Predicting Temperature-Dependence Viscosity of Vegetable Oils from Fatty Acid Composition

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ABSTRACT: The viscosities of 12 vegetable oils were experimentally determined as a function of temperature (5 to 95°C) by means of a temperature-controlled rheometer. Viscosities of the oil samples decreased exponentially with temperature. Of the three models [modified Williams-Landel-Ferry (WLF), power law and Arrhenius] that were used to describe the effects of temperature on viscosity, the modified WLF model gave the best fit. The amounts of monounsaturated FA or polyunsaturated fatty acids (PUFA) highly correlated ($R^2 > 0.82$) with the viscosities of the oil samples whereas poor correlations ($R^2 < 0.17$) were obtained between viscosities and the amounts of saturated or unsaturated FA. An exponential equation was therefore used to relate the viscosity of these vegetable oil samples to the amounts of monounsaturated FA or PUFA. The models developed are valuable for designing or evaluating systems and equipment that are involved in the storage, handling, and processing of vegetable oils.

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KEY WORDS: Fatty acid, models, monounsaturated, polyunsaturated, vegetable oil, viscosity.

About 79% of the over 100 million metric tons of edible oils and fats produced worldwide annually are derived from plant sources and are referred to as vegetable oils (1). Vegetable oils play important functional and sensory roles in food products, and they act as carriers of fat-soluble vitamins (A, D, E, and K) (2). They also provide energy and essential linoleic and linolenic acids, responsible for growth (3,4), and are one of the main ingredients in soaps, cosmetics, and pharmaceutical products (5,6).

In recent years, the production of vegetable oils has become more global with southeast Asia and South America becoming the most important suppliers of edible oils to regions and countries unable to meet local demand by home production. For example, between 1970 and 2003, the amount of vegetable oil that has been exported has increased by about eightfold (5.3 million metric tons in 1970 to 43.3 million metric tons in 2003) (7) with most of the increase occurring in the continents of Asia and South America. As a consequence, oils are exposed to varying temperatures for long periods of time during transportation from the place of production to the place of utilization. More importantly, the oils have to be pumped several times from one container or vessel to another during bulk movement.

One rheological parameter that is needed in the sizing and selecting of pumps and pipes for handling fluid products such as vegetable oils is viscosity (8). Instruments such as viscometers and rheometers are often used to measure the viscosity of vegetable oils (9). It has been well established that temperature has a strong influence on the viscosity of fluid products, with viscosity generally decreasing with increase in temperature (9). Several researchers have reported the viscosity of vegetable oils at room temperature (9–13). Studies have also been carried out on the effects of temperature on the viscosities of vegetable oils (14–16). These studies, however, have been carried out over different temperature ranges. It is extremely difficult to apply these viscosity–temperature equations outside the temperature ranges for which the equations were developed.

Viscosities of vegetable oil are sometimes estimated from parameters such as saponification value, iodine value, density, M.W., and number of carbon atoms per FA residue (6,17–19). None of these studies has directly related the viscosities of vegetable oils to the amounts of unsaturated (monounsaturated or polyunsaturated) FA. In addition, the effect of temperature was not taken into account in most of these studies.

The objectives of this study were (i) to obtain shear stress–shear rate data and estimate the viscosity of vegetable oils and (ii) to develop a relationship between the viscosity and amount of unsaturated (monounsaturated or polyunsaturated) FA in vegetable oils within a temperatures range of 5 to 95°C.

MATERIALS AND METHODS

Rheological test. Samples of the following 12 vegetable oils were used in this study: almond, canola, corn, grapeseed, hazelnut, olive, peanut, safflower, sesame, soybean, sunflower, and walnut. The samples were purchased from a local grocery store in Auburn, Alabama. Rheological tests were carried out by means of a Bohlin rheometer (Model CVO-100; Bohlin Instruments, Gloucestershire, United Kingdom). A programmable water bath (Model F25-HE; Julabo USA Inc., Allentown, PA) was used to ensure precise and stable control of temperature during measurements. The rheometer and the water bath were controlled by means of software provided by the manufacturer of the rheometer. The concentric cylinder measuring system was used to evaluate the rheological properties of the sample. This measuring system consisted of a 25-mm diameter rotating bob (inner cylinder) located in a 27.5-mm diameter fixed cup (outer cylinder). The bob was used to shear oil samples (13

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*To whom correspondence should be addressed at 200 Corley Bldg., Auburn University, Auburn AL 36849. E-mail: fasinoo@auburn.edu mL) contained in the annular gap between the cup and bob. Shear rates were ramped from 0.1 to 100 s^{-1} at temperatures of 5 to 95°C. All measurements were carried out in duplicate.

FA analysis of oils. Oils were methylated by using a 10% solution of boron trifluoride/methanol (Supelco, Bellefonte, PA) as described by Morrison and Smith (20). The FAME were then separated using a Varian 3900 gas chromatograph (Varian, Inc., Walnut Creek, CA) equipped with the following: an Omegawax fused-silica capillary column (0.25 mm internal diameter, 30 m; Supelco) with temperature of 50°C increasing to 220°C at 4°C per minute; a CP8400 autosampler; an 8410 autoinjector offset at 250°C; and an FID offset at 300°C (Varian Inc.). Helium was used as the carrier gas at a flow rate of 1 mL/min in the splitless mode. FA peaks were verified using known lipid standards (Nu-Chek-Prep, Elysian, MN). FAME were expressed as percentage by weight of total FA by calculating empirical correction factors using the procedure outlined by Christie (21).

RESULTS AND DISCUSSION

Figure 1 shows that the typical closeness in values of the shear stress–shear rate data obtained from duplicate measurements. This is confirmed by the plot of CV (percent ratio of SD to mean of viscosity obtained from duplicate readings) at each shear rate. Similar values of CV were obtained at other temperatures and for other oils. Consequently, the average shear stress at each shear rate was used for further data analysis. Within the temperature range of 5 to 95°C, the linear relationship of shear stress to shear rate indicates that all the vegetable oil samples tested in this study exhibit Newtonian behavior. Consequently, their viscosities at each temperature were obtained from the slope of the fit of experimental shear stress–shear rate data to Newton's law of viscosity equation (Eq. 1):

$$\sigma = \mu\dot{\gamma} \qquad [1]$$

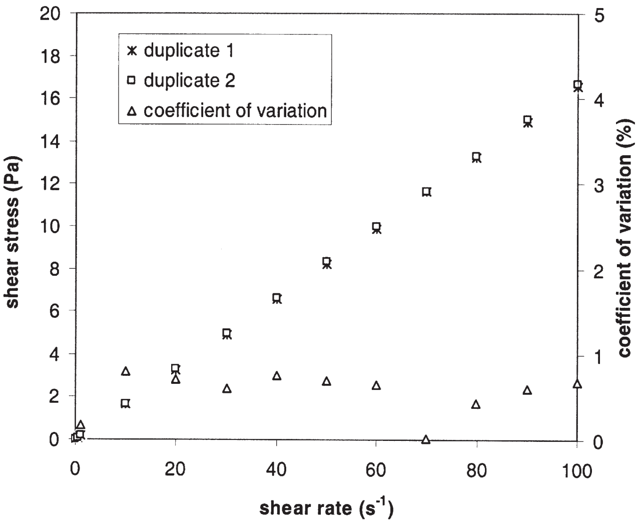

FIG. 1. Closeness of duplicate shear stress–shear rate data for canola oil at temperature of 5°C.

where σ is shear stress (mPa), $\dot{\gamma}$ is the shear rate (s^{-1}), and μ is viscosity (mPa·s). The values of the estimated viscosities are given in Table 1. In each case, the regression coefficient (R^2) obtained by fitting Equation 1 to the experimentally obtained shear stress–shear rate data was greater than 0.999.

As expected, the viscosities of the oil decreased in an exponential manner with increased temperature (Table 2). The viscosities at 5°C were about 20-fold greater than those at 95°C. This will have significant effects on the energy required to pump the oil at elevated temperatures compared with refrigerated temperatures. In addition, the viscosity values obtained in this study were within 12% of the viscosity values reported in the literature for soybean, corn, and sunflower oils (9,13,22).

Modeling. The dependence of the oil viscosities on temperature was modeled using Equations 2–4. Equation 2 is the Arrhenius model that is commonly used to model temperature dependence of a property (9,23). Equations 3 and 4 are, respectively, the modified form of the WLF (Williams-Landel-Ferry) and the power law models. Several researchers have used these equations to describe the viscosity–temperature relationship of food systems (24–28).

(i) Arrhenius model:

$$\mu = A\exp\left(\frac{E_a}{RT}\right) \qquad [2]$$

where E_a is the activation energy (kJ/kg), R is universal gas constant (8.314 kJ/kg mol K), T is absolute temperature (K), and A is a constant (mPa·s).

(ii) Modified WLF model:

$$\ln(\mu) = \frac{aT}{b+T} \qquad [3]$$

a and b are constants to be determined from Equation 3.

(iii) Power law model:

$$\mu = k(T - T_{ref})^n \qquad [4]$$

k and n are constants. T_{ref} is reference temperature of 273.15 K.

Constants A, a, b, k, and n in Equations 2–4 were estimated by using the nonlinear regression procedure NLIN in the SAS statistical package (29). The standard error of estimate (SEE: Eq. 5) was computed and used to compare the goodness of fit (an equation with lower SEE value gives a better fit to experimental data compared with an equation with higher SEE value) of the equations to the experimental data (30,31):

$$SEE = \sqrt{\frac{\sum_{i=l}^{n}(Y_i - Y_i'}{n-p}} \qquad [5]$$

where Y is the oil viscosity at a particular temperature, Y' is the predicted viscosity from Equations 2–4, n is the number of data points, and p is the number of parameters in each equation. The lower the estimated SEE for an equation, the better the fit of that equation to experimental data. The values of the estimated

TABLE 1
Viscosities[a] (mPa·s) of Vegetable Oil at Different Temperatures

	Sample temperature (°C)						
Source of oil	5	20	35	50	65	80	95
Almond	172.95	81.92	43.96	26.88	17.61	12.41	9.15
Canola	166.20	78.74	42.48	25.78	17.21	12.14	9.01
Corn	138.31	67.95	37.92	23.26	15.61	10.98	8.56
Grapeseed	165.23	76.00	41.46	25.27	16.87	11.98	9.00
Hazelnut	180.58	85.71	45.55	27.40	17.83	12.49	9.23
Olive	182.91	86.62	46.29	27.18	18.07	12.57	9.45
Peanut	192.60	83.99	45.59	27.45	17.93	12.66	9.40
Safflower	125.00	62.60	35.27	22.32	14.87	11.17	8.44
Sesame	155.15	74.75	41.14	24.83	16.82	11.91	8.91
Soybean	147.82	69.83	38.63	23.58	15.73	11.53	8.68
Sunflower	154.98	75.53	41.18	25.04	16.91	12.00	8.80
Walnut	116.55	59.00	33.72	21.20	14.59	10.51	8.21

[a] The viscosity values were obtained from the slope of the fit of experimental shear stress–shear rate data to the Newton's law of viscosity equation (Eq. 1).

constants for Equations 2–5 are given in Tables 3–5, respectively. For all the models and vegetable oil samples, the correlation coefficient obtained from the nonlinear regression procedure was > 0.99. Comparisons of the calculated SEE (Eq. 5), however, indicate that the temperature dependence of viscosity of vegetable oil sample was best described by the modified WLF model. The power law model gave the worst fit to the viscosity data. Similar results were obtained by Sopade *et al*. (25) for the viscosities of Australian honeys when the goodness of fit of the WLF model was compared with three other models (including the Arrhenius equation and the power law model).

FA composition and viscosity. The percentage amounts of monounsaturated FA, PUFA, and saturated and unsaturated FA in the various samples of vegetable oil are given in Table 6. These values are similar to those listed for these vegetable oils by the USDA (32) and Orthoefer (33). Correlation analysis using SAS statistical software (29) was carried out between viscosity and these FA types. The correlation ($R^2 << 1$) between oil viscosity and the amount of saturated or unsaturated FA was poor. The viscosities of vegetable oil (obtained from Table 2) were positively correlated with the amounts of monounsaturated FA (i.e., viscosity increased with increase in this type of FA) and negatively correlated with the amount of PUFA, respectively (i.e., viscosity decreased with increase in this FA) (Table 6). The results from the correlation analysis therefore indicate that the mass fraction of PUFA or monoun-

TABLE 2
Values of Constant A and Activation Energy (E_a) Obtained from Arrhenius Equation (Eq. 2) for the Various Samples of Vegetable Oil

Source of oil	A (mPa·s) × 10^6	E_a (MJ/kg mol K)	SEE[a] (Eq. 5)
Almond	191	31.7	0.480
Canola	197	31.6	0.481
Corn	321	30.0	0.355
Grapeseed	167	31.9	0.511
Hazelnut	178	32.0	0.452
Olive	185	31.9	0.446
Peanut	106	33.3	0.579
Safflower	394	29.3	0.336
Sesame	262	30.7	0.426
Soybean	217	31.1	0.414
Sunflower	269	30.7	0.433
Walnut	485	28.7	0.337

[a] SEE, standard error of estimate.

TABLE 3
Values of Constants *a* and *b* Obtained from the Modified WLF Model (Eq. 3) for the Various Samples of Vegetable Oils

Source of oil	*a*	*b*	SEE[a] (Eq. 5)
Almond	0.993	–224.8	0.025
Canola	0.985	–224.9	0.024
Corn	0.956	–224.5	0.025
Grapeseed	0.970	–225.5	0.023
Hazenut	0.998	–225.0	0.027
Olive	1.005	–224.8	0.027
Peanut	0.986	–226.3	0.024
Safflower	0.940	–224.3	0.024
Sesame	0.982	–224.3	0.024
Soybean	0.949	–225.6	0.025
Sunflower	0.984	–224.1	0.024
Walnut	0.936	–223.7	0.023

[a] For abbreviation see Table 2.

TABLE 4
Values of Constants *k* and *n* Obtained from the Power Law Model (Eq. 5) for the Various Samples of Vegetable Oils

Source of oil	*k*	*n*	SEE[a] (Eq. 5)
Almond	598.3	–0.77	1.38
Canola	571.5	–0.77	1.32
Corn	450.8	–0.73	1.20
Grapeseed	575.3	–0.77	1.26
Hazelnut	630.9	–0.78	1.48
Olive	637.7	–0.78	1.51
Peanut	703.8	–0.80	1.41
Safflower	397.3	–0.72	1.10
Sesame	518.7	–0.75	1.29
Soybean	499.7	–0.76	1.2
Sunflower	516.9	–0.75	1.28
Walnut	362.0	–0.70	1.02

[a] For abbreviation see Table 2.

TABLE 5
FA Compositions (percentage by weight of total FA) of the Vegetable Oil Samples

Source of oil	Saturated	Unsaturated	Monounsaturated	Polyunsaturated
Almond	8.84	91.16	65.64	25.52
Canola	11.53	88.47	52.98	35.49
Corn	14.93	85.07	25.60	59.47
Grapeseed	11.28	88.72	18.58	70.14
Hazelnut	8.92	91.08	77.63	13.45
Olive	16.88	83.12	76.06	7.06
Peanut	14.55	85.45	56.66	28.79
Safflower	8.28	91.72	13.52	78.20
Sesame	11.43	88.57	36.07	52.50
Soybean	16.24	83.76	22.41	61.35
Sunflower	8.15	91.85	52.52	39.32
Walnut	11.59	88.41	15.71	72.70

TABLE 6
Correlation Coefficients (obtained from correlation analysis) Between FA and Viscosity at Different Temperatures

	Temperature (°C)						
FA	5	20	35	50	65	80	95
Monounsaturated	0.82[a]	0.90	0.88	0.88	0.88	0.84	0.83
Polyunsaturated	–0.84	–0.90	–0.90	–0.88	–0.88	–0.83	–0.85
Saturated	–0.17	–0.10	–0.13	–0.05	–0.06	–0.01	–0.19
Unsaturated	0.17	0.10	0.13	0.05	0.06	0.01	0.19

[a] For example, the value of 0.82 implies that the correlation coefficient between monounsaturated FA and viscosity of vegetable oils at a temperature of 5°C was 0.82. Positive values indicate that viscosity of vegetable oils increased with an increase in amount of that FA, whereas negative values indicate that viscosity of vegetable oils decreased with increase in amount of that FA.

saturated FA in the oil influences the viscosities of vegetable oils. A mathematical relationship (Eq. 6) was therefore developed that relates viscosity to temperature and mass fraction of PUFA or mass fraction of monounsaturated FA (y: obtained from Table 5 for the vegetable oils used in the study) using the nonlinear regression procedure in SAS (29).

$$\mu = A\exp\left(\frac{B}{RT}\right) + y\exp\left(\frac{C}{RT}\right) \qquad [6]$$

where R is the universal gas constant (8.314 kJ/kg mol K) and T is the absolute temperature (K). The values of constants A, B, and C are given in Table 7. The high values of the correlation coefficient (0.99) and low values of the SEE indicated that the viscosity of vegetable oils can be predicted from the amount of PUFA or monounsaturated FA that were present. This information can be used for quality control and in the selection and design of equipment and processes for storing, handling, and using vegetable oils.

TABLE 7
Values of Constants (Eq. 6) That Can Be Used to Predict Viscosity of Vegetable Oil Based on Either Monounsaturated FA or PUFA

Parameter	Monounsaturated	Polyunsaturated
A	3.31×10^{-5}	2.31×10^{-4}
B	3.55×10^{4}	3.12×10^{4}
C	5.17×10^{3}	1.55×10^{4}
R^2	0.99	0.99
SEE[a] (Eq. 5)	0.96	1.08

[a] For abbreviation see Table 2.

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