 s.

$$\text{Acid value} = \frac{\text{mL KOH standardsolution} \times \text{molarity of KOH standard solution} \times 56.1}{wt \text{ of sample (g)}}$$

Acid value (mg KOH necessary to neutralize 1 g sample). May also be expressed in terms of % free fatty acids expressed as oleic acid

$$\% \text{ free fatty acid (as oleic acid)} = \frac{\text{Acid value}}{1.99}$$

3.1.4 Density Apparatus

- Density bottle.
- The analytical balance HR-200 with accuracy $\pm 0.00005\%$ was used to measure the mass.

3.2 Quality of Olive Oil

According to the International Olive Oil Council (IOOC), virgin olive oil is the oil obtained from the fruit of the olive tree solely by mechanical or other physical means under conditions that do not lead to alteration in the oil which has not undergone any treatment other than washing, decantation, centrifugation, or filtration, to the exclusion of oils obtained using solvents or using adjuvant having a chemical or biochemical action. The composition of olive oil is primarily triacylglycerols (~99%) and secondarily free fatty acids, mono- and diacylglycerols, and an array of lipids such as hydrocarbons, sterols, aliphatic alcohols, tocopherols, and pigments. Fig. (3.1) shows the structure of olive oil.

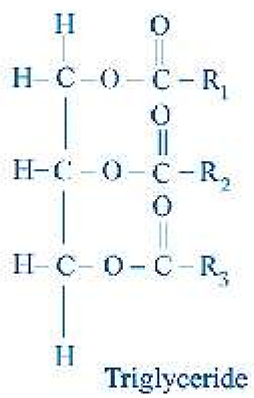


Figure (3.1): General chemical structure of olive oil. R_1, R_2 and R_3 are fatty acids

3.2.1 Fatty Acid Composition of Olive Oil

The major fatty acids in olive oil are: Oleic Acid (C18:1), a monounsaturated fatty acid. The oleic acid, the most representative fatty acid of olive oil, ranges from 55% to 83% of olive oil. Linoleic Acid (C18:2), a polyunsaturated fatty acid. That makes up about 3.5 to 21% of olive oil. Palmitic Acid (C16:0) is a saturated fatty acid that makes up 7.5 to 20% of olive oil. Stearic Acid (C18:0) is a saturated fatty acid that makes up 0.5 to 5% of olive oil. Linolenic Acid (C18:3) (specifically alpha-Linolenic Acid) is a polyunsaturated fatty acid that makes up 0 to 1.5% of olive oil.

The fatty acid composition of olive oil varies widely depending on the cultivar, maturity of the fruit, altitude, climate, and several other factors (Bechir B. *et al*, 2012; Boskou D., 2006).

3.2.2 Esters of Fatty Alcohols with Fatty Acids (Waxes)

Esters of fatty alcohols with fatty acids (waxes) are important minor olive oil constituents because they can be used as a criterion to differentiate various olive oil types. The main waxes detected in olive oil are esters of oleic or palmitic acid with 36, 38, 40, 42, 44, and 46 carbon atoms. The wax content and composition is affected by cultivar, crop year, and processing (Boskou D., 2006).

3.2.3 Trans Fatty Acids

Olive oil has no trans fatty acids. Olive oil is not a trans fatty acid because it has not been partially hydrogenated in a factory to make it solid at room temperature like margarine has (Boskou D., 2006).

3.2.4 Classification of Fatty Acids according to Chain Length

Long chain fatty acids have 12 to 22 carbon atoms. Medium chain fatty acids have 8 to 12 carbon atoms. Short chain fatty acids have 4 to 8 carbon atoms. The primary fatty acids in olive oil are all long chain fatty acids. Very long-chain fatty acids have greater than 20 carbon atoms. The oils having greater chain length have greater viscosity (Adnan Q. *et al*; 2009).

3.2.5 Free Fatty Acids Percent (%FFA) or the Acidity

The "acidity" in olive oil is the result of the degree of breakdown of the triacylglycerols, due to a chemical reaction called hydrolysis or lipolysis, in which free fatty acids are formed. These "broken off" fatty acids are called Free Fatty Acids. Table (3.1) shows the maximum levels have been fixed by the International Organization (IOOC) to establish the category (IOOC, 2000).

Table (3.1): Limits of free fatty acidity, as oleic acid percent, fixed by IOOC for each olive oil category

Category	FFA%
Extra virgin olive oil	≤ 0.8
Virgin olive oil	≤ 2.0
Ordinary virgin olive oil	≤ 3.3
Lampante oil	>3.3
Refined olive oil	≤0.3

Oils obtained from healthy fruits, regardless of the cultivar, processed just after harvesting, show very low values of free acidity well under 0.5% FFA. If fruits are damaged hydrolytic enzymes become active and the free acidity of the oil slightly increases. The increase in the acidity also might be due to delays between harvesting and extraction (especially if the fruit has been bruised or damaged during harvesting). The prolonged contact between oil and vegetation water (after extraction) increase the acidity. The careless extraction methods, as well as storing olives in heaps or silos also leads to increase the acidity of olive oil. The free fatty acidity is thus a direct measure of the quality of the oil and reflects the care taken right from blossoming and fruit set to the eventual sale and consumption of the oil.

The density or the specific gravity at different temperature, specific heat, other properties and information of olive oil were determined by many studies; Table 3.2 shows some of these properties (Adnan Q. *et al*, 2009; Robert C., 1980; http://olive oil source.com).

Table (3.2): Properties and information of olive oil determined by many studies

Density or Specific Gravity at 15 °C	0.918	(Robert C., 1980)
Melting point	−6 °C	(Robert C., 1980)
Viscosity at 20°C	84 (cP)	(Robert C., 1980)
Specific Heat	2.0 J/(g.)(°C)	(http:// olive oil source.com)
Thermal Conductivity at 20°C	0.17	(http:// olive oil source.com)
Dielectric Constant, e at 20°C	3.1	(http:// olive oil source.com)
Volumetric Heat Capacity at 20°C	1.650 106 J/m3	(http:// olive oil source.com)
Thermal Diffusivity at 20°C	10 x 10^{-8} m^2/s	(http:// olive oil source.com)
Smoke point	190°C	(http:// olive oil source.com)
Refractive index at 40°C	1.4679	(Robert C., 1980)
Average Sapontification value	130.32	(Adnan Q. *et al*, 2009)
Flow index	.84	(Adnan Q. *et al*, 2009)
Iodine value	81.1	(Robert C., 1980)

3.3 Statistical Analysis

The obtained results were tabulated and statistically analyzed. The statistical analysis of the data was done by using the statistical package (SPSS) program. The relationship between the viscosity of olive oils with temperature and storage age and the acidity with storage age were found by fitting equations using the SPSS program

Coefficient of determination R^2 and the P-value were used as a measure of the strength of the correlation between viscosity of olive oils with the temperature and storage age of the correlation between the acidity and storage age. Analysis of variance (ANOVA) test is used to determine significant differences between viscosity of olive oils and temperature. The P-value has two hypotheses:

1. Null hypothesis (H_o): there is no significant relationship between the dynamic viscosity and temperature.

2. Alternative hypothesis (H_a): there is significant relationship between the dynamic viscosity and temperature.

The P-value is the probability that the results observed in a study could have occurred by chance if the null hypothesis was true. The P-values do not simply provide researchers with a yes or no answer; it provides a sense of the strength of the evidence against the null hypothesis. The P-value ranged from zero to one, the lower the P-value, the stronger the evidence. The P-value ranged as follows:

Range I: $0.000 \leq P \leq 0.050$ strong significance (Alternative hypothesis).

Range II: $P = 0.050$ the threshold of statistical significance

Range III: $0.050 < P \leq 1.000$ no significance (null hypothesis) (Brian S. *at al*, 2004).

The coefficient of determination R^2 gives the proportion of the variance of one variable that is predictable from the other variable. It is a measure that allows determining how certain one can be in making predictions from a certain model.

R^2 represents the percent of the data that is the closest to the line of best fit. For example, if $R^2 = 0.850$, which means that 85% of the total variation in y can be explained by the linear relationship between x and y. The other 15% of the total variation in y remains unexplained (Brian S. *at al*, 2004).

Some empirical relations were found to describe the temperature dependence of dynamic viscosity by using Microsoft Excel program. The correlation constants for the best fit were estimated. The best fit equation was chosen based on the percentage of average absolute deviation (%AAD) and standard deviation (SD) of the data by following equations:

$$\%AAD = \frac{1}{N}\sum\frac{\left(\eta_{\exp}-\eta_{calc}\right)}{\eta_{exper}}$$

$$SD = \sqrt{\left[\frac{1}{N}\sum\left(\eta_{\exp}-\eta_{calc}\right)^2\right]}$$

Where η_{exp} is the measured dynamic viscosity, η_{cal} is the calculated dynamic viscosity from the empirical relation and N is the number of the measurements of dynamic viscosity of oil samples with temperature. (Dutt N. *et al*, 2007)

Chapter Four
Results and Analysis

4.1 Density Results

The density values of olive oil samples of different locations and different storage ages were measured at 15 ºC as given in Table 4.1.

Table (4.1): The density measurements of some olive oil samples of this work.

Density (g/cm^3)	Storage age (year)	Location
0.91287	0	Meithaloon
0.91384	0	Jenin
0.90982	0	Al-yamun
0.91176	0	Beita
0.91228	0	Sabastiya
0.91279	0	Ti'innik
0.91266	0	Saida
0.9124	1	Jeet
0.91259	5	Jeet
0.91174	5	Meithaloon
0.91166	13	Jeet

According to density measurements in Table 4.1 the average value of density of olive oil samples of crop 2010 is 0.91229 g/cm^3.

4.2 Viscosity Results

4.2.1 Temperature-Dependence of Dynamic Viscosity

4.2.1 I Yearly Basis

The dynamic viscosity of olive oil samples from two different locations (L_1 and L_2) and different storage ages in years were measured as a function of temperature. The measured data are given in Table 4.2.

Table (4.2): The measured values of dynamic viscosity of olive oil samples of two locations (L_1 and L_2) as a function of temperature.

t(°C)	L_1			L_2		
	Storage age: 0 year	Storage age: 5 years	Storage age: 13 years	Storage age: 2 years	Storage age: 9 years	Storage age: 12 years
	η(cP)					
35.0	54.9	53.1	50.3	59.0	47.8	39.0
37.0	50.8	48.9	46.1	54.5	44.8	34.0
40.0	44.5	41.7	40.0	48.3	38.4	27.7
42.0	41.3	39.2	36.6	43.9	35.4	25.0
45.0	36.6	35.7	32.0	38.5	32.2	21.5
47.0	34.2	32.8	29.3	36.9	30.0	
50.0	30.7	29.0	24.9	33.5	26.6	
52.0	28.7	27.4	23.2	31.2	24.1	
55.0	25.7	23.9	20.9	28.3	21.2	
57.0	24.0	23.2		26.6	20.3	
60.0	22.4	21.0		24.0		
62.0	20.9	20.0		22.9		
63.5	20.0					
65.0				20.8		

The dynamic viscosity of olive oil samples from two different locations (L_1 and L_2) of different storage ages as a function of temperature is plotted in Fig. 4.1 a and b.

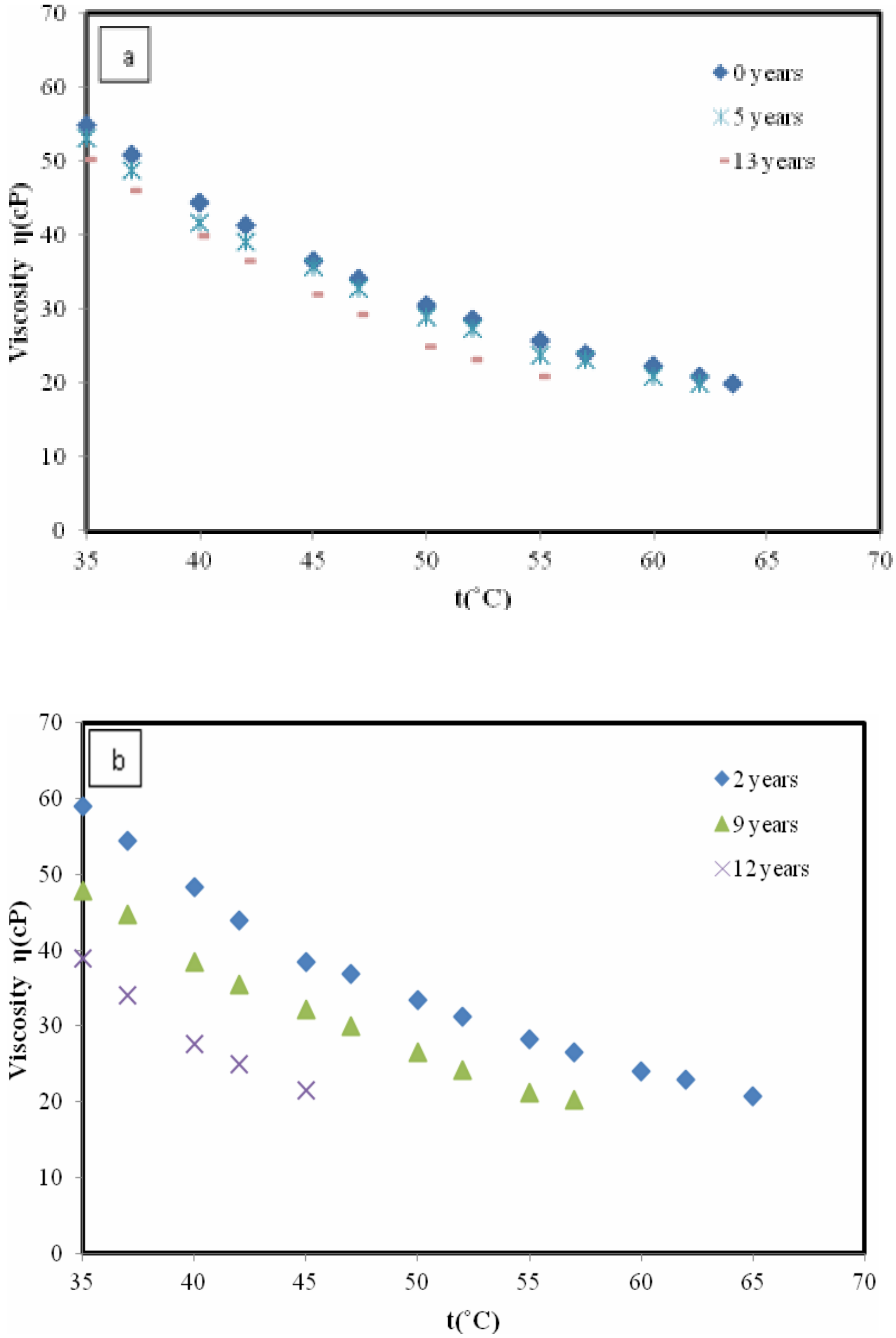


Figure (4.1): The measured values of dynamic viscosity of olive oil samples from two different locations a) L_1 and b) L_2 of different storage ages as function of temperature.

Our experimental results of dynamic viscosity of olive oil samples (η_{exp}) were compared with the previous calculated values (η_{cal}) found by using Abramovic's formula of two-constant $\eta = A - B\text{Log}t$ (Table 4.3) and

Andrade's formula of three-constant $Ln\eta = A + \frac{B}{T} + CT$ (Table 4.5). A, B and C are constants for olive oil. Tables 4.3 and 4.5 show η_{exp} and η_{cal} values while Tables 4.4 and 4.6 show results of computational quantities of AAD% and SD using Abramovic's and Andrade's formulas.

Table (4.3): Our experimental values and the calculated values of dynamic viscosity at different temperatures, using Abramovic's formula of two-constant.

t (°C)	L_1						L_2					
	Storage age: 0 year		Storage age: 5 years		Storage age: 13 years		Storage age: 2 years		Storage age: 9 years		Storage age: 12 years	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
35.0	54.9	43.8	53.1	43.8	50.3	43.8	59.0	43.8	47.8	43.8	39.0	43.8
37.0	50.8	40.8	48.9	40.8	46.1	40.8	54.5	40.8	44.8	40.8	34.0	40.8
40.0	44.5	36.6	41.7	36.6	40.0	36.6	48.3	36.6	38.4	36.6	27.7	36.6
42.0	41.3	34.0	39.2	34.0	36.6	34.0	43.9	34.0	35.4	34.0	25.0	34.0
45.0	36.6	30.2	35.7	30.2	32.0	30.2	38.5	30.2	32.2	30.2	21.5	30.2
47.0	34.2	27.9	32.8	27.9	29.3	27.9	36.9	27.9	30.0	27.9		
50.0	30.7	24.6	29.0	24.6	24.9	24.6	33.5	24.6	26.6	24.6		
52.0	28.7	22.4	27.4	22.4	23.2	22.4	31.2	22.4	24.1	22.4		
55.0	25.7	19.4	23.9	19.4	20.9	19.4	28.3	19.4	21.2	19.4		
57.0	24.0	17.5	23.2	17.5			27.0	17.5	20.3	17.5		
60.0	22.4	14.7	21.0	14.7			24.0	14.7				
62.0	20.9	13.0	20.0	13.0			22.9	13.0				
63.5	20.0	11.7										
65.0							20.8	10.4				

Table (4.4): AAD% and SD using Abramovic's formula of two-constant.

Location	Storage age (year)	Temp. Range (°C)	AAD%	SD (cP)
L_1	0	35.0 - 63.5	24.4	7.7
	5	35.0 – 62.0	19.2	6.1
	13	35.0 - 55.0	6.9	3.3
L_2	2	35.0 – 65.0	30.4	10.4
	9	35.0 - 57.0	7.6	2.5
	12	32.0 – 42.0	20.7	7.2

Table (4.5): Our experimental values and the calculated values of dynamic viscosity at different temperatures, using Andrade's formula of three-constant.

T(K)	L1						L2					
	Storage age: 0 year		Storage age: 5 years		Storage age: 13 years		Storage age: 2 years		Storage age: 9 years		Storage age: 12 years	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
308.0	54.9	46.0	53.1	46.0	50.3	46.0	59.0	46.0	47.8	46.0	39.0	46.0
310.0	50.8	42.6	48.9	42.6	46.1	42.6	54.5	42.6	44.8	42.6	34.0	42.6
313.0	44.5	38.1	41.7	38.1	40.0	38.1	48.3	38.1	38.4	38.1	27.7	38.1
315.0	41.3	35.5	39.2	35.5	36.6	35.5	43.9	35.5	35.4	35.5	25.0	35.5
318.0	36.6	32.0	35.7	32.0	32.0	32.0	38.5	32.0	32.2	32.0	21.5	32.0
320.0	34.2	30.0	32.8	30.0	29.3	30.0	36.9	30.0	30.0	30.0		
323.0	30.7	27.2	29.0	27.2	24.9	27.2	33.5	27.2	26.6	27.2		
325.0	28.7	25.6	27.4	25.6	23.2	25.6	31.2	25.6	24.1	25.6		
328.0	25.7	23.4	23.9	23.4	20.9	23.4	28.3	23.4	21.2	23.4		
330.0	24.0	22.0	23.2	22.0			27.0	22.0	20.3	22.0		
333.0	22.4	20.3	21.0	20.3			24.0	20.3				
335.0	20.9	19.2	20.0	19.2			22.9	19.2				
336.5	20.0	18.5										
338.0							20.8	17.8				

Table (4.6): AAD% and SD using Andrade's formula of three-constant.

Location	Storage age (year)	Temp. Range (K)	AAD%	SD(cP)
L_1	0	308.0 – 336.5	11.5	4.8
	5	308.0 – 335.0	7.5	3.5
	13	308.0 – 328.0	1.1	2.4
L_2	2	308.0 – 338.0	18.2	7.5
	9	308.0 – 330.0	1.8	1.4
	12	305.0 – 315.0	26.6	9.8

Table 4.4 shows that AAD% ranges from 6.9% to 30.4% and Table 4.6 shows AAD% ranges from 1.1% to 26.6%. This indicates that Abramovic's and Andrade's formulas are not the best fit for our experimental data of dynamic viscosity of olive oil samples.

Due to failure of Abramovic's and Andrade's formulas to fit our experimental data, a modification was introduced to Abramovic's and Andrade's formulas. The modification was in order to obtain a suitable description of our experimental measurements of dynamic viscosity as a function of temperature. As a result of this modification, the constants A, B for Abramovic's formula, and A, B and C for Andrade's formula were determined using Abramovic's and Andrade's formulas. Tables 4.7 and 4.9 show our experimental values (η_{exp}) and our calculated values (η_{cal}) using the modified form of Abramovic's and Andrade's formula of dynamic viscosity at different temperatures. Tables 4.8 and 4.10 tabulate AAD% and SD values.

Table (4.7): Our experimental values and our calculated values of dynamic viscosity at different temperatures, using the modified Abramovic's formula of two-constant.

t(°C)	L_1						L_2					
	Storage age: 0 year		Storage age: 5 years		Storage age: 13 years		Storage age: 2 years		Storage age: 9 years		Storage age: 12 years	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
35.0	54.9	53.1	53.1	51.3	50.3	49.8	59.0	56.9	47.8	47.5	39.0	39.1
37.0	50.8	49.9	48.9	48.1	46.1	46.2	54.5	53.5	44.8	44.4	34.0	34.9
40.0	44.5	45.3	41.7	43.6	40.0	41.0	48.3	48.8	38.4	39.9	27.7	29.0
42.0	41.3	42.5	39.2	40.8	36.6	37.7	43.9	45.8	35.4	37.1	25.0	25.3
45.0	36.6	38.5	35.7	36.9	32.0	33.1	38.5	41.6	32.2	33.2	21.5	20.0
47.0	34.2	36.0	32.8	34.4	29.3	30.3	36.9	38.9	30.0	30.7		
50.0	30.7	32.4	29.0	30.8	24.9	26.2	33.5	35.2	26.6	27.2		
52.0	28.7	30.1	27.4	28.6	23.2	23.5	31.2	32.8	24.1	25.0		
55.0	25.7	26.9	23.9	25.4	20.9	19.8	28.3	29.4	21.2	21.8		
57.0	24.0	24.8	23.2	23.3			27.0	27.2	20.3	19.7		
60.0	22.4	21.9	21.0	20.4			24.0	24.1				
62.0	20.9	20.0	20.0	18.5			22.9	22.1				
63.5	20.0	18.6										
65.0							20.8	19.2				

Table (4.8): Our values of A, B, AAD% and SD using the modified Abramovic's formula of two-constant.

Location	**Storage age (year)**	**A(cP)**	**B (cP)**	**Temp. Range (°C)**	**AAD%**	**SD (cP)**
L_1	0	259.0	133.3681	35.0 - 63.5	1.2	1.4
	5	255.0	131.9373	35.0 – 62.0	1.7	1.4
	13	286.0	152.9451	35.0 – 55.0	1.5	0.9
L_2	2	273.5	140.2751	35.0 – 65.0	1.5	1.6
	9	250.4	131.3744	35.0 -57.0	1.9	1.0
	12	308.7	174.6107	32.0 – 42.0	1.3	1.0

Table (4.9): Our experimental values and our calculated values of dynamic viscosity at different temperature using the modified Andrade's formula of three-constant.

T(K)	L_1						L_2					
	Storage age: 0 year		Storage age: 5 years		Storage age: 13 years		Storage age: 2 years		Storage age: 9 years		Storage age: 12 years	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
308.0	54.9	55.2	53.1	51.6	50.3	51.4	59.0	56.9	47.8	48.6	39.0	39.1
310.0	50.8	51.0	48.9	47.6	46.1	46.8	54.5	52.7	44.8	44.7	34.0	34.5
313.0	44.5	45.4	41.7	42.3	40.0	40.6	48.3	47.0	38.4	39.5	27.7	28.6
315.0	41.3	42.1	39.2	39.2	36.6	37.1	43.9	43.6	35.4	36.4	25.0	25.3
318.0	36.6	37.6	35.7	34.9	32.0	32.4	38.5	39.1	32.2	32.3	21.5	21.2
320.0	34.2	35.0	32.8	32.4	29.3	29.6	36.9	36.4	30.0	29.8		
323.0	30.7	31.4	29.0	29.0	24.9	25.9	33.5	32.7	26.6	26.6		
325.0	28.7	29.2	27.4	26.9	23.2	23.8	31.2	30.5	24.1	24.6		
328.0	25.7	26.3	23.9	24.2	20.9	20.9	28.3	27.5	21.2	22.0		
330.0	24.0	24.5	23.2	22.5			27.0	25.7	20.3	20.4		
333.0	22.4	22.1	21.0	20.3			24.0	23.2				
335.0	20.9	20.7	20.0	18.9			22.9	21.7				
336.5	20.0	19.7										
338.0							20.8	19.7				

Table (4.10): Our values of A, B, C, AAD% and SD using the modified Andrade's formula of three-constant.

.Location	Storage age (year)	A	B (K)	C (1/K) $\times 10^{-5}$	Temp. Range (K)	AAD%	SD (cP)
L_1	0	-07.72	3677.985	-69.00	308.0 – 336.5	1.2	0.6
	5	-08.00	3750.927	-76.00	308.0 – 335.0	1.5	0.8
	13	-10.84	4545.880	6.83	308.0 – 328.0	1.8	0.7
L_2	2	-07.38	3592.578	-79.00	308.0 – 338.0	2.6	1.1
	9	-09.21	4023.601	9.98	308.0 – 330.0	1.4	0.6
	12	-15.30	5932.681	-96.00	305.0 – 315.0	1.5	0.6

The modified forms of Abramovic's and Andrade's formulas give AAD% $\leq$1.9% and $\leq$ 2.6%, respectively (Table 4.8 and 4.10). This shows that the modified form of Abramovic's and Andrade's formulas don't fit exactly our experimental data.

Table 4.11 shows the constants A, B and C of Abramovic's and Andrade's formulas given by Abramovic for the dynamic viscosity of olive oil (Abramovic H. *et al*, 1998).

Table (4.11): The constants given by Abramovic using Abramovic's and Andrade's formulas.

Equation	A	B	C	Temperature range (K)
Abramovic's formula	235.40 cP	124.10 cP	-	298.15 to 328.15
Andrade's formula	-32.72	7462.27 K	0.04 1/K	

Our values of the constants of the modified form of Abramovic's and Andrade's formulas in Tables 4.8 and 4.10 are in disagreement with Abramovic values (Table 4.11). The different values were probably due to free fatty acid composition of different olive oil samples.

Three and multi-constant formulas were proposed to obtain a more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples. The η_{exp} and η_{cal} were used to propose the formulas that fit our experimental data. That is, AAD% and SD values are chosen to select the suitable prediction. If two-constant formula is proposed the fitting curves will not be in good agreement with the experimental data. Accordingly, the two-constant formula is not suitable for our experimental data where the AAD% gives very high value.

Our proposed formulas of three-constant $Ln\eta = A - \frac{B}{T+C}$ and multi-constant $\eta = A + \frac{B}{t} + CLn(t) + Dt^E$ fit our experimental data of dynamic viscosity. Our calculated values of the constants (A, B, C, D and E), AAD% and SD of the data are given in Tables 4.12and 4.13.

Table (4.12): Our values of A, B, C, AAD% and SD using our proposed two-constant formula.

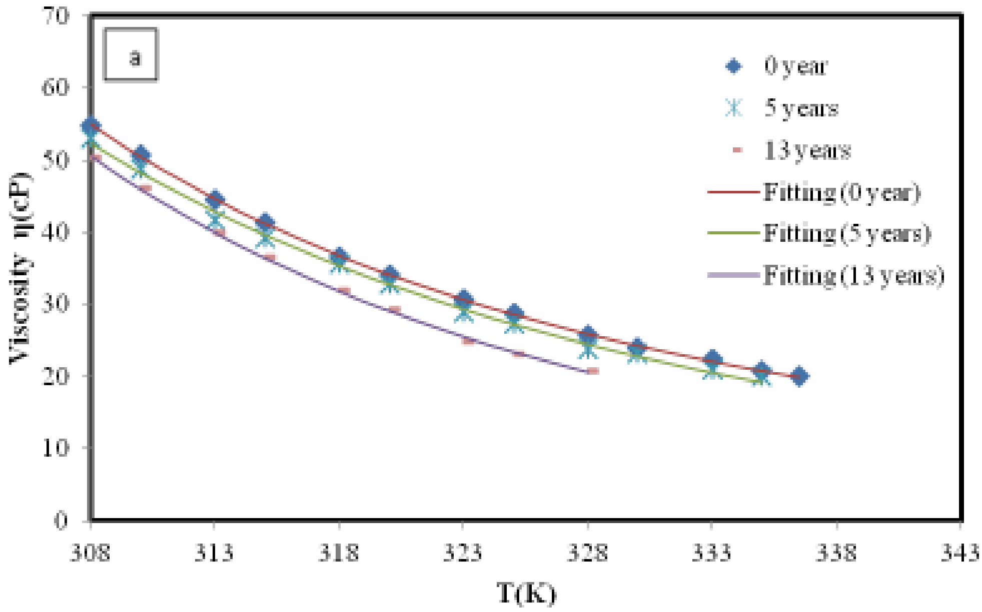
Location	Storage age (year)	A	B (K)	C (K)	Temp. Range (K)	AAD %	SD (cP)
L_1	0	-1.82578	-0786.38	-173.180000	308.0 – 336.5	0.0	0.2
	5	-8.35132	-3746.34	-3.656220	308.0 – 335.0	0.2	0.6
	13	-1.82740	-4547.45	0.299507	308.0 – 328.0	0.0	0.3
L_2	2	-7.74088	-3590.35	-3.909300	308.0 – 338.0	0.2	0.6
	9	-9.17109	-4021.00	0.304703	308.0 – 330.0	0.0	0.4
	12	-15.76780	-5932.87	-2.562840	305.0 – 315.0	0.1	0.4

Table (4.13): Our values of A, B, C, D, E, AAD% and SD using our proposed multi-constant formula.

Location	Storage age (year)	A (cP)	B (cP.°C)	C (cP)	D (cP/°C^E)	E	Temp. Range (°C)	AAD%	SD (cP)
L_1	0	-136.6100	3822.114	23.21082	694.2263	-2624.33	35.0 - 63.5	0.0	0.2
	5	-152.5700	3888.662	26.56520	694.2263	-2624.33	35.0 – 62.0	0.0	0.5
	13	-84.5450	3369.510	10.90927	694.2263	-2624.33	35.0 – 55.0	0.0	0.3
L_2	2	-126.0240	3891.562	20.78368	694.2263	-2624.33	35.0 – 65.0	0.0	0.5
	9	-20.5408	2501.031	-0.82095	694.2263	-2624.33	35.0 – 57.0	0.0	0.4
	12	-485.7750	6473.887	95.43480	694.2263	-2624.33	32.0 – 42.0	0.0	0.3

Table 4.12 shows that AAD% ≤ 0.2%. Table 4.13 shows that AAD% = 0.0%. Accordingly, our proposed two and multi-constant formulas are more suitable to describe the temperature dependence of dynamic viscosity of olive oil samples. In addition, our proposed multi-constant formula gives values closer to our experimental values than the values resulting from our proposed two-constant formula.

Fig. 4.2 a and b and 4.3 a and b show our experimental data and our fitting curves using our proposed three and multi-constant formulas of dynamic viscosity of olive oil samples from two different locations (L_1 and L_2) of different storage ages as a function of temperature.



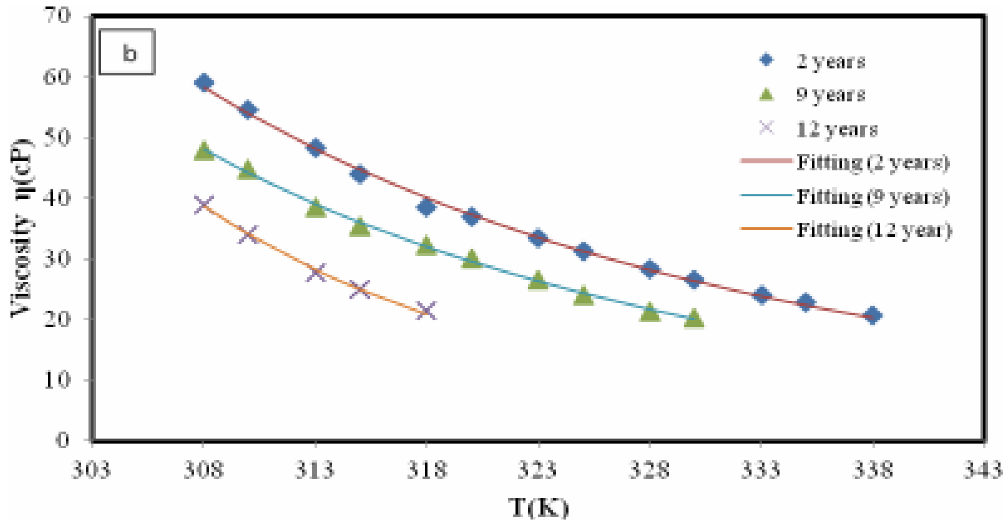
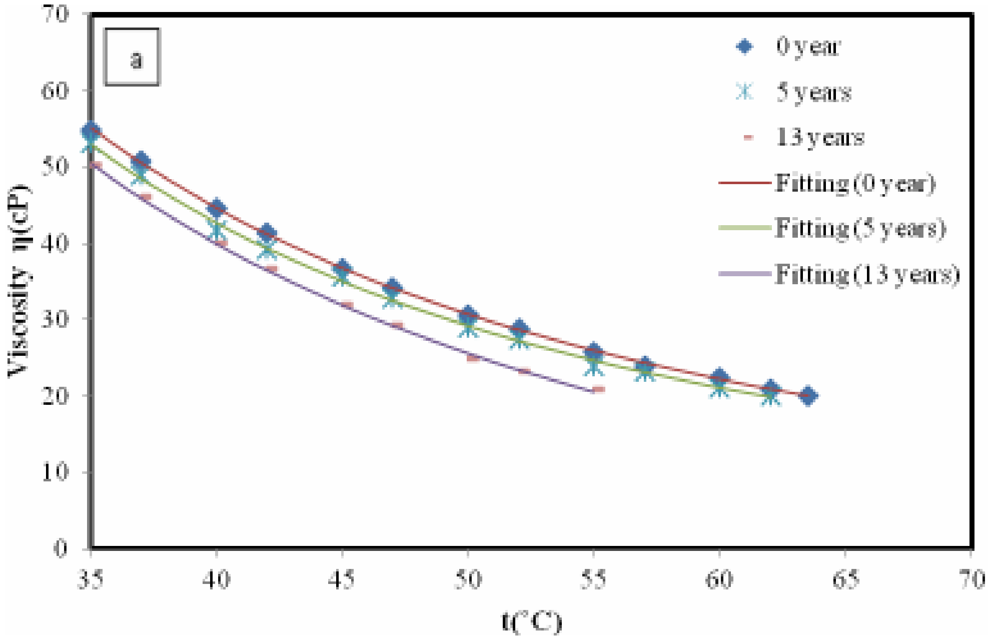


Figure (4.2): The dynamic viscosity of olive oil samples from two different locations a) L_1 and b) L_2 of different storage ages as function of temperature. The lines are representing our proposed three-constant formula and the points are representing our experimental data.



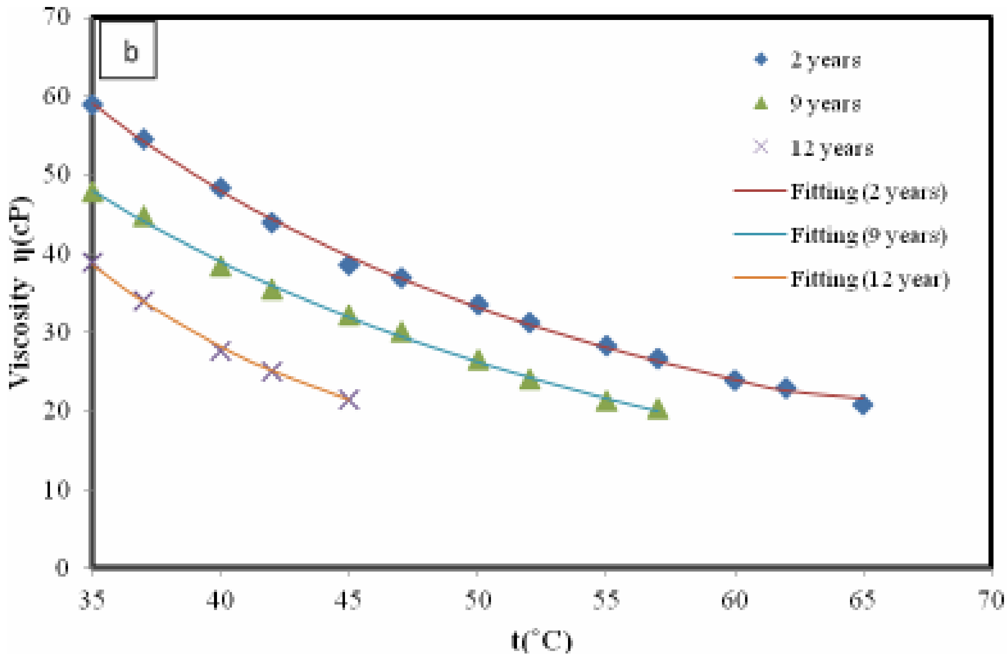


Figure (4.3): The dynamic viscosity of olive oil samples from two different locations a) L_1 and b) L_2 of different storage ages as function of temperature. The solid lines are representing our proposed multi-constant formula and the points are representing our experimental data.

4.2.1 II Weekly Basis

The dynamic viscosity of olive oil samples of the crop 2010 from two different locations (L_3 and L_4) at different temperatures was measured at different stages of storage in weeks, as given in Table 4.14.

Table (4.14): The measured values of the dynamic viscosity of olive oil samples from L_3 and L_4 as a function of temperature.

t(°C)	L_3			L_4			
	Storage age: 1week	Storage age: 3 weeks	Storage age: 8 weeks	Storage age: 1 week	Storage age: 3 weeks	Storage age: 6 weeks	Storage age: 7 weeks
	η (cP)						
42.0	37.7	36.6	35.9	39.9	37.4	33.1	32.9
45.0	33.2	33.1	31.9	35.6	32.9	29.3	28.3
47.0	30.9	30.6	29.0	32.1	30.7	26.6	26.0
50.0	27.6	27.5	26.1	28.4	27.6	23.6	23.0
52.0	25.7	25.0	23.5	26.6	25.9	22.3	20.6
55.0	23.2	22.5	21.7	24.2	23.2		
57.0	21.6	21.5	20.2	23.1	22.2		
60.0				20.4			

The dynamic viscosity of olive oil samples from different locations (L_3 and L_4) as a function of temperature, which was measured after some weeks, is plotted in Fig. 4.4 a and b.

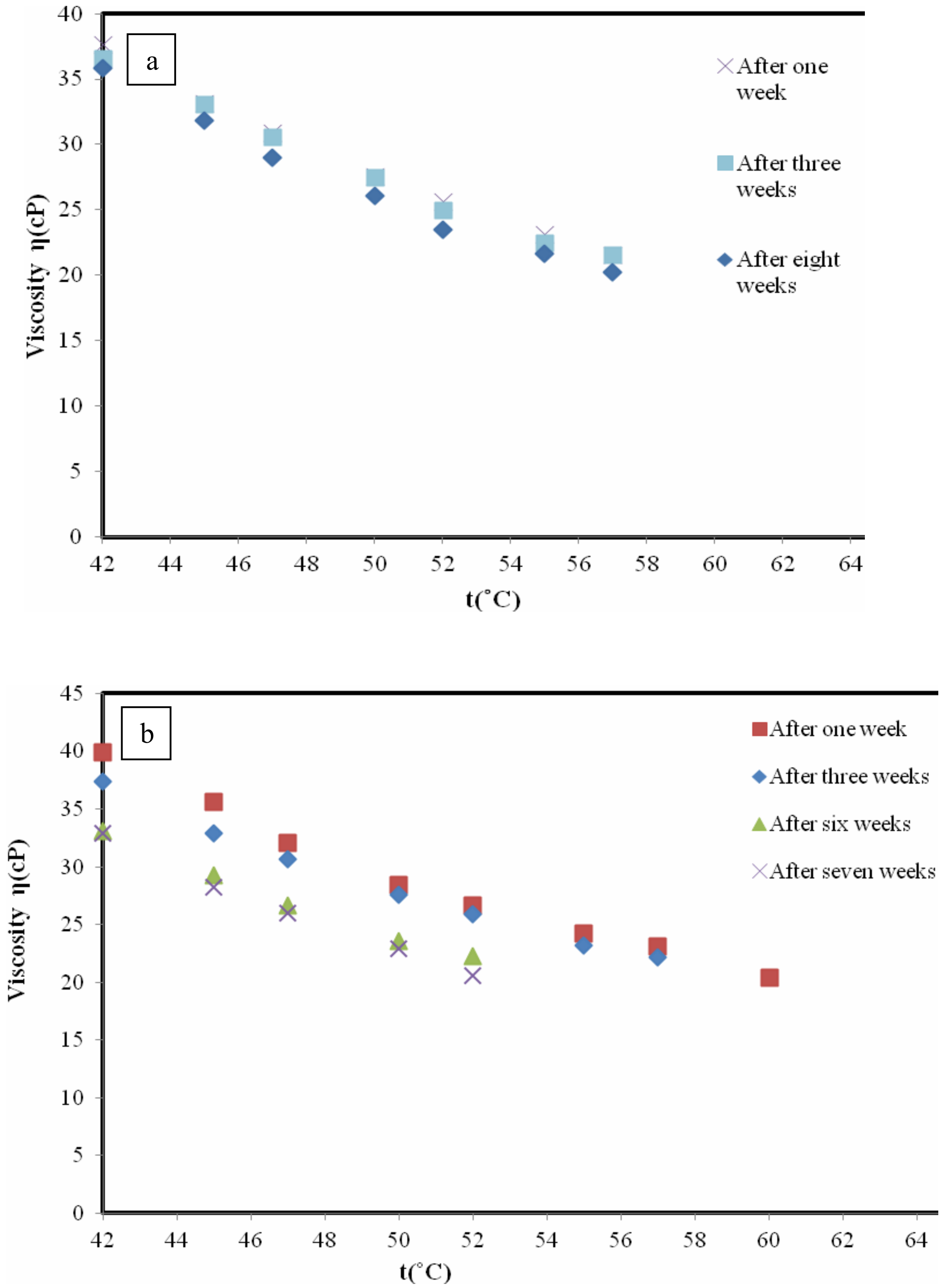


Figure (4.4): The measured values of the dynamic viscosity of olive oil samples from two different locations a) L_3 and b) L_4 for different storage age in weeks as a function of temperature.

A comparison was made between the measured experimental data of dynamic viscosity (η_{exp}) and the previously calculated values (η_{cal}). This calculated values found by two-constant formula of

Abramovic's $\eta = A - BLogt$ and three-constant formula of Andrade's $Ln\eta = A + \frac{B}{T} + CT$. A, B and C are constants for olive oil. It was found that the literature values didn't fit our experimental data. Tables 4.15, 4.16, 4.18 and 4.19 show η_{exp} and η_{cal} values. The computed results of AAD% and SD are given in Tables 4.17 and 4.20.

Table (4.15): Our experimental values and the calculated values of the dynamic viscosity of olive oil samples from L_3, using Abramovic's formula of two-constant.

t(°C)	Storage age: 1 week		Storage age: 3 weeks		Storage age: 8 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP))	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
42.0	37.7	34.0	36.6	34.0	35.9	34.0
45.0	33.2	30.2	33.1	30.2	31.9	30.2
47.0	30.9	27.9	30.6	27.9	29.0	27.9
50.0	27.6	24.6	27.5	24.6	26.1	24.6
52.0	25.7	22.4	25.0	22.4	23.5	22.4
55.0	23.2	19.4	22.5	19.4	21.7	19.4
57.0	21.6	17.5	21.5	17.5	20.2	17.5

Table (4.16): Our experimental values and the calculated values of the dynamic viscosity of L_4 at different temperatures using Abramovic's formula of two-constant.

t(°C)	Storage age: 1 week		Storage age: 3weeks		Storage age: 6 weeks		Storage age: 7 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP))	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
42.0	39.9	34.0	37.4	34.0	33.1	34.0	32.9	34.0
45.0	35.6	30.2	32.9	30.2	29.3	30.2	28.3	30.2
47.0	32.1	27.9	30.7	27.9	26.6	27.9	26.0	27.9
50.0	28.4	24.6	27.6	24.6	23.6	24.6	23.0	24.6
52.0	26.6	22.4	25.9	22.4	22.3	22.4	20.6	22.4
55.0	24.2	19.4	23.2	19.4				
57.0	23.1	17.5	22.2	17.5				
60.0	20.4	14.7						

Table (4.17): AAD% and SD using Abramovic's formula of two-constant.

Location	Storage age (week)	Temp. Range (°C)	AAD%	SD (cP)
L_3	1	42.0 – 57.0	12.4	3.4
	3	42.0 – 57.0	11.8	3.2
	8	42.0 – 57.0	6.9	1.8
L_4	1	42.0 – 60.0	18	5
	3	42.0 – 57.0	12.5	3.4
	6	42.0 – 55.0	3.1	0.9
	7	42.0 – 55.0	6.7	1.7

Table (4.18): Our experimental values and the calculated values of the dynamic viscosity of olive oil samples from L3 using Andrade's formula of three-constant.

T(°C)	Storage age: 1 week		Storage age: 3 weeks		Storage age: 8 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
315.0	37.7	35.5	36.6	35.5	35.9	35.5
318.0	33.2	32.0	33.1	32.0	31.9	32.0
320.0	30.9	30.0	30.6	30.0	29.0	30.0
323.0	27.6	27.2	27.5	27.2	26.1	27.2
325.0	25.7	25.6	25.0	25.6	23.5	25.6
328.0	23.2	23.4	22.5	23.4	21.7	23.4
330.0	21.6	22.0	21.5	22.0	20.2	22.0

Table (4.19): Our experimental values and calculated values of the dynamic viscosity of L4 at different temperature using Andrade's formula of three-constant.

t(°C)	Storage age: 1 week		Storage age: 3weeks		Storage age: 6 weeks		Storage age: 7 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
315.0	39.9	35.5	37.4	35.5	33.1	35.51	32.9	35.5
318.0	35.6	32.0	32.9	32.0	29.3	32.02	28.3	32.0
320.0	32.1	30.0	30.7	30.0	26.6	29.95	26.0	30.0
323.0	28.4	27.2	27.6	27.2	23.6	27.19	23.0	27.2
325.0	26.6	25.6	25.9	25.6	22.3	25.55	20.6	25.6
328.0	24.2	23.4	23.2	23.4				
330.0	23.1	22.0	22.2	22.0				
333.0	20.4	20.3						

Table (4.20): AAD% and SD using Andrade's formula of three-constant.

Location	Storage age (week)	Temp. Range (K)	AAD%	SD (cP)
L_3	1	315.0 – 330.0	1.6	1.0
	3	315.0 – 330.0	0.8	1.0
	8	315.0 – 330.0	4.7	1.3
L_4	1	315.0 – 333.0	5.5	2.3
	3	315.0 – 330.0	1.8	0.9
	6	315.0 – 325.0	11.8	3.1
	7	315.0 – 325.0	15.8	4.0

Using Abramovic's and Andrade's formulas, the AAD% values were found to be from 3.1% to 12.4% (Table 4.17) and from 0.8% to 15.8%, (Table 4.20), respectivaly. As a result, their formulas were not the best fit for our experimental data of dynamic viscosity of olive oil samples.

Abramovic's and Andrade's formulas didn't fit for our experimental data of dynamic viscosity of olive oil samples. Accordingly, a modification was introduced to their formula in order to obtain a suitable description of our experimental data of dynamic viscosity as a function of temperature. The constants of Abramovic's and Andrade's formulas were determined using the modification. Our experimental values (η_{exp}) and calculated values (η_{cal}), using the modified form of Abramovic's and Andrade's formulas of dynamic viscosity at different temperatures are given in Tables 4.21, 4.21, 4.24 and 4.25. Tables 4.23 and 4.26 tabulate AAD% and SD values.

Table (4.21): Our experimental values and calculated values of the dynamic viscosity of L3 at different temperatures, using the modified Abramovic's formula of two-constant.

t(°C)	Storage age: 1 week		Storage age: 3 weeks		Storage age: 8 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
42.0	37.7	37.4	36.6	37.0	35.9	35.7
45.0	33.2	33.9	33.1	33.4	31.9	32.2
47.0	30.9	31.6	30.6	31.2	29.0	30.0
50.0	27.6	28.4	27.5	27.9	26.1	26.8
52.0	25.7	26.3	25.0	25.9	23.5	24.8
55.0	23.2	23.4	22.5	23.0	21.7	21.9
57.0	21.6	21.6	21.5	21.1	20.2	20.0

Table (4.22): Our experimental values and our calculated values of the dynamic viscosity of L4 at different temperatures, using the modified Abramovic's formula of two-constant.

t(°C)	Storage age: 1 week		Storage age: 3weeks		Storage age: 6 weeks		Storage age: 7 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
42.0	39.9	39.4	37.4	37.0	33.1	32.4	32.9	32.9
45.0	35.6	35.6	32.9	33.6	29.3	28.8	28.3	29.0
47.0	32.1	33.3	30.7	31.4	26.6	26.6	26.0	26.6
50.0	28.4	29.9	27.6	28.4	23.6	23.4	23.0	23.1
52.0	26.6	27.8	25.9	26.4	22.3	21.3	20.6	20.9
55.0	24.2	24.8	23.2	23.7				
57.0	23.1	22.9	22.2	21.9				
60.0	20.4	20.1						

Table (4.23): Our values of A, B, AAD% and SD using the modified Abramovic's formula of two-constant of olive oil samples from L3 and L4.

Location	Storage age (week)	A(cP)	B (cP)	Temp. Range (°C)	AAD%	SD (cP)
L_3	1	231.5	119.5513	42.0 – 57.0	1.5	0.5
	3	231.2	119.6388	42.0 – 57.0	1.3	0.5
	8	228.0	118.4390	42.0 – 57.0	1.7	0.7
L_4	1	241.3	124.4046	42.0 – 60.0	1.6	0.9
	3	222.2	114.0817	42.0 – 57.0	1.4	0.6
	6	225.0	118.6790	42.0 – 55.0	1.8	0.6
	7	243.0	129.4211	42.0 – 55.0	1.5	0.5

Table (4.24): Our experimental values and our calculated values of the dynamic viscosity of L3 at different temperatures, using the modified Andrade's formula of three-constant.

T(K)	Storage age: 1 week		Storage age: 3 weeks		Storage age: 8 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
315.0	37.7	37.1	36.6	37.2	35.9	36.0
318.0	33.2	33.1	33.1	33.1	31.9	31.9
320.0	30.9	30.7	30.6	30.7	29.0	29.5
323.0	27.6	27.5	27.5	27.4	26.1	26.2
325.0	25.7	25.5	25.0	25.5	23.5	24.2
328.0	23.2	22.9	22.5	22.9	21.7	21.6
330.0	21.6	21.3	21.5	21.3	20.2	20.0

Table (4.25): Our experimental values and calculated values of the dynamic viscosity of L4 at different temperatures, using the modified Andrade's formula of three-constant.

T(K)	Storage age: 1 week		Storage age: 3weeks		Storage age: 6 weeks		Storage age: 7 weeks	
	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)	η_{exp} (cP)	η_{cal} (cP)
315.0	39.9	39.3	37.4	36.5	33.1	32.7	32.9	32.3
318.0	35.6	35.0	32.9	32.7	29.3	28.8	28.3	28.1
320.0	32.1	32.4	30.7	30.4	26.6	26.5	26.0	25.6
323.0	28.4	28.9	27.6	27.3	23.6	23.4	23.0	22.3
325.0	26.6	26.8	25.9	25.5	22.3	21.6	20.6	20.4
328.0	24.2	24.0	23.2	22.9				
330.0	23.1	22.3	22.2	21.4				
333.0	20.4	20.0						

Table (4.26): Our values of A, B, AAD% and SD using the modified Andrade's formula of three-constant of olive oil samples from L3 and L4.

Location	**Storage age (weeks)**	**A**	**B** (K)	**C** (K^2) $\times 10^{-5}$	**Temp. Range (K)**	**AAD %**	**SD**
L_3	1	-3.64	3050.001	-771	315.0 – 330.0	0.9	0.3
	3	-3.60	3052.000	-785	315.0 – 330.0	0.6	0.3
	8	-3.00	3050.289	-984	315.0 – 330.0	0.7	0.4
L_4	1	-3.31	3050.287	-858	315.0 – 333.0	0.7	0.5
	3	-4.14	3050.281	-618	315.0 – 330.0	1.6	0.5
	6	-2.60	3050.291	-1142	315.0 – 325.0	1.4	0.4
	7	-1.13	3050.299	-1612	315.0 – 325.0	1.5	0.4

Table 4.23 shows AAD% ≤ 1.8%. Table 4.26 shows AAD% ≤ 1.6%. The results indicate that the modified form of Abramovic's and Andrade's formulas didn't fit exactly our experimental data.

The values of the constants of the modified form of Abramovic's and Andrade's formulas in Tables 4.23 and 4.26 are in disagreement with Abramovic's values (Table 4.11). This is might be due to free fatty acid composition of different olive oil samples.

Three and multi-constant formulas were proposed by this work to obtain more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples. The η_{exp} and η_{cal} were used to propose the formulas that fit our experimental. That is, AAD% and SD values are chosen to select the suitable prediction.

If two-constant formula is proposed the fitting curves will not be in good agreement with the experimental data. Accordingly, the two-constant formula is not suitable for our experimental data where the AAD% gives very high value.

It was found that the proposed formula of three-constant $Ln\eta = A - \frac{B}{T+C}$ and multi-constant $\eta = A + \frac{B}{t} + CLn(t) + Dt^E$ fit our experimental data of dynamic viscosity. Our calculated values of A, B, C, D, E, AAD% and SD of the data, are given in Tables 4.27 and 4.28.

Table (4.27): Our values of A, B, C, AAD% and SD using our proposed three-constant formula of olive oil samples of L3 and L4.

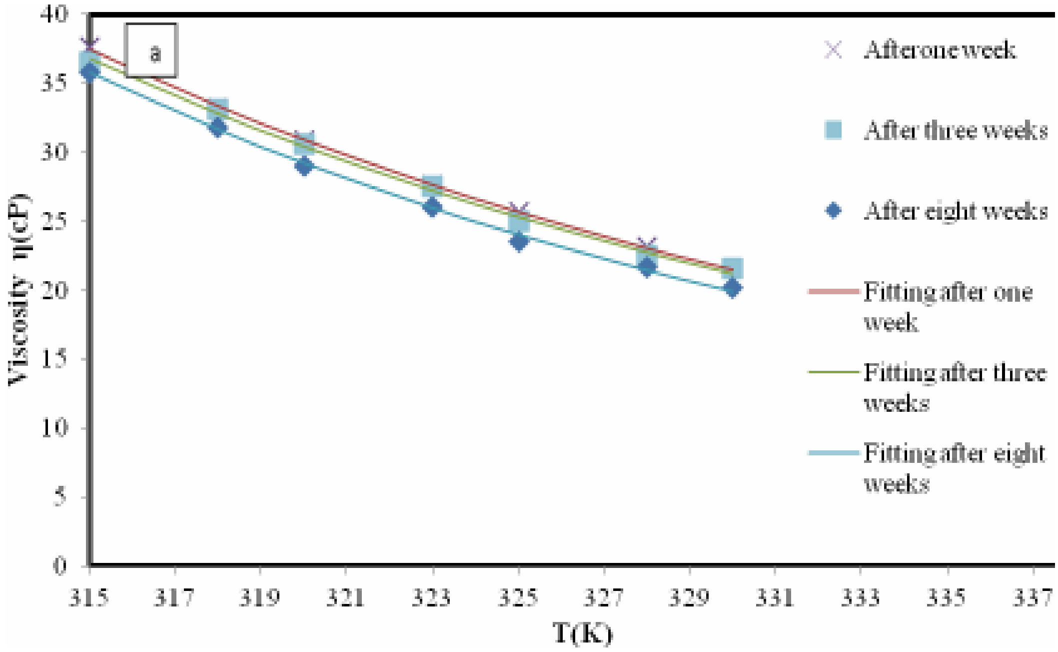
Location	Storage age (weeks)	A	B (K)	C (K)	Temp. Range (K)	AAD %	SD (cP)
L_3	1	-7.30653	-3053.11	-35.6963	315.0 – 330.0	0.0	0.1
	3	-7.25578	-3053.05	-33.9289	315.0 – 330.0	0.0	0.3
	8	-7.62857	-3053.43	-42.5131	315.0 – 330.0	0.0	0.3
L_4	1	-7.36674	-3053.25	-38.5983	315.0 – 333.0	0.1	0.4
	3	-7.04828	-3052.78	-28.6302	315.0 – 330.0	0.0	0.2
	6	-7.87487	-3053.66	-46.5050	315.0 – 325.0	0.0	0.2
	7	-8.57047	-3054.37	-61.7518	315.0 – 325.0	0.0	0.2

Table (4.28): Our values of A, B, C, D, E, AAD% and SD using our proposed multi-constants formula.

Location	Storage age (week)	A (cP)	B (cP.°C)	C (cP)	D(cP/°C^E)	E	Temp Range (°C)	AAD %	SD (cP)
L_3	1	-150.31904	3820.695	25.94402	694.2263	-2624.33	42.0 – 57.0	0.0	0.1
	3	41.22569	1897.006	-13.18860	694.2263	-2624.33	42.0 – 57.0	0.0	0.4
	8	-299.88700	5270.429	56.30426	694.2263	-2624.33	42.0 – 57.0	0.0	0.2
L_4	1	-355.97400	6073.650	67.27800	694.2263	-2624.33	42.0 – 60.0	0.2	0.3
	3	-229.89000	4514.184	42.72617	694.2263	-2624.33	42.0 – 57.0	0.0	0.1
	6	-1134.18000	13876.920	225.60200	694.2263	-2624.33	42.0 – 55.0	0.0	0.4
	7	-1116.07000	13878.850	220.74040	694.2263	-2624.33	42.0 – 55.0	0.0	0.6

Tables 4.27 and 4.28 show that AAD% $\leq$ 0.2%; therefore, our proposed two and multi-constant formulas are more suitable to describe the temperature dependence of dynamic viscosity of olive oil samples.

Fig. 4.5 a and b and 4.6 a and b show our experimental data and our fitting curves using our proposed three and multi-constant formulas of dynamic viscosity of olive oil samples from two different locations (L_3 and L_4) of different storage ages as a function of temperature.



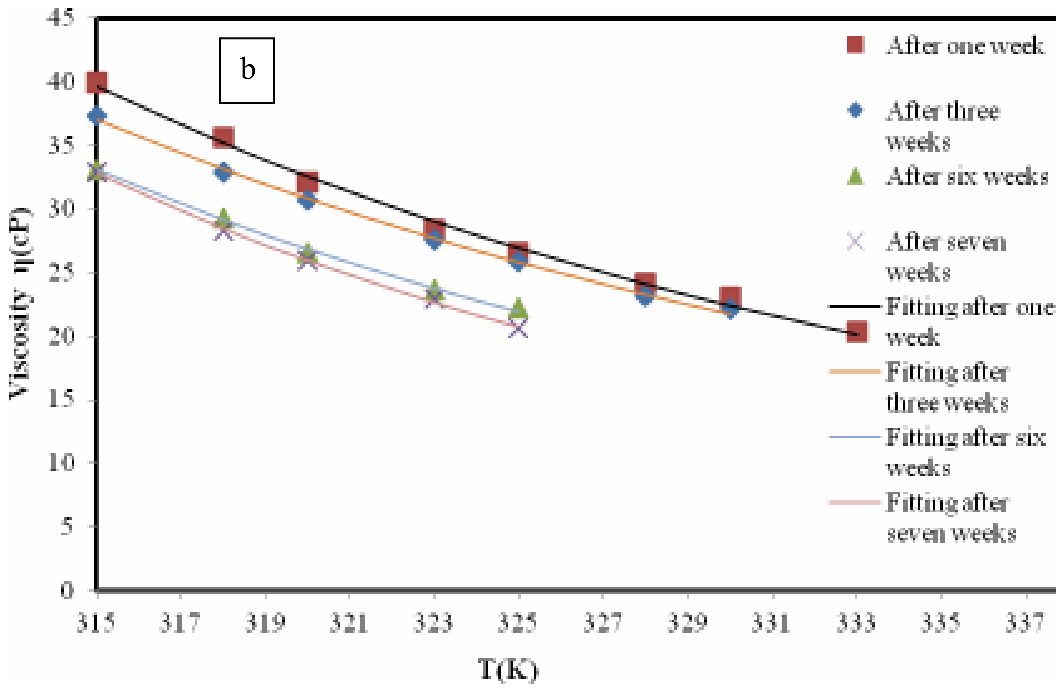
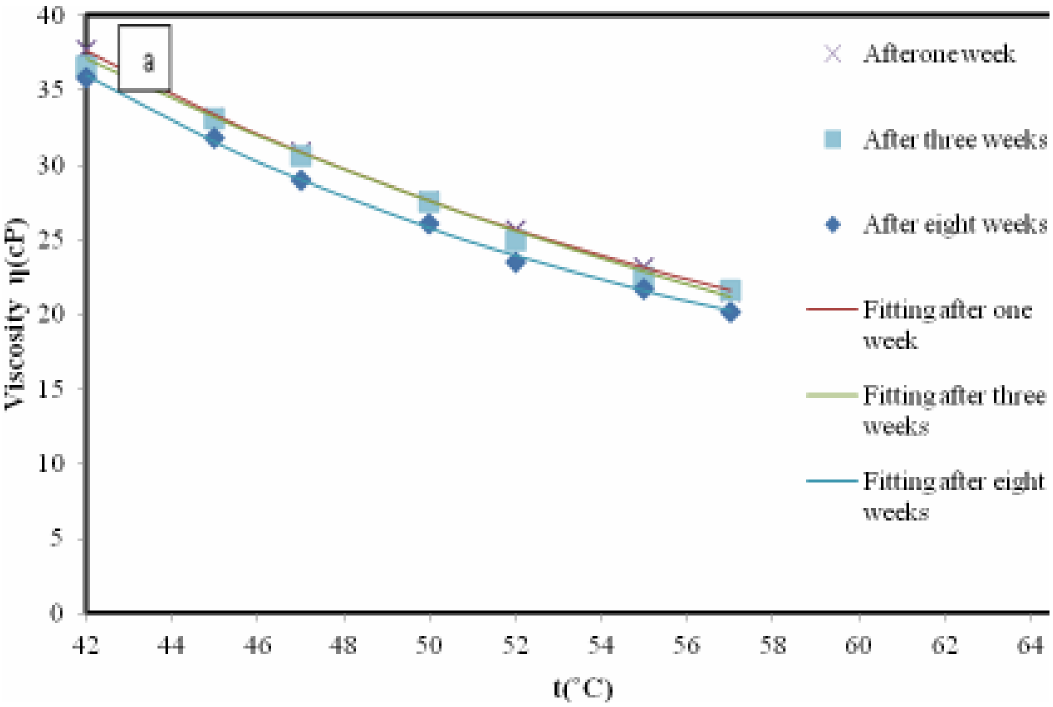


Figure (4.5): The dynamic viscosity of olive oil samples from two different locations a) L_3 and b) L_4 of different storage ages as function of temperature. The solid lines are representing our proposed three-constant formula and the points are representing our experimental data.



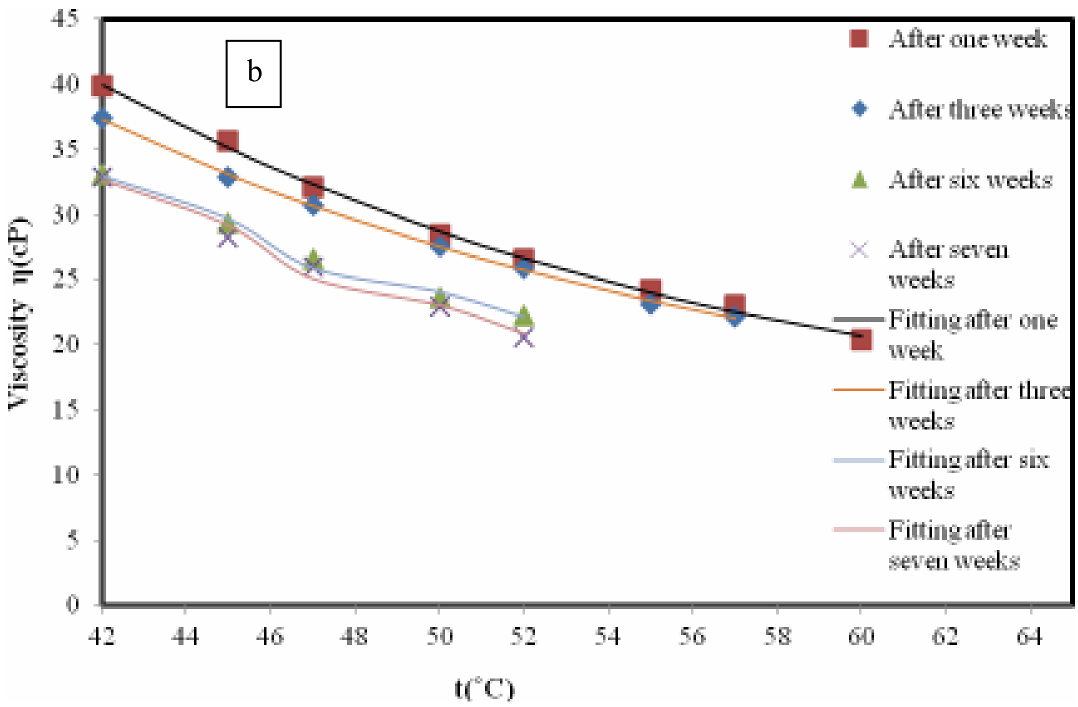


Figure (4.6): The dynamic viscosity of olive oil samples from two different locations a) L_3 and b) L_4 of different storage ages as function of temperature. The solid lines are representing our proposed multi-constant formula and the points are representing our experimental data.

4.2.1. III Olive Oil Crop 2010

The dynamic viscosity of olive oil of crop 2010 from L_5 as a function of temperature was measured. The experimental values of dynamic viscosity as a function of temperature are tabulated in Table 4.29.

Table (4.29): The measured values of dynamic viscosity of olive oil from L5 olive oil as a function of temperature.

t(°C)	η(cP)	t(°C)	η(cP)	t(°C)	η(cP)	t(°C)	η(cP)	t(°C)	η(cP)
19.0	86.3	29.0	51.0	39.0	34.8	49	26.2	59.0	21.0
19.5	83.0	29.5	50.0	39.5	34.0	49.5	26.0	59.5	20.8
20.0	80.3	30.0	48.8	40.0	33.5	50.0	26.0	60.0	20.7
20.5	77.7	30.5	47.8	40.5	33.0	50.5	25.7	60.5	20.3
21.0	75.2	31.0	47.0	41.0	32.3	51.0	25.3		
21.5	72.8	31.5	46.0	41.5	32.0	51.5	25.0		
22.0	70.8	32.0	45.2	42.0	31.5	52	24.8		
22.5	69.0	32.5	44.2	42.5	31.0	52.5	24.3		
23.0	67.5	33.0	43.3	43.0	30.5	53.0	24.3		
23.5	65.8	33.5	42.5	43.5	30.0	53.5	24.0		
24.0	64.0	34.0	41.8	44.0	29.5	54.0	23.7		
24.5	62.3	34.5	41.0	44.5	29.2	54.5	23.5		
25.0	60.7	35.0	40.5	45.0	29.0	55.0	23.2		
25.5	59.3	35.5	39.8	45.5	28.5	55.5	23.0		
26.0	58.2	36.0	39.2	46.0	28	56.0	22.7		
26.5	56.7	36.5	38.3	46.5	27.7	56.5	22.5		
27.0	55.5	37.0	37.5	47.0	27.2	57.0	22.2		
27.6	54.5	37.5	37.3	47.5	27.0	57.5	21.8		
28.0	53.0	38.0	36.0	48.0	26.7	58.0	21.7		
28.5	52.0	38.5	35.3	48.5	26.3	58.5	21.3		

The dynamic viscosity of olive oil of crop 2010 from L_5 as a function of temperature through increasing temperature is shown in Fig. (4.7).

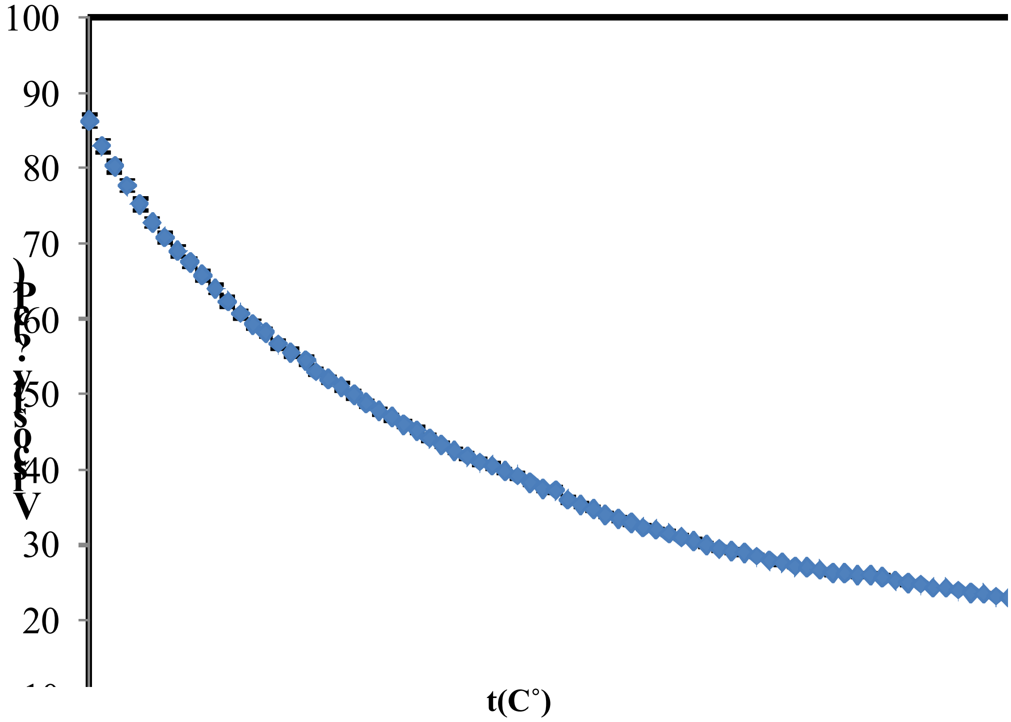


Figure (4.7): The measured values of dynamic viscosity of olive oil from L_5 as a function of temperature (with vertical error bars).

The previously calculated values (η_{cal}), found by Abramovic's formula of two-constant $\eta = A - BLogt$, and Andrade's formula of three-constant $Ln\eta = A + \frac{B}{T} + CT$, were compared with our experimental values of dynamic viscosity (η_{exp}). A, B and C are constants for olive oil. However, Abramovic's and Andrade's formulas failed to fit our measured experimental values of dynamic viscosity. Tables 4.30 and 4.32 show η_{exp} and η_{cal} values. Results of computation of values of AAD% and SD are tabulated in Tables 4.31 and 4.33.

Table (4.30): Our experimental values and calculated values of dynamic viscosity at different temperatures, using Abramovic's formula of two-constant.

t(°C)	η_{exp} (cP)	η_{cal} (cP)	t(°C)	η_{exp} (cP)	η_{cal} (cP)	t(°C)	η_{exp} (cP)	η_{cal} (cP)
19.0	86.3	76.7	33.5	42.5	46.1	48.0	26.7	26.8
19.5	83.0	75.3	34.0	41.8	45.3	48.5	26.3	26.2
20.0	80.3	73.9	34.5	41.0	44.6	49.0	26.2	25.6
20.5	77.7	72.6	35.0	40.5	43.8	49.5	26.0	25.1
21.0	75.2	71.3	35.5	39.8	43.0	50.0	26.0	24.6
21.5	72.8	70.0	36.0	39.2	42.3	50.5	25.7	24.0
22.0	70.8	68.8	36.5	38.3	41.5	51.0	25.3	23.5
22.5	69.0	67.6	37.0	37.5	40.8	51.5	25.0	23.0
23.0	67.5	66.4	37.5	37.3	40.1	52.0	24.8	22.4
23.5	65.8	65.3	38.0	36.0	39.3	52.5	24.3	21.9
24.0	64.0	64.1	38.5	35.3	38.6	53.0	24.3	21.4
24.5	62.3	63.0	39.0	34.8	37.9	53.5	24.0	20.9
25.0	60.7	61.9	39.5	34.0	37.3	54.0	23.7	20.4
25.5	59.3	60.8	40.0	33.5	36.6	54.5	23.5	19.9
26.0	58.2	59.8	40.5	33.0	35.9	55.0	23.2	19.4
26.5	56.7	58.8	41.0	32.3	35.3	55.5	23.0	18.9
27.0	55.5	57.8	41.5	32.0	34.6	56.0	22.7	18.4
27.6	54.5	56.6	42.0	31.5	34.0	56.5	22.5	18.0
28.0	53.0	55.8	42.5	31.0	33.3	57.0	22.2	17.5
28.5	52.0	54.9	43.0	30.5	32.7	57.5	21.8	17.0
29.0	51.0	53.9	43.5	30.0	32.1	58.0	21.7	16.6
29.5	50.0	53.0	44.0	29.5	31.4	58.5	21.3	16.1
30.0	48.8	52.1	44.5	29.2	30.8	59.0	21.0	15.6
30.5	47.8	51.2	45.0	29.0	30.2	59.5	20.8	15.2
31.0	47.0	50.3	45.5	28.5	29.6	60.0	20.7	14.7
31.5	46.0	49.5	4.0	28	29.1	60.5	20.3	14.3
32.0	45.2	48.6	46.5	27.7	28.5			
32.5	44.2	47.8	47.0	27.2	27.9			
33.0	43.3	47.0	47.5	27.0	27.3			

Table (4.31): AAD% and SD of the data using Abramovic's formulas of two-constant.

AAD%	SD (cP)	Temperature range (°C)
0.6	3.4	19.0 – 60.5

Table (4.32): Our experimental values and calculated values of dynamic viscosity at different temperatures, using Andrade's formula of three-constant.

T(K)	η_{exp} (cP)	η_{cal} (cP)	T(K)	η_{exp} (cP)	η_{cal} (cP)	T(K)	η_{exp} (cP)	η_{cal} (cP)
292.0	86.3	91.4	306.5	42.5	48.8	321.0	26.7	29.0
292.5	83.0	89.3	307.0	41.8	47.8	321.5	26.3	28.5
293.0	80.3	87.2	307.5	41.0	46.9	322.0	26.2	28.1
293.5	77.7	85.2	308.0	40.5	46.0	322.5	26.0	27.6
294.0	75.2	83.3	308.5	39.8	45.1	323.0	26.0	27.2
294.5	72.8	81.4	309.0	39.2	44.2	323.5	25.7	26.8
295.0	70.8	79.5	309.5	38.3	43.4	324.0	25.3	26.4
295.5	69.0	77.7	310.0	37.5	42.6	324.5	25.0	26.0
296.0	67.5	76.0	310.5	37.3	41.8	325.0	24.8	25.6
296.5	65.8	74.3	311.0	36.0	41.0	325.5	24.3	25.2
297.0	64.0	72.6	311.5	35.3	40.3	326.0	24.3	24.8
297.5	62.3	71.0	312.0	34.8	39.5	326.5	24.0	24.4
298.0	60.7	69.5	312.5	34.0	38.8	327.0	23.7	24.1
298.5	59.3	68.0	313.0	33.5	38.1	327.5	23.5	23.7
299.0	58.2	66.5	313.5	33.0	37.5	328.0	23.2	23.4
299.5	56.7	65.1	314	32.3	36.8	328.5	23.0	23.0
300.0	55.5	63.7	314.5	32.0	36.1	329.0	22.7	22.7
300.6	54.5	62.1	315.0	31.5	35.5	329.5	22.5	22.4
301.0	53.0	61.0	315.5	31.0	34.9	330.0	22.2	22.0
301.5	52.0	59.8	316.0	30.5	34.3	330.5	21.8	21.7
302.0	51.0	58.5	316.5	30.0	33.7	331.0	21.7	21.4
302.5	50.0	57.3	317.0	29.5	33.1	331.5	21.3	21.1
303.0	48.8	56.1	317.5	29.2	32.6	332.0	21.0	20.8
303.5	47.8	55.0	318.0	29.0	32.0	332.5	20.8	20.6
304.0	47.0	53.9	318.5	28.5	31.5	333.0	20.7	20.3
304.5	46.0	52.8	319.0	28	31.0	333.5	20.3	20.0
305.0	45.2	51.8	319.5	27.7	30.5			
305.5	44.2	50.7	320.0	27.2	30.0			
306.0	43.3	49.7	320.5	27.0	29.5			

Table (4.33): AAD% and SD of the data using Andrade's formula of three-constant.

AAD%	SD (cP)	Temperature range (K)
9.5	5.2	292.0 – 333.5

Abramovic's and Andrade's formulas were not the best fit for our experimental data of dynamic viscosity of olive oil sample because the AAD% values found to be 0.6% and 9.5%, respectively (Tables 4.31 and 4.33).

Abramovic's and Andrade's formulas failed to fit our experimental data. This work, therefore, introduced a modification to Abramovic's and Andrade's formulas in order to obtain a suitable description of our experimental data of dynamic viscosity. This modification, by using Abramovic’s and Andrade's formulas, determined the constants of Abramovic's and Andrade's formulas. Tables 4.34 and 4.36 show our experimental values (η_{exp}) and calculated values (η_{cal}) using the modified form of Abramovic’s and Andrade's formula of dynamic viscosity at different temperatures. Tables 4.35 and 4.37 tabulate AAD% and SD values.

Table (4.34): Our experimental values and calculated values of dynamic viscosity at different temperatures, using the modified Abramovic's formula of two-constant.

t(°C)	η_{exp} (cP)	η_{cal} (cP)	t(°C)	η_{exp} (cP)	η_{cal} (cP)	t(°C)	η_{exp} (cP)	η_{cal} (cP)
19.0	86.3	75.4	33.5	42.5	46.0	48.0	26.7	27.3
19.5	83.0	74.0	34.0	41.8	45.2	48.5	26.3	26.8
20.0	80.3	72.7	34.5	41.0	44.4	49.0	26.2	26.3
20.5	77.7	71.4	35.0	40.5	43.7	49.5	26.0	25.7
21.0	75.2	70.2	35.5	39.8	43.0	50.0	26.0	25.2
21.5	72.8	69.0	36.0	39.2	42.2	50.5	25.7	24.7
22.0	70.8	67.8	36.5	38.3	41.5	51.0	25.3	24.2
22.5	69.0	66.6	37.0	37.5	40.8	51.5	25.0	23.7
23.0	67.5	65.5	37.5	37.3	40.1	52.0	24.8	23.2
23.5	65.8	64.4	38.0	36.0	39.4	52.5	24.3	22.7
24.0	64.0	63.3	38.5	35.3	38.8	53.0	24.3	22.2
24.5	62.3	62.2	39.0	34.8	38.1	53.5	24.0	21.7
25.0	60.7	61.1	39.5	34.0	37.4	54.0	23.7	21.2
25.5	59.3	60.1	40.0	33.5	36.8	54.5	23.5	20.7
26.0	58.2	59.1	40.5	33.0	36.1	55.0	23.2	20.3
26.5	56.7	58.1	41.0	32.3	35.5	55.5	23.0	19.8
27.0	55.5	57.2	41.5	32.0	34.9	56.0	22.7	19.3
27.6	54.5	56.0	42.0	31.5	34.2	56.5	22.5	18.9
28.0	53.0	55.3	42.5	31.0	33.6	57.0	22.2	18.4
28.5	52.0	54.4	43.0	30.5	33.0	57.5	21.8	18.0
29.0	51.0	53.5	43.5	30.0	32.4	58.0	21.7	17.5
29.5	50.0	52.6	44.0	29.5	31.8	58.5	21.3	17.1
30.0	48.8	51.7	44.5	29.2	31.3	59.0	21.0	16.6
30.5	47.8	50.8	45.0	29.0	30.7	59.5	20.8	16.2
31.0	47.0	50.0	45.5	28.5	30.1	60.0	20.7	15.8
31.5	46.0	49.2	4.0	28	29.5	60.5	20.3	15.3
32.0	45.2	48.3	46.5	27.7	29.0			
32.5	44.2	47.5	47.0	27.2	28.4			
33.0	43.3	46.8	47.5	27.0	27.9			

Table (4.35): Our values of A, B, AAD% and SD using the modefied Abramovic's formula of two-constant.

A(cP)	B (cP)	Temp Range (°C)	AAD%	SD (cP)
228.0487	119.3898	19.0 – 60.5	0.4	3.3

Table (4.36): Our experimental values and our calculated values of dynamic viscosity at different temperatures, using the modified Andrade's formula of three-constant.

T(K)	η_{exp} (cP)	η_{cal} (cP)	T(K)	η_{exp} (cP)	η_{cal} (cP)	T(K)	η_{exp} (cP)	η_{cal} (cP)
292.0	86.3	83.0	306.5	42.5	41.7	321.0	26.7	26.4
292.5	83.0	80.7	307.0	41.8	40.9	321.5	26.3	26.0
293.0	80.3	78.5	307.5	41.0	40.1	322.0	26.2	25.7
293.5	77.7	76.4	308.0	40.5	39.4	322.5	26.0	25.4
294.0	75.2	74.4	308.5	39.8	38.7	323.0	26.0	25.1
294.5	72.8	72.4	309.0	39.2	38.0	323.5	25.7	24.9
295.0	70.8	70.5	309.5	38.3	37.3	324.0	25.3	24.6
295.5	69.0	68.7	310.0	37.5	36.6	324.5	25.0	24.3
296.0	67.5	67.0	310.5	37.3	36.0	325.0	24.8	24.1
296.5	65.8	65.3	311.0	36.0	35.4	325.5	24.3	23.8
297.0	64.0	63.7	311.5	35.3	34.8	326.0	24.3	23.6
297.5	62.3	62.1	312.0	34.8	34.2	326.5	24.0	23.4
298.0	60.7	60.6	312.5	34.0	33.6	327.0	23.7	23.1
298.5	59.3	59.2	313.0	33.5	33.1	327.5	23.5	22.9
299.0	58.2	57.8	313.5	33.0	32.5	328.0	23.2	22.7
299.5	56.7	56.4	314	32.3	32.0	328.5	23.0	22.5
300.0	55.5	55.1	314.5	32.0	31.5	329.0	22.7	22.3
300.6	54.5	53.6	315.0	31.5	31.1	329.5	22.5	22.1
301.0	53.0	52.6	315.5	31.0	30.6	330.0	22.2	21.9
301.5	52.0	51.5	316.0	30.5	30.1	330.5	21.8	21.8
302.0	51.0	50.3	316.5	30.0	29.7	331.0	21.7	21.6
302.5	50.0	49.2	317.0	29.5	29.3	331.5	21.3	21.4
303.0	48.8	48.2	317.5	29.2	28.9	332.0	21.0	21.3
303.5	47.8	47.2	318.0	29.0	28.5	332.5	20.8	21.1
304.0	47.0	46.2	318.5	28.5	28.1	333.0	20.7	21.0
304.5	46.0	45.2	319.0	28	27.7	333.5	20.3	20.8
305.0	45.2	44.3	319.5	27.7	27.4			
305.5	44.2	43.4	320.0	27.2	27.0			
306.0	43.3	42.6	320.5	27.0	26.7			

Table (4.37): Our values of A, B, C, AAD% and SD using the modified Andrade's formula of three-constant

A	B (K)	C (K)	Temp. Range (K)	AAD%	SD (cP)
-86.11	15609.03	0.126963	292.0 – 333.5	1.4	0.8

Table 4.35 shows AAD% = 0.4% and Table 4.37 shows AAD% = 1.4%. This indicates that Abramovic's and Andrade's formulas don't fit exactly our experimental data.

The values of the constants A, B and C of the modified form of Abramovic's and Andrade's formulas in Tables 4.35 and 4.37 are in disagreement with Abramovic's values (Table 4.11). The different values were probably due to free fatty acid composition of different olive oil samples.

To obtain a more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples, three and multi-constant formulas were proposed. To estimate the equations, the η_{exp} and η_{cal} were used. That is, AAD% and SD values are chosen to select the suitable prediction.

If two-constant formula is proposed the fitting curves will not be in good agreement with the experimental data. Accordingly, the two-constant formula is not suitable for our experimental data where the AAD% gives very high value.

This study found that our proposed formula of three-constant $Ln\eta = A - \frac{B}{T+C}$ and multi-constant $\eta = A + \frac{B}{t} + CLn(t) + Dt^{E}$ fit our experimental data of dynamic viscosity. Our calculated values of the constants (A, B, C, D and E), AAD% and SD of the data are given in Table 4.38.

Table (4.38): Our values of A, B, C, D and E, AAD% and SD using our proposed formula.

our proposed formula	A	B	C	D	E	Temp. Range	AAD%	SD (cP)
three-constant	1.261552	-163.511 K	-240.637 K	-	-	292.0 – 333.5 K	0	0.3
multi-constant	-70.4707 cP	2222.396 cP.°C	694.2263 cP	-2624.33 cP/°C^E	13.22235	19.0 – 60.5 °C	0	0.3

Table 4.38 shows that AAD% = 0%; therefore, our proposed two and multi-constant formulas are more suitable to describe the temperature dependence of dynamic viscosity of olive oil sample.

Fig. 4.8 and 4.9 show our experimental data and our fitting curves using our proposed three and multi-constant formulas of dynamic viscosity of olive oil sample from L_5 as a function of temperature.

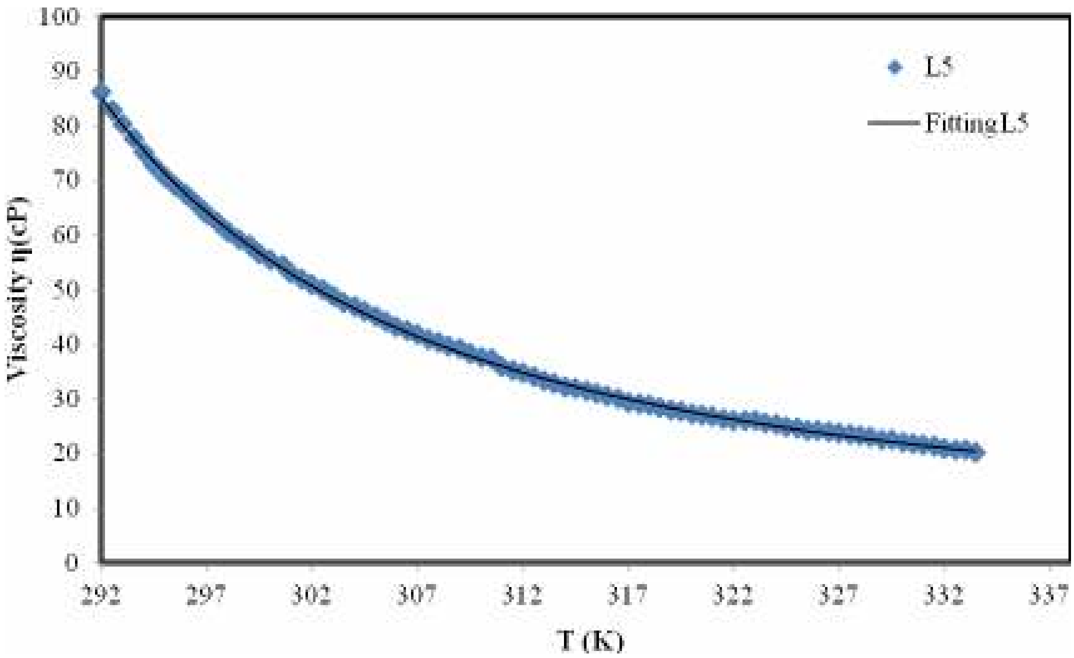


Figure (4.8): The dynamic viscosity of olive oil from L5 as a function of temperature. The solid line is representing our proposed three-constant formula and the points are representing our experimental data.

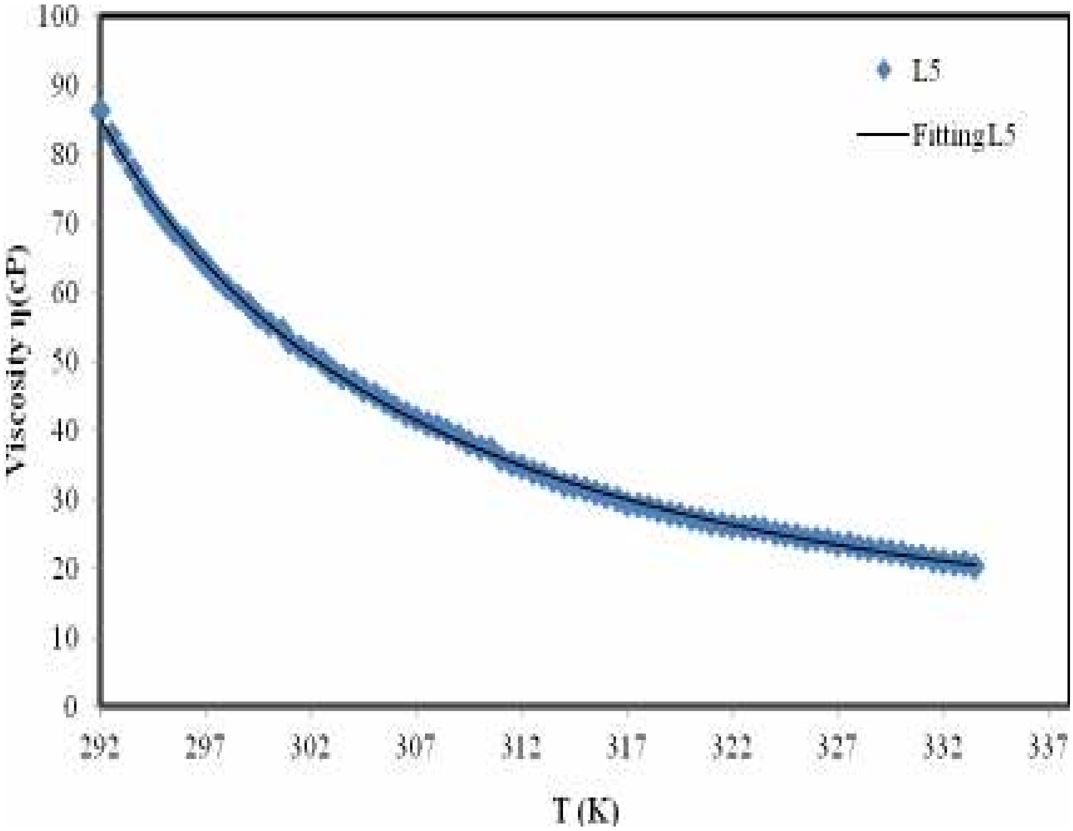


Figure (4.9): The dynamic viscosity of olive oil from L_5 as a function of temperature. The solid line is representing our proposed multi-constant formula and the points are representing our experimental data.

4.2.2 Storage Age-Dependence of Dynamic Viscosity

4.2.2 I Yearly Basis

The dynamic viscosity of olive oil samples from two locations (L_1 and L_2) was measured as a function of storage age in years at 45 ºC as given in Table 4.39.

Table (4.39): The measured values of dynamic viscosity of olive oil samples from L1 and L2 as a function storage age.

L_1		L_2	
Storage age (year)	η (cP)	Storage age (year)	η (cP)
0	36.6	2	38.5
5	35.7	9	32.2
13	32.0	12	21.5

The experimental values of dynamic viscosity of olive oil samples from L_1 and L_2 as a function of storage age at 45ºC are shown in Fig. (4.10).

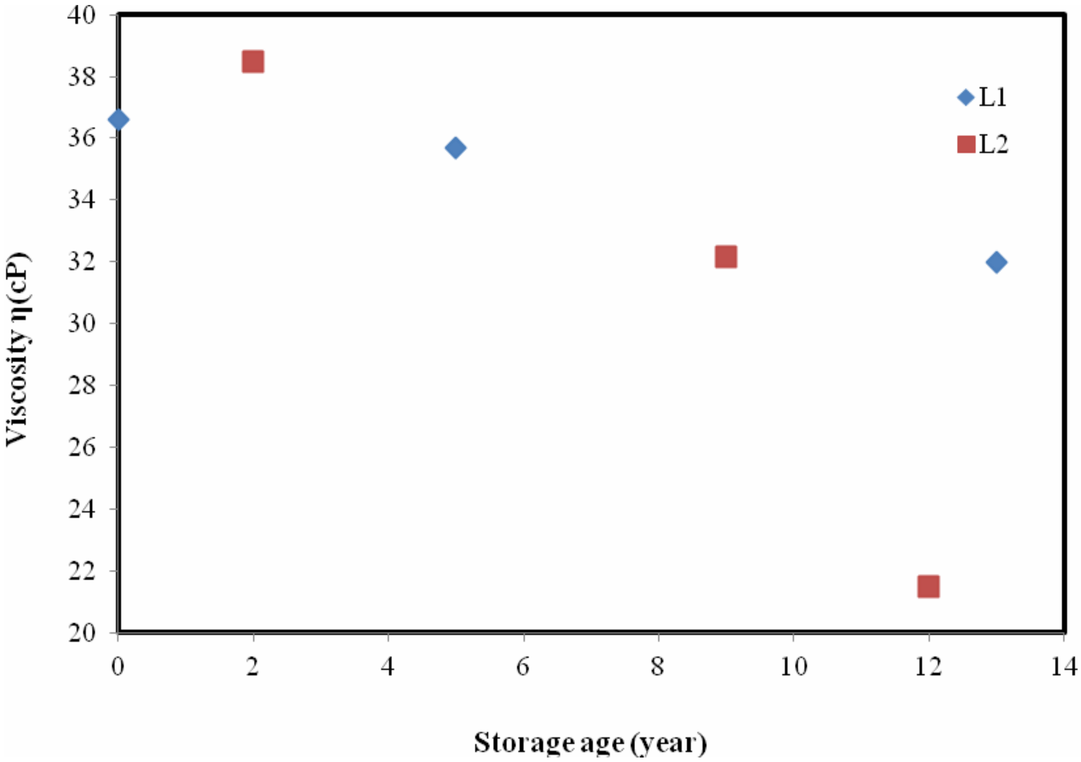


Figure (4.10): The measured values of dynamic viscosity of olive oil samples from L1 and L_2 as function of storage age.

Multi-constant formula is proposed by this work to obtain more suitable prediction of storage age dependence of dynamic viscosity of olive oil samples. The η_{exp} and η_{cal} were used to propose the formula that fits our experimental data. That is, AAD% and SD values are chosen to select the suitable prediction.

The experimental values of the dynamic viscosity of olive oil samples from L_1 and L_2 of different storage ages were fitted by using our multi-constant formula. Our multi-constant formula is proposed to be:

$$\eta = At^2 + Bt + C + De^{Et} \tag{4.1}$$

Where η is the dynamic viscosity in cP, t is the storage age in years, A, B, C, D and E are constants. Our calculated values of A, B, C, D, E, AAD% and SD of the data, are given in Table 4.40.

Table (4.40): Our values of A, B, C, D and E, AAD% and SD using our proposed formula.

The location	A ($cP/years^2$)	B (cP/year)	C (cP)	D (cP)	E	AAD%	SD
L_1	-0.149	2.252	27.918	8.682	-0.709	0.0	0.0
L_2	-0.311	3.199	27.039	9.396	-0.199	0.0	0.0

Table 4.40 shows that AAD% = 0%. Accordingly, our proposed multi-constant formula is suitable to describe the storage age dependence of dynamic viscisity of olive oil sample.

Fig. 4.11 shows our experimental data and our fitting curves using equation 4.1 of dynamic viscosity of olive oil samples from L_1 and L_2 as a function of storage age in years.

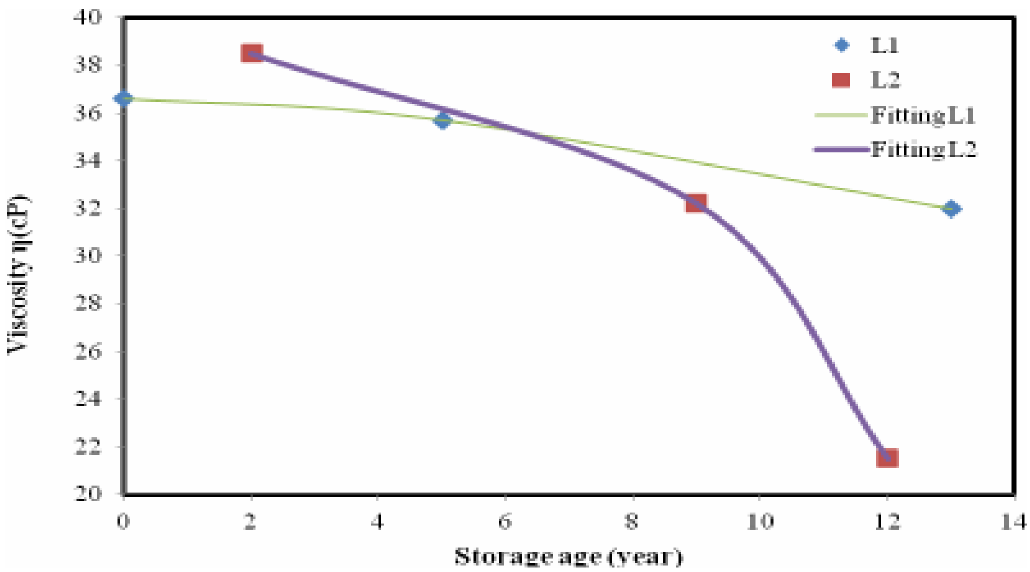


Figure (4.11): The dynamic viscosity of olive oil samples from L_1 and L_2 as a function of storage age in years. The solid lines are representing equation 4.1 and the points are representing our experimental data.

4.2.2 II Weekly Basis

Our experimental results of dynamic viscosity measurements at different storage ages in weeks for olive oil samples from two locations (L_3 and L_4) at 47°C are given in Table 4.41.

Table (4.41): The measured values of dynamic viscosity of olive oil samples from two different locations (L3 and L4) as a function storage age.

L_3		L_4	
Storage age (week)	η (cP)	Storage age (week)	η (cP)
1	30.9	1	32.1
3	30.6	3	30.7
8	29.0	6	26.6
		7	26.0

The dynamic viscosity of olive oil samples from two locations ($L_3$and L_4) was measured as a function of storage age in weeks at 47ºC as shown in Fig. (4.12).

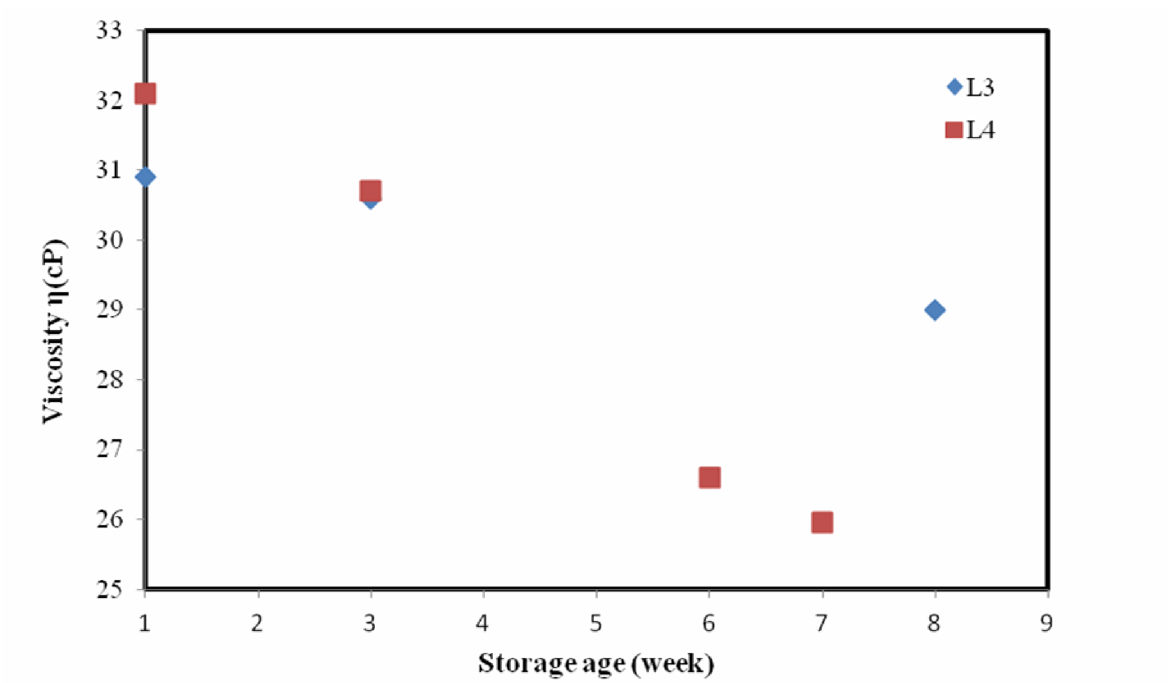


Figure (4.12): The measured values of dynamic viscosity of olive oil samples from $L_3$and L_4 of as function of storage age in weeks.

The experimental values of the dynamic viscosity of olive oil samples from L_3 and L_4 of different storage ages were fitted by using our multi-constant formula. Our multi-constant formula is proposed to be:

$$\eta = At^2 + Bt + C + De^{Et} \qquad (4.2)$$

Where η is the dynamic viscosity in cP, t is the storage age in weeks, A, B, C, D and E are constants. Our calculated values of A, B, C, D, E, AAD% and SD of the data, are given in Table 4. 42.

Table (4.42): Our values of A, B, C, D and E, AAD% and SD using our proposed formula.

The location	A (cP/week^2)	B (cP/week)	C (cP)	D (cP)	E	AAD%	SD
L_3	-0.118	1.469	23.846	7.378	-0.257	0.0	0.0
L_4	0.207	-3.300	38.930	-16.197	-1.466	0.0	0.0

Table 4.42 shows that AAD% = 0%; therefore, our proposed multi-constant formula are suitable to describe the storage age dependence of dynamic viscosity of olive oil sample.

Fig. 4.13 shows our experimental data and our fitting curves using equation 4.2 of dynamic viscosity of olive oil samples from L_3 and L_4 as a function of storage age in weeks.

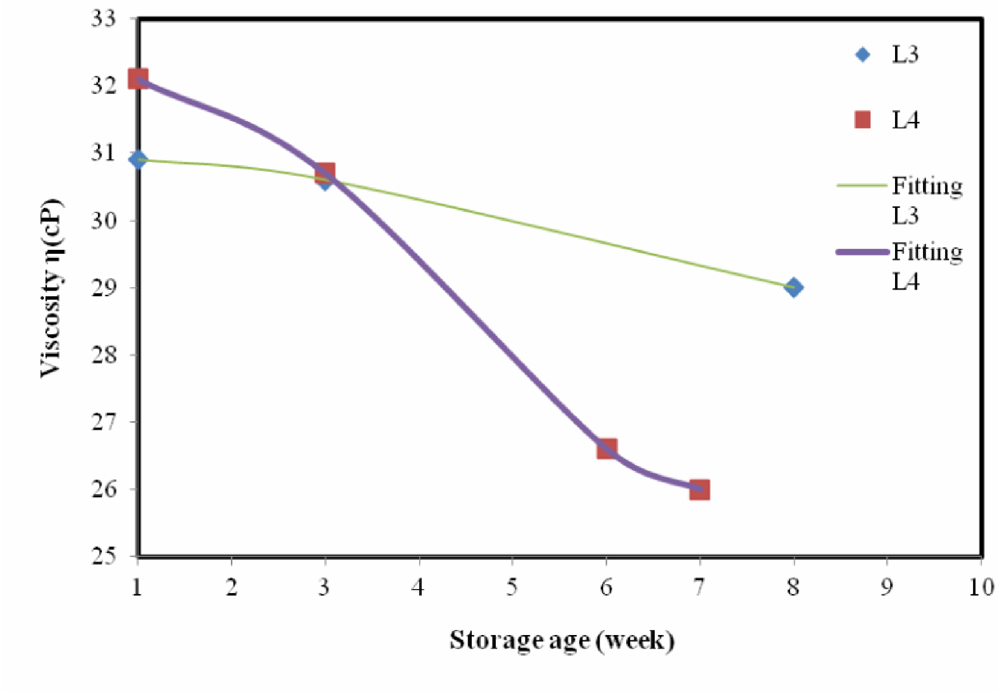


Figure (4.13): The dynamic viscosity of olive oil samples from L_3 and L_4 as a function of storage age in weeks. The solid lines are representing equation 4.2 and the points are representing our experimental data.

4.2.3 Acidity Results

4.2.3 I Olive oil crop 2010

The acidity of olive oil samples of crop 2010 of 5 months storage age from different locations in Palestine was measured. The experimental data are given in Table 4.43.

Table (4.43): The measured values of acidity of olive oil samples of crop 2010 from different locations.

Acidity (FFA %)	Location	Code
0.64	A'nin	R_1
0.53	Zbuba	R_2
0.50	Ti'innik	R_3
0.30	Silat al harithiya	R_4
0.95	Rummana	R_5
0.51	Arafa	R_6
0.54	Kafr dan	R_7
0.61	AL Tayba	R_8
1.55	Aqraba	R_9
1.34	burqa	R_{10}
0.65	Tubas	R_{11}
1.23	Marda	R_{12}
0.87	Kofor Tholoth	R_{13}
0.51	Jaba'	R_{14}
0.96	Barta'a	R_{15}
1.59	Yasid	R_{16}
0.90	AL-Jadida	R_{17}

Table 4.43 shows most of olive oil samples of crop 2010 from different locations have FFA% ≤ 0.65% which indicates that most of olive oil samples of crop 2010 from different locations are extra virgin olive oil (<0.8%). On the other hand, the olive oil samples which have FFA% between 0.8% and 2% are considered to be virgin olive oil. The acidity of olive oil influenced by different parameters such as degree of ripeness, industrial processes employed for oil extraction, the cultivator, altitude, and climate and several other factors.

The measured values of acidity of olive oil samples of crop 2010 from different locations are shown in Fig. (4.14).

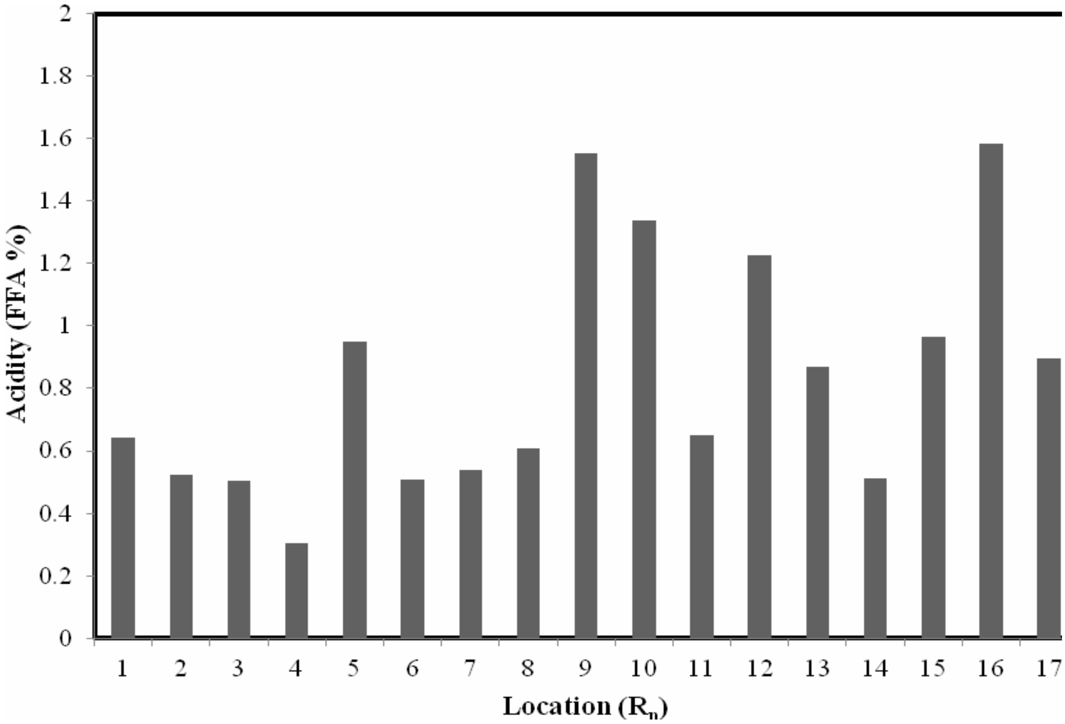


Figure (4.14): The measured values of acidity of olive oil samples from different location of crop 2010.

4.2.3 II Storage Age Dependence of Olive Oil Acidity

4.2.3 II.I Yearly Basis

The acidity of olive oil samples from four different locations (L_1, L_2, L_6 and L_7) of different storage ages was measured. The experimental data are given in Table 4.44.

Table (4.44): The measured acidity values of olive oil samples from L1, L2, L6 and L7 of different storage ages.

L_1		L_2		L_6		L_7	
Storage age (years)	Acidity (FFA %)	Storage age (years)	Acidity (FFA %)	Storage age (years)	Acidity (FFA %)	Storage age (years)	Acidity (FFA %)
0	0.97	1	1.70	0	0.30	0	0.90
1	1.69	9	7.15	6	2.40	1	1.55
10	2.19	10	8.79	11	3.73	2	1.90
11	3.69	12	12.50	12	5.22	3	2.15
13	5.51	13	19.94	13	9.89	5	2.34

The acidity of olive oil samples from L_1, L_2, L_6 and L_7 as a function of storage age in years is shown in Fig. (4.15).

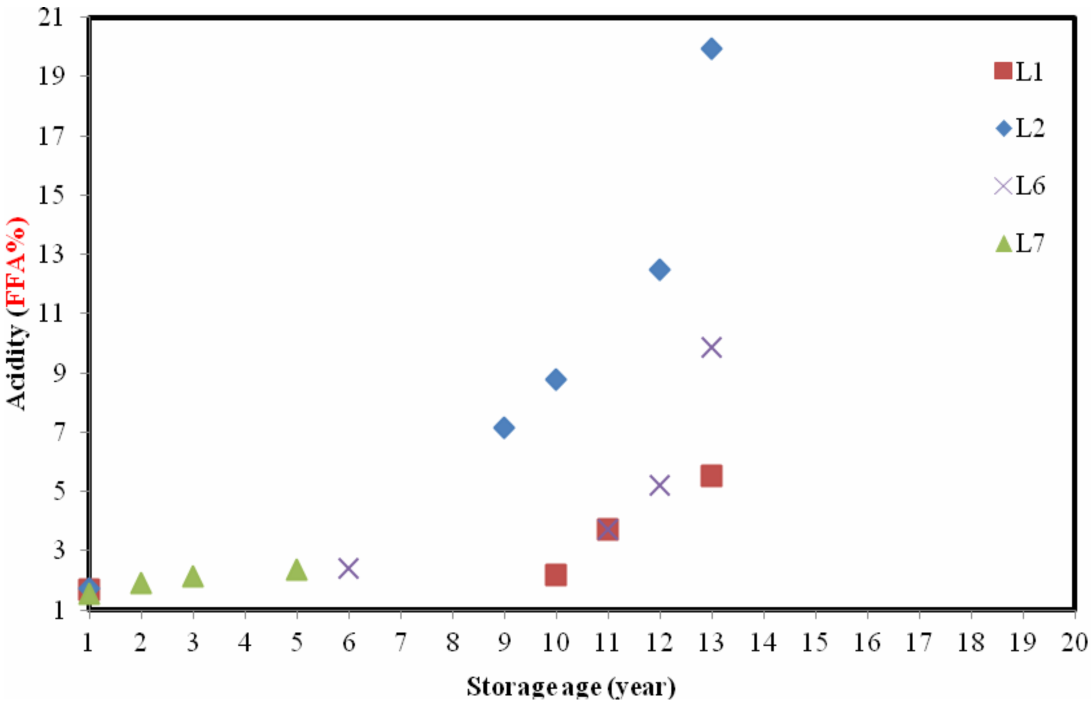


Figure (4.15): The measured values of acidity of olive oil samples from L_1, L_2, L_6 and L_7 as a function of storage age in years.

The acidity of olive oil sample of 12-year storage age from L_8 (Asira Al-Shamaliyeh) was measured to be 2.92%.

Multi-constant formula is proposed by this work to obtain more suitable prediction of storage age dependence of acidity of olive oil samples. The η_{exp} and η_{cal} were used to propose the formula that fits our experimental data. That is, AAD% and SD values are chosen to select the suitable prediction.

The experimental values of the acidity of olive oil samples from L_1, L_2, L_6 and L_7 of different storage ages were fitted by using our multi-constant formula. Our multi-constant formula is proposed to be:

$$acidity\,(FFA\ \%) = At^2 + Bt + C + De^{Et} \tag{4.3}$$

Where acidity is presented as grams of oleic acid per 100 grams oil, t is the storage age in years, A, B , C, D and E are constants. Our calculated values of A, B, C, D, E, AAD% and SD of the data, are given in Table 4.45

Table (4.45): Our values of A, B, C, D and E, AAD% and SD using our proposed formula.

The location	A (1/years^2)	B (1/year)	C	D	E	AAD%	SD
L_1	0.0809	-0.8047	2.4088	-1.5000	-10.0000	0.6	0.2
L_2	0.0996	-0.3124	1.9170	5.2346	0.0003	0.0	0.0
L_6	0.4251	-7.0564	29.4518	-29.1479	-10.0000	0.0	0.4
L_7	-0.2093	0.2277	-1.1053	2.0070	0.2647	0.0	0.0

Table 4.45 shows that most of AAD% = 0%; therefore, our proposed multi-constant formula are suitable to describe the storage age dependence of acidity of olive oil sample.

Fig. 4.16 shows our experimental data and our fitting curves using equation 4.3 of acidity of olive oil samples from L_1, L_2, L_6 and L_7 as a function of storage age in years.

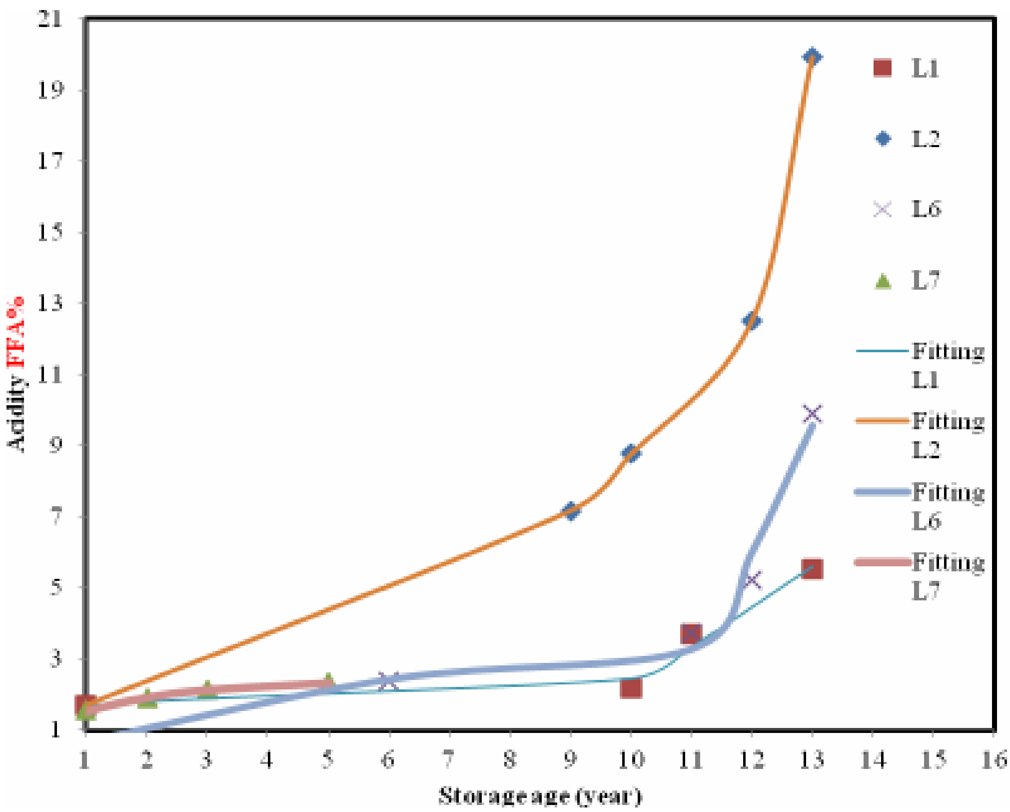


Figure (4.16): The acidity of olive oil samples from L_1, L_2, L_6 and L_7 as a function of storage age in years. The solid lines are representing equation 4.3 and the points are representing our experimental data.

4.2.3 II Weekly Basis

The acidity of olive oil samples from three different locations (L_3, L_4 and L_7) was measured at different storage ages in weekly basis. The values are given in Table 4.46.

Table (4.46): The measured acidity values of olive oil samples from L3, L4 and L7 at different storage ages.

L_7		L_4		L_3	
Acidity (FFA %)	Storage age (weeks)	Acidity (FFA%)	Storage age (weeks)	Acidity (FFA%)	Storage age (weeks)
1.79	4	1.48	1	0.64	2
1.83	5	1.54	2	0.65	4
1.86	6	1.60	3	0.67	6
1.87	7	1.60	6	0.71	7
2.06	16	1.63	7	0.72	10
2.12	20	1.69	9	0.80	17
2.17	21	1.69	10	0.82	18
2.19	22	1.72	11	0.82	20
2.23	24	1.72	16	0.88	21
2.36	25	1.81	19	0.88	22
2.60	30	1.82	21	0.91	25
3.02	33	1.89	22	1.03	30
3.27	34	2.00	24	1.24	31
		2.00	25	1.40	33
		2.01	34	1.66	34

The acidity of olive oil samples from L_3, L_4 and L_7 as a function of storage age in weeks is plotted in Fig. (4.17).

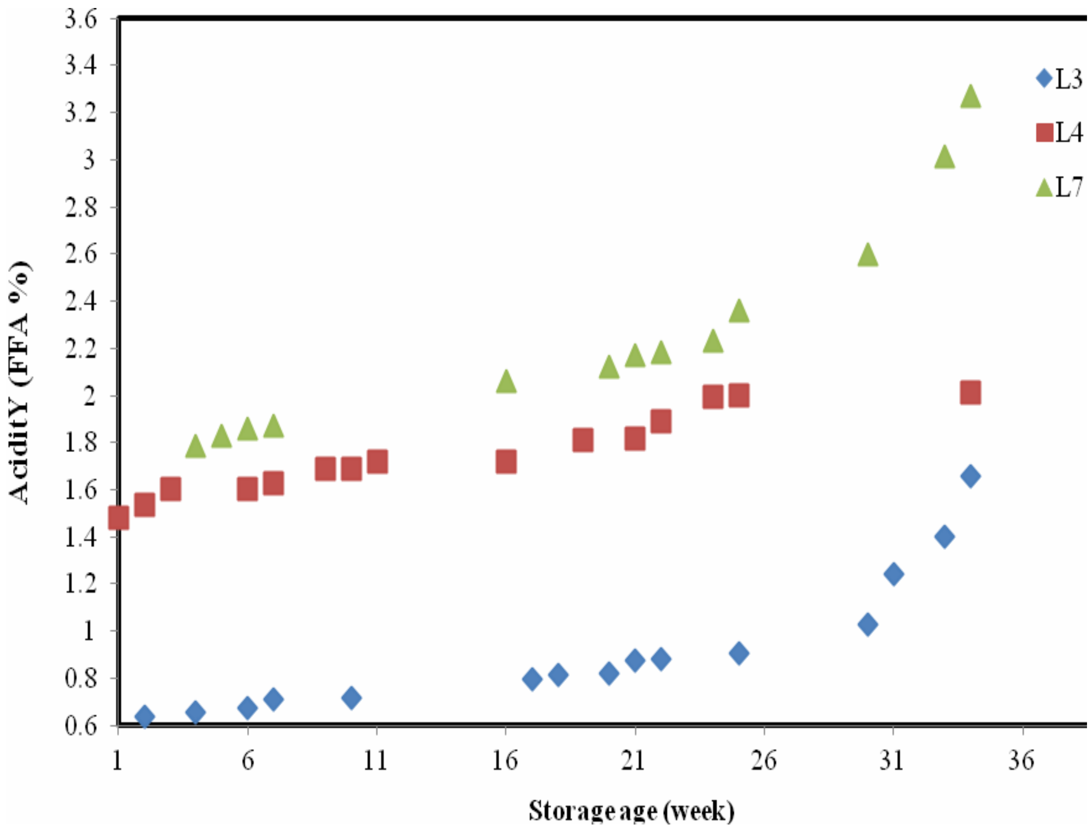


Figure (4.17): The measured values of acidity of olive oil samples from L_3, L_4 and L_7 as a function of storage age in weeks.

The experimental values of the acidity of olive oil samples from L_3, L_4 and L_7 of different storage ages were fitted by using our multi-constant formula. Our multi-constant formula is proposed to be:

$$acidity\,(FFA\ \%) = A\,t^{B} + Ct + D + Ee^{Ft} \tag{4.4}$$

Where acidity is presented as grams of oleic acid per 100 grams oil, t is the storage age in weeks, A, B , C, D and E are constants. Our calculated values of A, B, C, D, E, AAD% and SD of the data, are given in Table4.47.

Table (4.47): Our values of A, B, C, D and E, F, AAD% and SD using our proposed formula.

The location	A ($1/week^2$)	B (1/week)	C	D	$E\times10^{-6}$	F	AAD%	SD
L_3	0.4871	0.0290	0.0089	0.1190	8.7517	0.3308	0.0	0.0
L_4	0.2039	-0.0400	0.0192	1.3006	-1.0548	0.3418	0.0	0.0
L_7	0.3102	-0.0431	0.0231	1.4137	7.098	0.3425	0.0	0.0

Table 4.47 shows that AAD% = 0%. Accordingly, our proposed multi-constant formula are suitable to describe the storage age dependence of acidity of olive oil sample.

Fig. 4.18 shows our experimental data and our fitting curves using equation 4.4 of acidity of olive oil samples from L_3, L_4 and L_7 as a function of storage age in weeks.

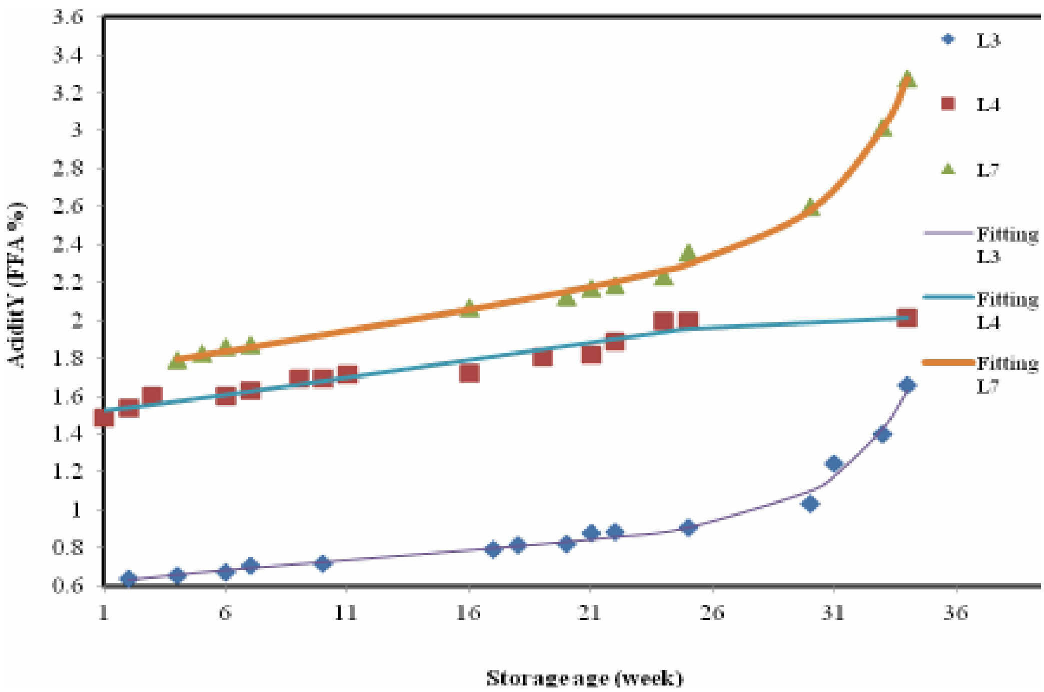


Figure (4.18): The acidity of olive oil samples from L_3, L_4 and L_7 as a function of storage age in weeks. The solid lines are representing equation 4.4 and the points are representing our experimental data.

Chapter Five
Discussion

The average of experimental results of density measurements for olive oil samples of crop 2010 at 15°C was found to be 0.91229 g/cm^3. Robert obtained the density of olive oil to be 0.918 g/cm^3 at 15°C (Robert C. *et al*, 1980). Our value is in good agreement with Robert's value. The slight difference in values is probably due to the influences of some structural characteristics on viscosity (the fatty acid composition of olive oil).

Our dynamic viscosity of olive oil sample was measured to be 80.5 cP at 20°C, 60.7 cP at 25°C, and 33.5 cP at 40°C. Adnan and Robert obtained the dynamic viscosity of olive oil to be 84 cP at 20°C, 63.61 cP at 25°C, 36.3 cP at 40°C (Adnan Q. et al; 2009, Robert C. et al; 1980). Our value of dynamic viscosity of olive oil at different temperatures is not in good agreement with Adnan's and Robert's values. The small discrepancy in values might be due to the influences of the fatty acid composition of olive oil. The machinery groups also effect on the viscosity of olive oil. The viscosity is influences by the wax content and composition which is affected by cultivar, crop year, and processing (Boskou D., 2006).

The experimental measurements of dynamic viscosity of olive oil samples of different storage ages in years from two different locations (L_1 and L_2) at 42°C showed that for location L_1 $\eta = 41.3$ cP (0-year storage age) and 36.6 cP (13-year storage age). For location L_2 $\eta = 59.0$ cP (2-year storage age) and $\eta = 25$ cP (12-year storage age). The overall results in this study of the effect of dynamic viscosity as a function of storage age in years indicate a decrease of dynamic viscosity as olive oil is stored. The decrease of dynamic viscosity of olive oil as a function of storage age in years occurred more rapidly in samples from L_2 than that in those of L_1. The effect of dynamic viscosity as a function of storage age in weeks at 42°C showed that for location L_3 η = 37.7 cP (1-week storage age) and η=35.85 cP (8-week storage age) and for location L_4 η = 39.9 cP (1-week storage age) and 32.9 cP (7-week storage age). The dynamic viscosity results of weekly basis in this study indicate that the dynamic viscosity of olive oil samples decreases as a function of storage age in weeks. The dynamic viscosity of olive oil decreased as a function of storage age at a greater rate in samples from L_4 than in those of L_3.

All experimental measurements of dynamic viscosity of olive oil samples of different locations in Palestine give values which slightly differ from one location to another. For instance, the dynamic viscosity of olive oil samples of crop 2010 from two different locations L_1 and L_5 at 42°C were obtained to be 41.3 cP and 31.5 cP, respectively. The difference might be due to different parameters that influence on the fatty acid composition of olive oil. The fatty acid composition of olive oil varies widely depending on the cultivator, maturity of the fruit, altitude and climate. Hot climate affects the fatty acid composition of olive oils. The cooler regions will yield oil with higher oleic acid than warmer climates; therefore, a cool region olive oil may be more monounsaturated in content than warm region oil. The altitude of location L_1 is ranges between 440 to 510 m and the amount of rain of crop season 2010 was 580.8 mm (cool region) while the altitude of L_5 is between 100 to 270 m and the amount of rain of crop season 2010 was 513.5 mm (hot climate). Appendix B shows the altitude of some locations in Palestine. The amount of rain for the different locations and different crop seasons in Palestine is given in Appendix C. One can observe that the results of the dynamic viscosity values of olive oil of crop 2010 from location L_1 (cool region): η = 41.3 cP are greater than the values of olive oil from location L_5 (hot climate): η = 31.5 cP. The dynamic viscosity values of olive oil from L_1: η = 36.6 cP (13-year storage age) are also greater than the values of olive oil samples from L_2: η = 25 cP (12-year storage age). The altitude of location L_2 is 350 m. The dynamic viscosity values of some olive oil samples from location L_1 show values less than the sample from location L_2 of 2-year storage age: η = 43.9 cP. The highest values for viscosity were found in the case of olive oil from location L_2 of 2 years storage age which indicates that there are other factors that affect the viscosity of olive oil. This sample may be exposed to factors that increase its dynamic viscosity. For instance, olive oil quality and behavior can be influenced by the industrial processes employed for oil extraction (Amirante *et al*, 2002). The degree of ripeness is also an important quality factor. Appendix A shows the characteristic of the olive oil during olive ripening.

The dynamic viscosity values of olive oil sample of crop 2010 from L_4: η = 39.9 cP (1 week storage age) are greater than the values from L_3: η=37.7 cP (1week storage age). The altitude of location L_3 is 140 – 230 m while the amount of rain was 514 mm. The altitude of location L_4 is 520 – 600 m and the amount of rain of location was 333.2 mm. which gives a reasonable cause that justifies the slight difference in dynamic viscosity values of olive oil from L_3 and L_4.

The measured experimental results of dynamic viscosity of olive oil samples are compared against the previously calculated values found by Abramovic's formula of two-constant $\eta = A - BLogt$ and Andrade's formula of three-constant $Ln\eta = A + \frac{B}{T} + CT$ for olive oil. For instance, the calculated values of dynamic viscosity at 45°C were found to be 30.2 cP and 32.0 cP, respectively. Our measured experimental value at 45°C (36.6cP) shows significant difference between our result and the literature value. This indicates that Abramovic's and Andrade's formulas are not the best fit to be used for our experimental data of dynamic viscosity of olive oil samples. Abramovic's and Andrade's formulas were modified to fit our experimental values. As a result of this modification, the constants A, B and C were determined using Abramovic's and Andrade's formulas. The calculated dynamic viscosity using the modified form of Abramovic's and Andrade's formulas at 45°C were found to be 38.5 cP and 37.6 cP, respectively, which indicate that Abramovic's and Andrade's modified formulas don not fit exactly our experimental data. Two $(Log\eta = AT + B)$, three $(Ln\eta = A - \frac{B}{T + C})$ and multi $(\eta = A + \frac{B}{t} + CLn(t) + Dt^{E})$ -constant formulas are proposed to obtain more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples in our regions. The constants of our proposed formulas were estimated to give the best fit.

The effect of acidity as a function of storage age in yearly basis shows that: for location L_1 from 0.97% (0-year storage age) to 5.51% (13-year storage age). Location L_2 is from 1.70% (1-year storage age) to19.94% (13-year storage age), for location L_6 from 0.305% (0-year storage age) to 9.89% (13-year storage age). Location L_7 is from 0.90% (0-year storage age) to 2.34% (5-year storage age).

The overall results in this study of the effect of acidity as a function of storage age in yearly basis were over the limits established by IOOC ($\geq$3.3%). This indicates a deterioration of oil quality as olive oil is stored. The values of the acidity of some olive oil samples (from L_7) are below the maximum levels ($\leq$ 3.3%) established by IOOC which suggest that the oil can be stored for a long period (> 12 years) without deterioration.

Our acidity results of the olive oils of weekly basis show an increase as a function of storage age in weeks. The values of acidity increases as follows: For location L_3 from 0.64% (2-week storage age) to 1.66% (34-week storage age). Location L_4 is from 1.48% (1-week storage age) to 2.01% (34-week storage age). Location L_7 is from 1.79% (4-week storage age) to 3.27% (34-week storage age).

The overall results of weekly basis in this study indicate that the fatty acid levels in the analyzed olive oil samples increased incrementally, but that it was within the limits established by IOOC ($\leq$ 3.3%).

Our acidity value of extra olive oil increased from 0.65% to 0.79% after 3 months and 1.03% after 6 months. Falque in his study found that the values of the initial acidity of the extra-virgin olive oils for glass bottle is 0.39%, and the values of acidity after 3 and 6 months are 0.42% and 0.45%, respectively (Falque E. et al; 2007). Our results are in quit good agreement with those of Falque. The slightly different values from one location to another are probably due to different parameters that influence the acidity of oil. The degree of ripeness is an important quality factor (Appendix A). Olive oil quality and properties can be influenced by the industrial processes employed for oil extraction. The acidity increasis if the olive fruits are damaged. The main olive pests/diseases in Palestine which damage the fruits are the olive fly and the peacock eye spot. Fruits are damaged also if olives are picked by sticks from the trees. Acidity in previous studies (Bechir B. et al; 2012, Bento A. et al; 2002) indicates a progressive deterioration of oil quality as the fruit is stored.

Some empirical relations that describe the dependence of dynamic viscosity and acidity of olive oil on storage age were fitted to the experimental data. The constants for the best fit are calculated.

Chapter Six

Conclusion and Future Works

The values of the acidity of some olive oil samples (from L_1) suggest that the oil can be stored for a period not more than 12 years without deterioration. A lot of study is needed to study the influence of storage age in other quality factors such as peroxide index, impurity content (%), phenols content, iodine index, saponification index, fatty acid content and absorption coefficients K270 and K232. The absorption coefficients K270 and K232 are used as quality factor because the absorbency at 232nm is caused by hydroperoxides (primary stage of oxidation) and conjugated dienes (intermediate stage of oxidation). The absorbency at 270nm is caused by carbonylic compounds (secondary stage of oxidation) and conjugated trienes (technological treatments). The degree of oxidation of olive oil is reflected by its specific extinction at 232 nm and 270 nm.

These studies will determine the storage age of olive oil without deterioration. In addition, future studies are needed to study the quality parameters as a function of storage age in ideal storage conditions. The ideal storage conditions when each bottle flushes with nitrogen after filling in order to remove oxygen and olive oil must be stoned storage in temperature range 16 – 18˚C in dark.

One of the most interesting topics left for future study is the behavior of viscosity of olive oil from different location in Palestine as a function of shear rate (Newtonian or non Newtonian behavior).

This work studies the dynamic viscosity of olive oil samples from different locations in Palestine as a function of temperature. The acidity and the viscosity as a function of storage age for these samples were also studied. Another works is needed to study a lot of olive oil samples from other locations in Palestine than the location which we did our study on them.

References

Abed M. *et al*, **"Characterization of the main Palestinian olive cultivars and olive oil"**, 1st Ed., (2010).

Abramovic H., klofutar G., ***"The temperature dependence of dynamic viscosity for some vegetables oils"*, Acta Chim. Slov**. **45**(1), 69-77 (1998).

Adnan Q., Ahmad M., Akhtar N., Farzana K. and Mehmood A., ***"Rheological studies and characterization of different oils"***, **J. Chem. Soc. Pak.**, **31**(2), 201 - 206 (2009).

Ahmad M., Amran A.,Giap S. G. E. and Nik W. M. N. W., ***"The assessment of rheological model reliability in lubricating behavior of vegetable oils"***, **Engineering e-Transaction**, **4**(2), 81-89 (2009).

Amirante P., Dugo G. and Gomes T., ***"Influence of technological innovation in improving the quality of extra virgin olive oil"***, **Olivae**, **93**, 34-42, (2002).

Andrade E. N. C., **Nature**, **125**, 309-318(1930).

AOAC., official methods of analysis, 17th Ed., 969.17(1997).

Ayadi M., Bouaziz M., Ines F., Jemai H. and Sayadi S., ***"Effect of storage on refined and husk olive oils composition: stabilization by addition of natural antioxidants from Chemlali olive leaves"***, **Food Chemistry**, **108,** 253–262 (2008).

Bakshi N.N. and Parthasarathy S., ″***Relation between velocity of sound and viscosity in liquids***″, **Proc. Phys. Soc. 66B**:368–370 (1953).

Barnett R. E., Rodger J. W. and Thorpe T. E., ″***On the relations between the viscosity (internal friction) of liquids and their chemical nature***″, **Part II, Phil. Trans. 189**, 71-107(1897).

Bayrak Y., Iscan M., Topallar H., ″***Kinetics of autoxidative polymerization of sun flower seed oil***″, **Tr. J. of chemistry**, **21**, 118-125 (1997).

Bechir B., Chedly A., Mokhtar Z., Nabil B., Nizar D. and Youssef O., ″***Effect of olive storage period at two different temperatures on oil quality of two tunisian cultivars of Olea europea Chemlali and Chetoui***″, **African Journal of Biotechnology**, **11**(4), 888 – 895 (2012).

Bell J. D., Cannon M. R., Manning R. E., ″***Viscosity measurement***″, **Anal. Chem.**, **32**, 355-358 (1960).

Bento A., Casal S., Oliveira M. and Pereira J., ″***Influence of olive storage period on oil quality of three portuguese cultivars of olea europea, cobrancüosa, madural, and verdeal transmontana***″, **J. Agric. Food Chem.**, **50**, 6335 – 6340 (2002).

Bu L., Lin X. and Yaws C.L., ″***Calculate viscosities for 355 liquids***″, **Chem.Eng. 101**(4) 119-20, 122, 124, 126, 128, (1994).

Boskou D., ″**Olive oil chemistry and technology**″, 2nd Ed. (2006).

Buszewski B and Ligor M., ***"The comparison of solid phase microextraction-GC and static headspace-GC for determination of solvent residues in vegetable oils"***, **J. Sep. Sci.** 31: 364-371(2008).

Brahmi F., Dabbou S., Gharbi I., Hammami M. and Nakbi A., ***"Impact of packaging material and storage time on olive oil quality",*** **African Journal of Biotechnology**, **10**(74), 16937-16947, (2011).

Brian S. and Landau S., **"A hand book of statistical analyses using SPSS"**, (2004).

Bridgman P. W., ***"Viscosity of liquids under pressure",*** **Physics**, **11**, 603-606 (1925).

Brookfield Engineering Laboratories, Inc., Middlebore, USA, manual no. M/92-021-K1098, pp. 34 (1999).

Calligaris S., Manzocco L., Nicoli M. C., Sovrano S., ***"Influence of crystallization on the oxidative stability of extra virgin olive oil"***, J. **Agric. Food Chem**., **54** (2), 529–535 (2005).

Clements C., Craig-Schmidt M., Fasina O. O. and Hallman H., ***"Predicting temperature-dependence viscosity of vegetable oils from fatty acid composition"***, **Journal of the American Oil Chemists' Society, 83**(10), 899-903 (2006).

Clements L. D., Noureddini H. and Teoh B. C., ***"Viscosity of vegetables oils and fatty acids"***, **J. Am. Oil Chem. Soc**., **69** (12), 1189-1191 (1992).

Danner R. P. and Daubert T. E., ″**Physical and thermodynamic properties of pure chemicals –data compilation design institute for Physical properties data**″, AIChE, Taylor and Francis, Washington DC (1994).

De Guzman J., ″***Relation between fluidity and heat of fusion***″, **Anales Soc. Espan. Fis. Y. Quim. 11**, 353-362 (1913).

Duhne C. R., ″***Viscosity-temperature correlations for liquids***″, **Chem. Eng.**, **86** (15), 83 (1979).

Dumitru A., Geacai S.,Neagu N. A., Sterpu A., ″***Study of the behavior of some vegetable oils during the thermal treatment***″, **Ovidius University Annals of Chemistry**, **21**(1),5-8 (2010).

Dutt N. and Prasad D. H., ″**Representation of the temperature dependence of the viscosity of pure liquids, private communication**″, chemical engineering division, Indian institute of chemical technology, Hyderabad (2004).

Dutt N., Ghosh T. K., Prasad D. H. L., Rani K. Y. and Viswanath D. S., ″**Viscosity of Liquids Theory, Estimation, Experiment, and Data**″, 444-553 (2007).

El-hefian E. A., Jabir O. M., Yahaya A. H., ″**Temporal behavior of olive oil: with and without chitosan**″, 12th, Asian Chemical Congress (12ACC), (2007).

Falque E. and Mendez A. I., ″***Effect of storage time and container type on the quality of extra-virgin olive oil***″, **Since Direct Food Control**, **18**, 521–529, (2007).

Giap S. G. E., ″***The hidden property of arrhenius-type relationship: viscosity as a function of temperature***″, **Journal of Physical Science, 21**(1), 29–39 (2010).

Goletz E., Jr. and Tassios D., ″***An Antoine type equation for liquid viscosity dependency to temperature***″, **Ind. Eng. Chem. Proc. Des. Dev., 16**(1), 75-79 (1977).

Guushaa A., Hosier L., Swingler S. G. and Vaughan A. S., ″***Selection of a suitable vegetable oil for high voltage insulation applications***″, **J. Phys**., **183**(1), 1-5 (2009).

Haighton J., Van Putte K. and Vermaas L. F., ″***Determination of the solid contents of fats by wide-line nuclear magnetic resonance. Signal of liquid oils***″, **J. Am. Oil Chemist's Soc., 49**(3), 153-156 (1972).

Hsieh F.H., Rodenbush C.M. and Viswanath D.S., ″***Density and Viscosity of Vegetable Oils***″, **JAOCS.**, **76**, 1415–1419 (1999).

http//www.olive oil source.com/page/chemical-characteristics.

International Olive oil Council ″**Trade standards applying to olive oil and olive pomace oil**″, E. /Conv. /Doc. no.1 /16 November 2000. International Olive Oil Council, Madrid, Spain.

James F., ″**Rheological methods in food process engineering**″, 2nd Ed., 1-35 (1996).

Kiritsakis A., Papadopoulou P. and Vekiari S. A., ″***Effects of processing methods and commercial storage conditions on the extra virgin olive oil quality indexes***″, **Grasas Y Aceites.**, **58**(3), 237-242 (2007).

Natarajan G. and Viswanath D. S., ″**Data book on viscosity of liquids**″, Hemisphere, New York (1989).

Palestinian meteorological authority in the ministry of transport

Poling B. E., Prausnitz J. M., and Reid R. C., ″**Properties of gases and liquids**″, McGraw-Hill, New York, 4th Ed. (1987).

Qun-Fang L., Rui-Sen L. and Yu-Chun H., ″***Correlation of viscosities of pure liquids in a wide temperature range***″, **Fl. Ph. Equilib**.**140**(1-2), 221-231 (1997).

Rao, M.A., ″**Rheology of fluid and semisolid foods: principles and applications**″, Aspen Publishers, Inc., Gaithersburg, Maryland (1999).

Robert C., ″**CRC Handbook of Chemistry and Physics**″, 59th Ed. (1979).

Tan Hsiao Wei, ″**Rheology and stability of olive oil cream emulsion stabilized by sucrose fatty acid esters nonionic surfactants**″, (2009).

Vogel H., ″***Das temperaturabhängigkeitsgesetz der viskosität von flüssigkeiten***″, **Physics**. **22**, 645-646 (1921).

Appendix

Appendix A

	October	November
Free acidity (%)	0.28	0.32 ± 0.16
Fatty acid composition (%)		
Palmitic	12.53	15.53 ± 2.19
Palmitoleic	0.59	0.98 ± 0.44
Heptadecanoic	0.25	0.11 ± 0.05
Heptadecenoic	0.25	0.13 ± 0.06
Stearic	4.05	3.48 ± 0.09
Oleic	70.54	64.11 ± 4.88
Linoleic	10.41	14.06 ± 2.30
Linolenic	0.61	0.89 ± 0.11
Eicosanoic	0.41	0.45 ± 0.04
Eicosenoic	0.36	0.24 ± 0.01

The characteristic of the olive oil during olive ripening (Abed *et al*, 2010).

Appendix B

Code	Location	Altitude (meter)
L_1	Jeet	450 - 510
L_2	Saida	350
L_3	Al-Yamun	140 - 230
L_4	Beta	520 - 600
L_5	Jenin	100 - 270
L_6	Arraba	320
L_7	Meithaloon	380 - 410
L_8	Asira Al-Shamaliyeh	648

The altitude of some locations in Palestine (Palestinian meteorological authority in the ministry of transport).

Appendix C

Code	Location	The rain season	The amount of rain (mm)
L_1	Jeet	2010	580.8
		2005	789.9
		2004	567.8
		1999	341
		1998	758.6
		1997	789.1
L_2	Saida	2010	735.5
		2009	564.9
		2008	445
		2001	763.3
		2000	592.9
		1998	544.9
L_3	Al-Yamun	2010	514
L_4	Beta	2010	333.2
L_5	Jenin	2010	513.5
L_6	Arraba	2010	587
		2004	461.5
		1999	222.8
		1998	599.3
		1997	580
L_7	Meithaloon	2010	521.6
		2009	531.5
		2008	391.9
		2007	356
		2005	519.2

The amount of rain for different locations and different crop seasons in Palestin (Palestinian meteorological authority in the ministry of transport).

جامعة النجاح الوطنية
كلية الدراسات العليا

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قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الفيزياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

2012م

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الملخص

تم دراسة اللزوجة واعتمادها على درجات الحرارة لعينات من زيت الزيتون من منطقتين مختلفتين في فلسطين ذات أعمار تخزين مختلفة تصل إلى ثلاث عشرة سنة. كما تم دراسة اللزوجة واعتمادها على درجات الحرارة لعينات من زيت الزيتون من محصول عام 2010 من منطقتين مختلفتين في فلسطين بعد تخزينها لعدة أسابيع. تم مقارنة قيم اللزوجة واعتمادها على درجات الحرارة لهذة العينات مع نتائج دراسات سابقة و التي تصف اعتماد اللزوجة على درجات الحرارة بمعادلات تحوي على عدد من الثوابت اثنان أوثلاثة ثوابت وأظهرت النتائج أن هذه المعادلات لا تصف بتوافق كبير اللزوجة واعتمادها على درجات الحرارة لعينات من زيت الزيتون من مناطق مختلفة في فلسطين. لذلك تم اقتراح معادلات تصف اعتماد اللزوجة على درجة الحرارة بتوافق كبير تحوي عدداً من الثوابت اثنان او ثلاثة اوعدة ثوابت.

أظهرت نتائج الدراسة أن اللزوجة تتأثر عكسيا مع درجة الحرارة وعمر التخزين.

وكذلك تم دراسة حموضة عينات من زيت الزيتون من محصول عام 2010 من عدة مناطق من فلسطين وأظهرت الدراسة أن معظم العينات هي زيت زيتون فاخر (≤ 0.8%).

كما تم دراسة حموضة عينات زيت زيتون من أربع مناطق مختلفة في فلسطين ذات أعمار تخزين تصل إلى ثلاث عشرة سنة. أظهرت النتائج أن الحموضة تتأثر طرديا مع عمر التخزين بالسنوات بحيث تتجاوز نسبة الحموضة مقاييس الجودة العالمية (≤3.3 %). وتجدر

الاشارة إلى أن عمر تخزين زيت الزيتون لا يمكن أن يتجاوز إثنتى عشرة سنة بدليل أن حموضة بعض العينات التي تم تخزينها لفترة عشر سنوات احتفظت بنسبة حموضة ضمن المقاييس العالمية المعتمدة لجودة زيت الزيتون.

وأيضا تم دراسة حموضة عينات من زيت الزيتون من ثلاث مناطق مختلفة في فلسطين بعد تخزينها لعدة أسابيع. كما أظرت النتائج أن تأثر الحموضة بعمر التخزين بالأسابيع كان طفيفاً جدا وبقيت نسبة الحموضة ضمن مقاييس الجودة العالمية(≤3.3 %).

في هذه الدراسة تم اقتراح معادلات تصف اعتماد كل من اللزوجة والحموضة على عمر التخزين.