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Temperature and Storage Age (Yearly Basis)-Dependence of Olive Oil Viscosity in Different Locations in Palestine

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Abstract
The dynamic viscosity of olive oil samples of different storage ages in yearly 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 basis indicate a decrease of dynamic viscosity. This work propose three and multi-constant formulas to obtain more suitable prediction of temperature dependence of dynamic viscosity of olive oil samples from different locations in Palestine. The best AAD% was calculated using our proposed formulas to be 0%. The relationships between the viscosity of olive oil samples with temperature and storage age have been found by fitting equations.

Keywords: olive oil; storage ages; dynamic viscosity; constant formulas; fitting equation.

1. Introduction
Viscosity is a fundamental characteristic property of all liquids and it is an important factor that determines the overall quality and stability of food systems.

Two, three and multi-constant formula have been proposed for the representation of liquid viscosity as a function of temperature by numerous researchers. In his study, Giap derived an equation to replace the well-known Arrhenius-type relationship. Giap used six vegetable oils to test his model and to prove its accuracy. Giap S. G. E., [1]. A functional form describe the effect of temperature (t) in ºC on liquid viscosity (η) in cP was proposed by Thorpe et.al. [2]. Three-constant form to describe liquid viscosity as a function of temperature was proposed by De Guzman [3]. A three-constant representation also was proposed by Vogel [4]. In addition, a polynomial form was proposed by Reid et.al. [5]. A new formula to represent the dynamic viscosity data as a function of temperature was utilized by Danner [6].

Abramovic used modified versions of the Andrade equation to describe the dependence of dynamic viscosities of number of vegetable oils on temperature. Abramovic et.al. [7]. In addition, Abramovic suggested new forms to represent the dynamic viscosity data as a function of temperature which has been also used by several investigators. Abramovic.et.al. [8 - 10].

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. The relationship between the dynamic viscosity of olive oil with temperature and storage age will be found by fitting equations.

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:

$$\eta = \frac{\tau}{\frac{\partial u}{\partial x}} \qquad (1)$$

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). Viswanath et.al. [11]. The Kinematic viscosity requires knowledge of mass density of the liquid (ρ) at that temperature and pressure. It is defined as:

$$\nu = \frac{\eta}{\rho} \quad (2)$$

Where, ν is kinematic viscosity in centistokes (cSt), ρ is in g/cm^3. Viswanath et.al. [11].

1.1 Pure-Liquid Viscosity Theories

Two, three and multi –constant formulas have been proposed for the representation of liquid viscosity as a function of temperature. The simplest formula to represent the liquid dynamic viscosity as a function of temperature was proposed by De Guzman.et.al. [3, 7], which is:

$$\eta = A e^{\frac{B}{T}} \quad (3)$$

Two-constant formulas describe the effect of temperature on dynamic viscosity were proposed by Abramovic Abramovic's formulas have the following forms:

$$Log\,\eta = \frac{A}{T} - B \quad (4)$$

$$\eta = A - B\,Log\,t \quad (5)$$

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 equations (4), (5) and (6) are constants. Abramovic presented the constants of equations (5) and (6) of olive oil and other oils. Abramovic.et.al. [8].Andrade's equations of three-constant formula were used by Abramovic that are represented in the following equations:

$$Ln\,\eta = A + \frac{B}{T} + \frac{C}{T^2} \quad (6)$$

$$Ln\,\eta = A + \frac{B}{T} + CT \quad (7)$$

Antoine's type of three-constant equation was utilized by Natarajan, which is:

$$Log\,\eta = \frac{B}{C - T} + A \quad (8)$$

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 Abramovicet.al. [7, 8]. The constants of equation (9) for dynamic viscosity (η) of olive oil and some liquids are presented. Haighton et.al. [12, 13].

Clements in his study used multi-constant formula of the form:

$$Ln\,\eta = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \dots \quad (9)$$

Where, η is the dynamic viscosity in cP and T is the temperature in Kelvin. A, B, C and D are constants. Clements et.al. [14].

2. Experimental

2.1Methodology

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 dynamic viscosity of olive oil samples of different ages from two different locations (Jeet (L_1) and Saida (L_2)) was measured as a function of temperature. The experimental data were fitted and the correlation constants of the best fits were estimated.

2.2 *Experimental Apparatus*

Two models of viscometer of different ranges were used to measure the range of viscosity of olive oils samples: Low viscosity readings of olive oil samples were measured using the Digital Viscometer Model NDJ-8S with accuracy ± 1%. A Brookfield Viscometer Model DV-I+ with accuracy ± 1% also was used to measure the viscosity of olive oil samples. The SP-1 spindle was operated at 60 rpm. The calibration of the Brookfield Viscometer Model DV-I+ was verified by using standard fluid with a viscosity of 4840 cP with accuracy ± 1% at room temperature and RV-3 Spindle at 2 rpm was used. [15].

Temperature was measured using Digital Prima Long Thermometer with accuracy ± 1% which measure 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. Results and Discussion

3.1 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. The fatty acid composition of olive oil varies widely depending on the cultivar, maturity of the fruit, altitude, climate, and several other factors. Boskou et.al. [16,17].

3.2 *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 wax content and composition is affected by cultivar, crop year, and processing [15].

3.3 *Statistical Analysis*

Microsoft Excel program was used to propose some empirical relations that describe the dynamic viscosity as a function of temperature. The correlation constants for the best fit were estimated. Percentage of average absolute deviation (%AAD) and standard deviation (SD) of the data were used to choose the best fit equation. Viswanath et.al. [11].

3.4 *Temperature-Dependence of Dynamic Viscosity*

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. 1 a and b.

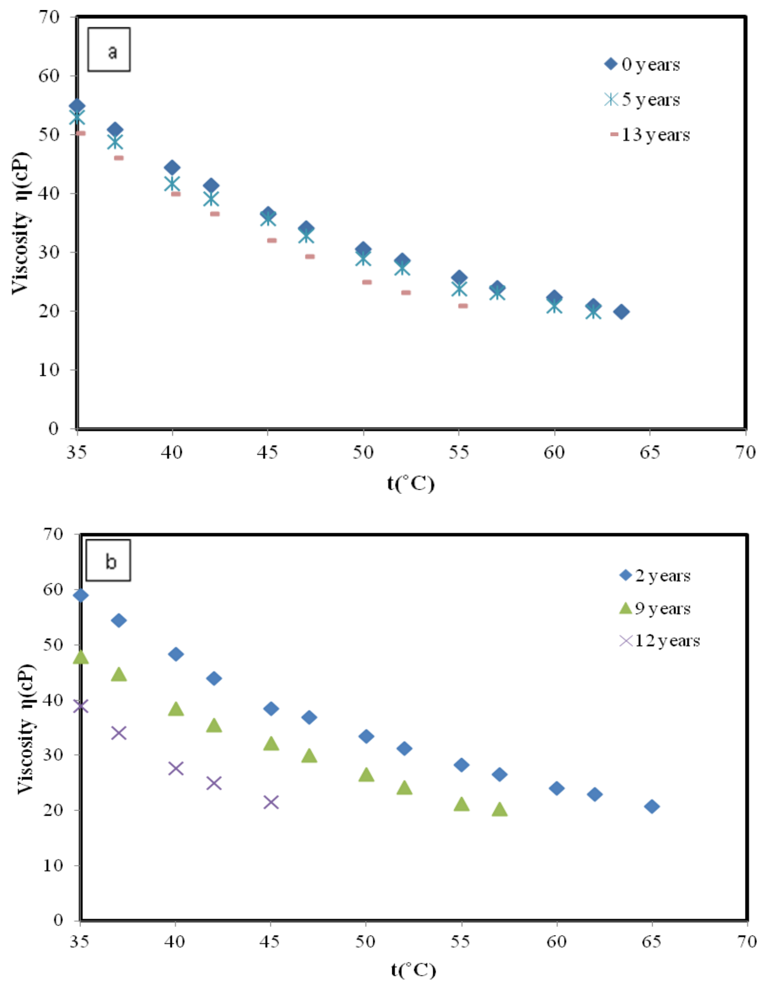


Fig.1. The measured values of dynamic viscosity of olive oil samples from two different locations a) L_1 and b) L_2 of different storage ages as function of temperature.

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 $\eta = A - BLogt$ and Andrade's formula of three-constant $Ln\eta = A + \frac{B}{T} + CT$. A, B and C are constants for olive oil. Using Abramovic's and Andrade's formulas, the AAD% values were found by this work to be from 6.9% to 30.4% and from 1.1% to 26.6% respectively. 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. 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 are given. Tables 1 and 2 tabulate AAD% and SD values.

Table (1): 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 (2): 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) $\times10^{-5}$	**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 1 and 2). This shows that the modified form of Abramovic's and Andrade's formulas don't fit exactly our experimental data.

Our values of the constants of the modified form of Abramovic's and Andrade's formulas in Tables 1 and 2 are in disagreement with Abramovic values (Table 3). The different values were probably due to free fatty acid composition of different olive oil samples.

Table (3): 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	

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 and 5.

Table (4): 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 (5): 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 shows that AAD% ≤ 0.2%. Table 5 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.

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:

$$\eta = At^2 + Bt + C + De^{Et} \qquad (10)$$

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 6.

Table (6): 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 6 shows that AAD% = 0%. Accordingly, our proposed multi-constant formula is suitable to describe the storage age dependence of dynamic viscosity of olive oil sample.

Fig. 2 a and b and 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.

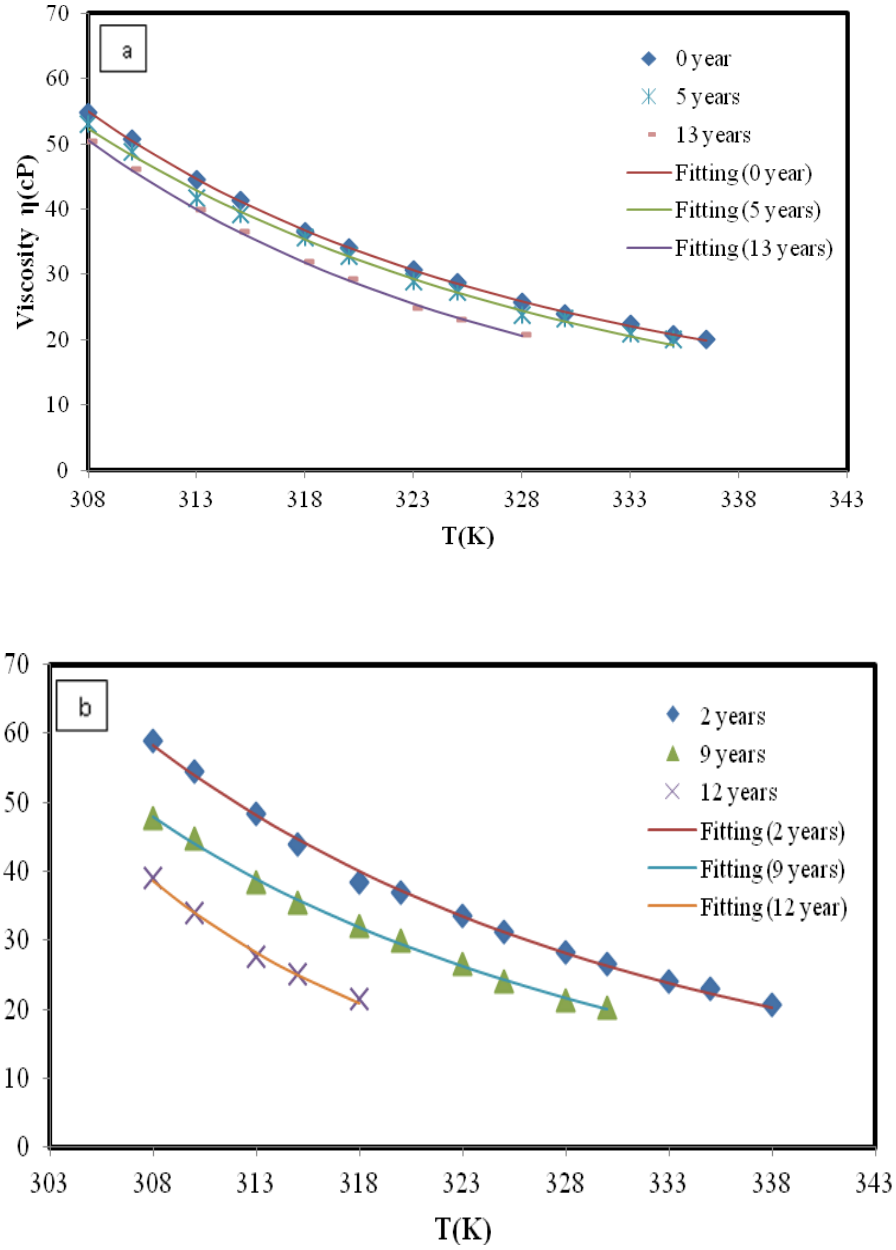
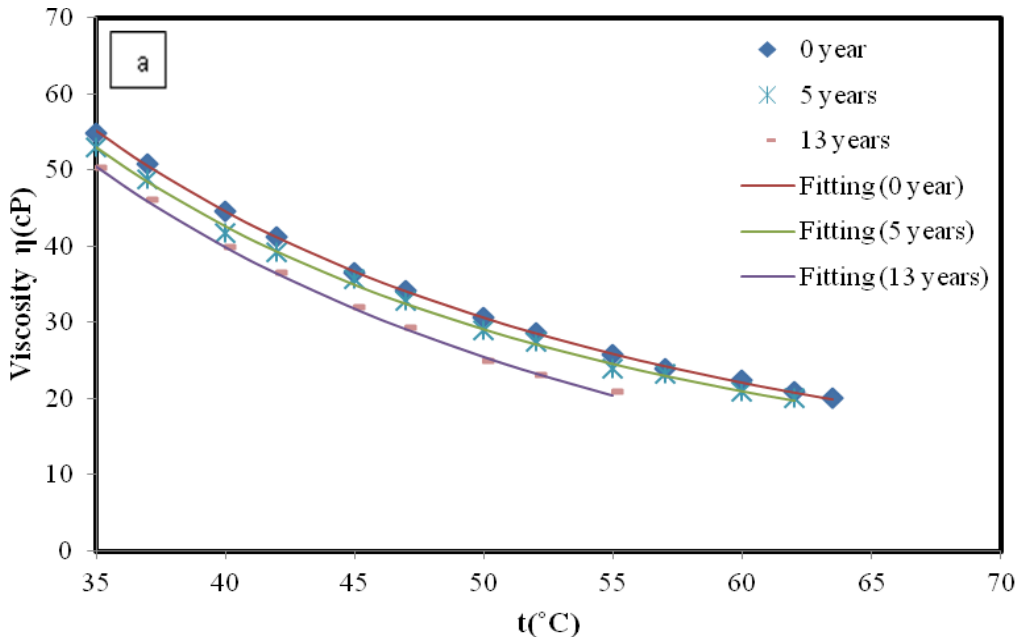


Fig.2. The dynamic viscosity of olive oil samples from two different locations a) L_1 and b) L_2 of different storage ages as function of temperature. The lines are representing our proposed three-constant formula and the points are representing our experimental data.



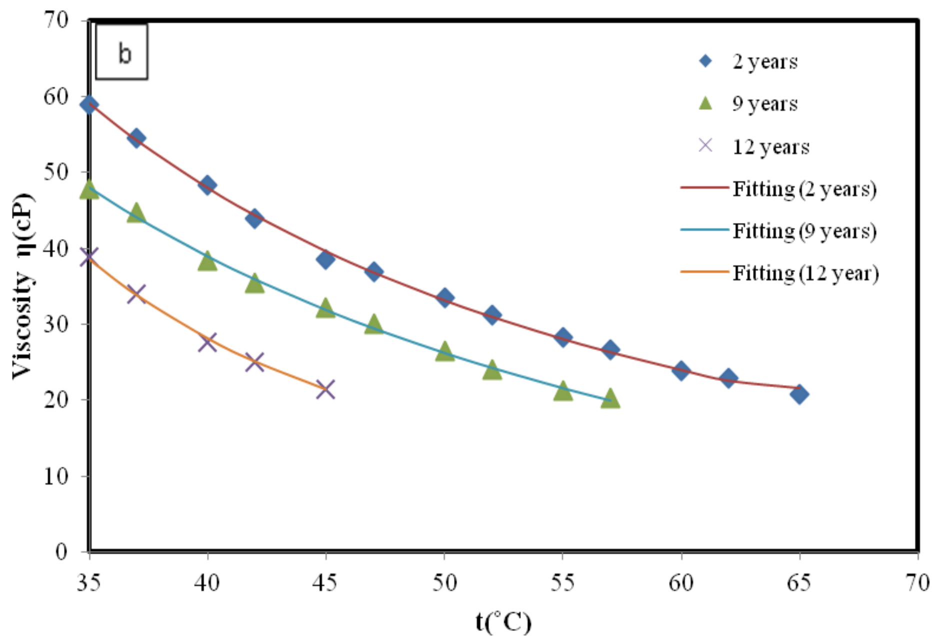


Fig.3. The dynamic viscosity of olive oil samples from two different locations a) L_1 and b) L_2 of different storage ages as function of temperature. The solid lines are representing our proposed multi-constant formula and the points are representing our experimental data.

3.5 *Storage Age-Dependence of Dynamic Viscosity*

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).

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.

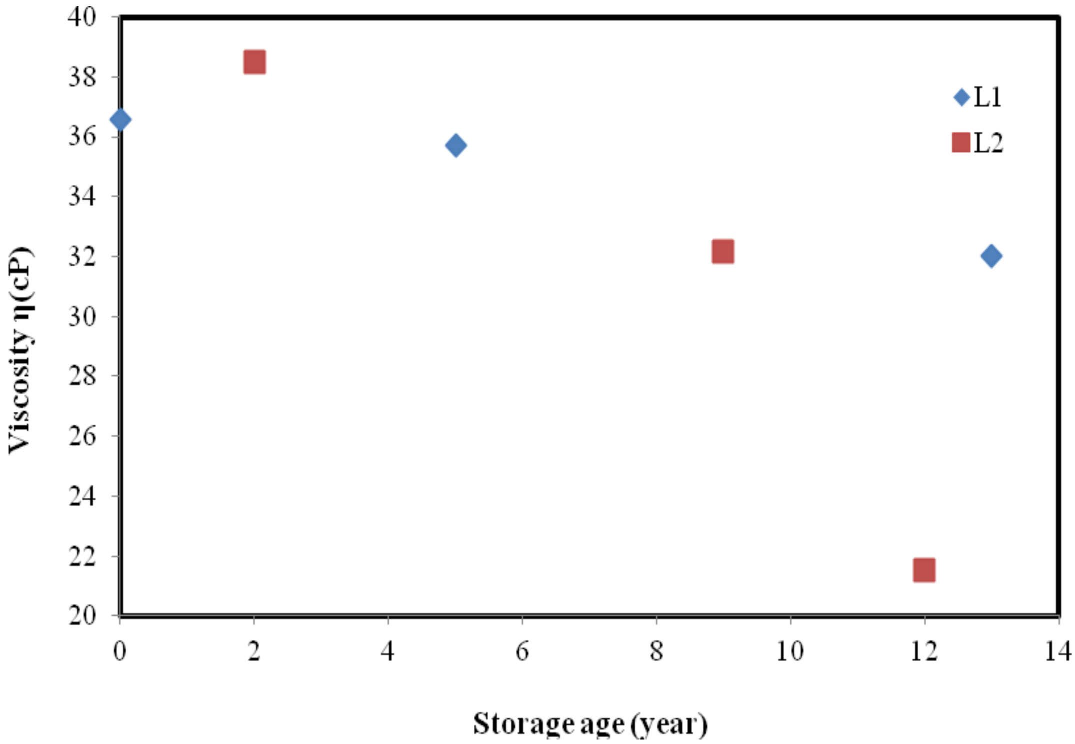


Fig. 4. The measured values of dynamic viscosity of olive oil samples from L_1 and L_2 as function of storage age.

Fig. 5 shows our experimental data and our fitting curves using equation 11 of dynamic viscosity of olive oil samples from L_1 and L_2 as a function of storage age in years.

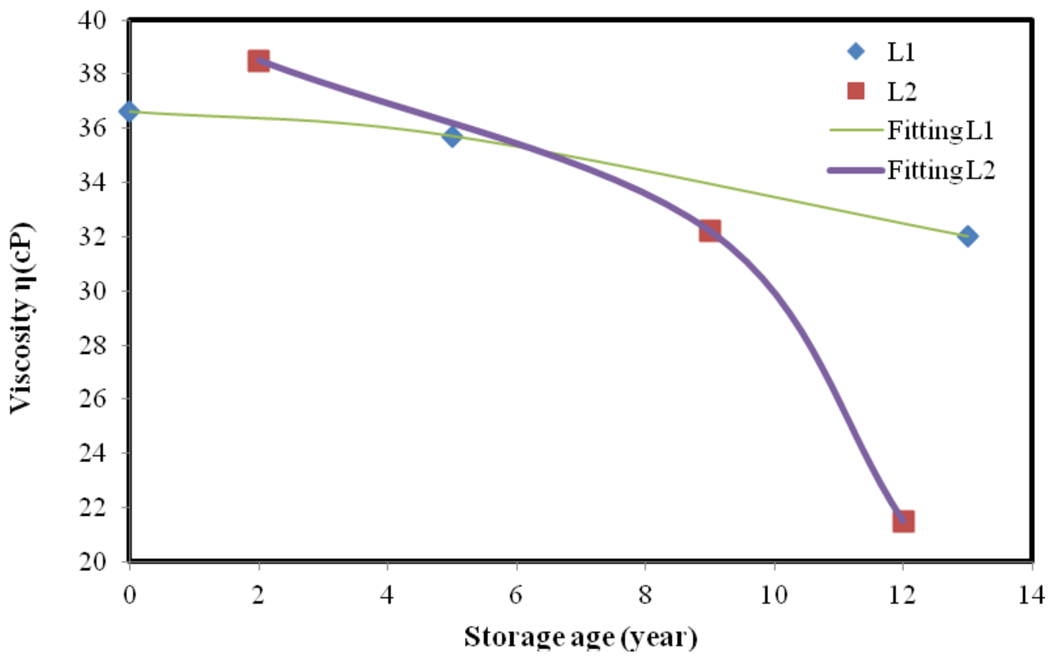


Fig. 5. The dynamic viscosity of olive oil samples from L_1 and L_2 as a function of storage age in years. The solid lines are representing equation 11 and the points are representing our experimental data.

Conclusion

Our dynamic viscosity of olive oil sample was measured to be 44.5cP at 40°C. Robert obtained the dynamic viscosity of olive oil to be 36.3 cP at 40°C [18]. Our value of dynamic viscosity of olive oil at different temperatures is not in good agreement with Robert's value. 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 [19]. The viscosity is influences by the wax content and composition which is affected by cultivar, crop year, and processing. Viswanath et.al. [11 ,16, 17].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 η = 41.3 cP (0-year storage age) and 36.6cP (13-year storage age). For location L_2 η = 59.0 cP (2-year storage age) and η = 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. 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. 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. Viswanath et.al. [11, 16, 17, 20]. 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 1997 was 789.1 mm (cool region) while the altitude of L_2 is 350 m and the amount of rain of crop season 1998 was 544.9 mm. One can observe that the results of the dynamic viscosity values of olive oil from L_1: η = 36.6 cP (13-year storage age) are greater than the values of olive oil samples from L_2: η = 25 cP (12-year storage age). 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. [19]. The degree of ripeness is also an important quality factor. Boskou D. [16, 20].

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. 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.

References

1. Giap S. G. E., *J. Phy. Sci.***,** 21(1), (2010) 29–39.
2. Thorpe T. E., Rodger J. W. and Barnett R. E., On the relations between the viscosity (internal friction) of liquids and their chemical nature, Part II, *Phil. Trans.* **189** (1897) 71-107.
3. De Guzman J., Relation between fluidity and heat of fusion, *Anales Soc. Espan. Fis. Y. Quim.* 11 (1913) 353.

4. Vogel H., Physics. 22, 645-646 (1921) 353-362.
5. Reid R. C., Prausnitz J. M. and Poling B. E., Properties of gases and liquids, McGraw-Hill, New York, 4th Ed. (1987).
6. Daubert T. E. and Danner R. P., Physical and thermodynamic properties of pure chemicals –data compilation design institute for Physical properties data**,** AIChE, Taylor and Francis, Washington DC (1994).
7. Andrade E. N. C., *Nature*, 125, (1930) 309-318.
8. Abramovic H. and klofutar G., *Acta Chim. Slov.* 45(1), (1998) 69-77.
9. Rao, M.A., Rheology of fluid and semisolid foods: principles and applications", Aspen Publishers, Inc., Gaithersburg, Maryland (1999).
10. Calligaris S., Sovrano S., Manzocco L. and Nicoli M. C., *J. Agric. Food Chem.*, 54 (2), (2005) 529–535.
11. Viswanath S., Ghosh K., Prasad H., Dutt V., Rani Y., *Viscosity of Liquids Theory, Estimation, Experiment and Data*, ISBN 10 : 9048173787 (2007) 444-553.
12. Haighton A., Van Putte K. and Vermaas L. F., *J. Am. Oil Chemist's Soc***.,** 49 (3), (1972) 153-156.
13. Viswanath D. S. and Natarajan G., Data book on viscosity of liquids, Hemisphere, New York (1989).
14. Clements L. D., Noureddini H. and Teoh B. C., *J. Am. Oil Chem. Soc.*, 69 (12), (1992) 1189-1191.
15. Brookfield Engineering Laboratories, Inc., Middlebore, USA, manual no. M/92-021-K1098, 34 (1999).
16. Boskou D., Olive oil chemistry and technology, 2nd Ed. (2006).
17. Nabil B., Youssef O., Nizar D., Bechir B., Chedly A. and Mokhtar Z. *Afr. J. Biotch.*, 11(4) (2012) 888 – 895.
18. Robert C., CRC Handbook of Chemistry and Physics, 59th Ed. (1979).
19. Amirante P., Dugo G. and Gomes T., *Olivae*, 93, (2002) 34-42.
20. Abed M. Characterization of the main Palestinian olive cultivars and olive oil, 1st Ed., (2010).

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