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VISCOSITY AND SPECIFIC HEAT OF VEGETABLE OILS AS A FUNCTION OF TEMPERATURE: 35°C TO 180°C

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The viscosities and specific heat capacities of twelve vegetable oils were experimentally determined as a function of temperature (35 to 180°C) by means of a temperature controlled rheometer and differential scanning calorimeter (DSC). Viscosities of the oil samples decreased exponentially with temperature. Out of the three models (modified WLF, power law, and Arrhenius) that were used to describe the effect of temperature on viscosity, the modified WLF model gave the best fit. The specific heat capacity of the oil samples however increased linearly with increase in temperature. The equations developed in the study could be valuable for designing or evaluating handling and processing systems and equipment that are involved in the storage, handling and utilization of vegetable oils.

Keywords: ***Vegetable oil, Viscosity, Models, Specific heat.***

INTRODUCTION

About 79% of the over 100 million tonnes 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 carrier 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 they are one of the main ingredients used to manufacture soaps, cosmetics, and pharmaceutical products.[5,6]

Vegetable oils are mostly used for cooking and frying of foods and snacks. In both applications, the oils are subjected to elevated temperatures in the range of 35 to 180°C. The optimum design of heating and cooling systems for cooking and frying, and the fundamental understanding of cooking and frying processes require that the thermo-physical properties of the major ingredients involved (such as vegetable oil)[7] in these processes be known. Two of the important thermophysical properties are viscosity and specific heat. The sizing and selection of pumps and pipes for handling the hot oil also require that the viscosity of the oil be known.[8]

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.[9,10,11,12,13] Studies have also been carried out on the effect of temperature on the viscosity of some

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vegetable oils at temperatures less than 110°C[9,14,15,16] and at temperatures between 150–180°C[17]. The authors did not find any reported study on the viscosity of vegetable oils at temperatures between 110–150°C. Moreover, these studies that have been carried out on temperature effect on viscosity of vegetable oils have been carried out at different temperature ranges.

Additionally, no published data exist on the effect of temperature on the specific heat of vegetable oils throughout the temperature range of 35–180°C. Some of the reported studies on specific heat of vegetable oil include the following: Paul and Mittal[18]—specific heat of canola oil (after being used for frying) at 45–60°C; Maskan and Bagci[7]—sunflower seed oil (after being used for frying) at 0–50°C; and Bhatnagar et al.[19] of vegetable oils of corn, peanut, coconut, soybean and palm at temperatures of 20–100°C. The objectives of this study were to (a) obtain shear stress-shear rate data; and (b) to estimate the viscosity and specific heat of vegetable oils within temperatures range of 35–180°C.

MATERIALS AND METHODS

Rheological Test

The following 12 vegetable oil samples were used in this study: almond, canola, corn, grapeseed, halzenut, olive, peanut, safflower, sesame, soybean, sunflower, and walnut oil. The samples were purchased from a local grocery store in Auburn, AL. Rheological tests were carried out by means of a Bohlin rheometer (Model CVO-100, Bohin Instruments, Gloucestershire, UK)). A programmable water bath (Model F25-HE, Julabo USA Inc. Allentown, PA) was used to ensure correct and stable control of temperature during measurements. The rheometer and the water bath were controlled by means of a 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 ml) contained in the annular gap between the cup and bob. The samples were sheared at a shear rate of 1 to 100 s^{-1} and at temperatures of 35–180°C. All measurements were carried out in duplicate.

Specific Heat

A differential scanning calorimeter - DSC (Model Q100, TA Instruments, New Castle, DE) was used to estimate the specific heat of the twelve oil samples. The DSC was calibrated with indium before use. About 8 to 10 mg of oil sample was placed in hermetically sealed aluminum pans. An empty aluminum pan was used as reference. DSC runs were performed from 35–180°C at a scan rate of 20°C/min. Based on the measured amount of energy (heat) absorbed a sample during a run, the DSC manufacturer's software (TA Universal Analysis and TA Advantage Speciality Library) were used to analyze the heat flow data and calculate the specific heat of the oil samples. Results are the average of duplicate samples.

RESULTS AND DISCUSSION

Viscosity

Figure 1 shows that the typical closeness in values of the shear stress—the shear rate data obtained from duplicate measurements. This is confirmed by the plot of coefficient of

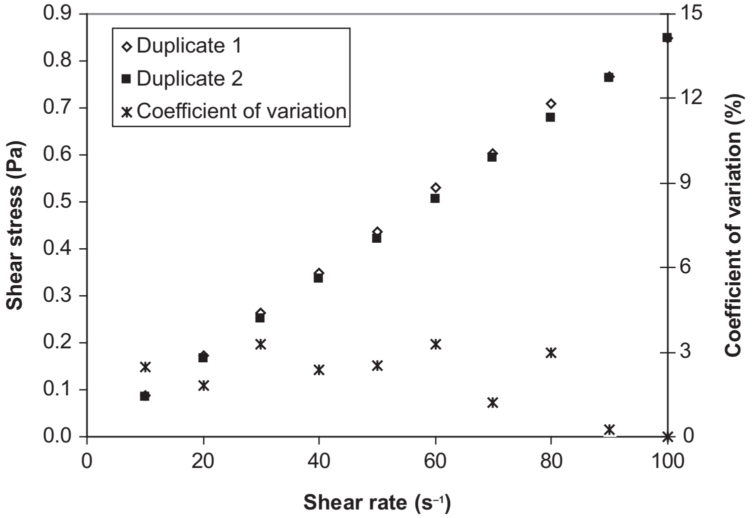

Figure 1 Closeness of duplicate shear stress—shear rate data for corn oil at temperature of 95°C.

variation at each shear rate. Similar values of coefficient of variation 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 35–180°C, the linear relationship of shear stress to shear rate indicate that all the vegetable oil samples tested in this study exhibit Newtonian behavior. The viscosities at each temperature were therefore obtained from the slope of the fit of experimental shear stress—shear rate data to the Newton's law of viscosity equation (Eq. 1). The values of the estimated viscosities are given in Table 1. In each case, the regression coefficient (R^2) that was obtained due to the fit of Eq. 1 to the experimentally obtained shear stress-shear rate data was greater than 0.995.

$$\sigma = \mu\dot{\gamma}, \tag{1}$$

where σ is shear stress (mPa), $\dot{\gamma}$ is the shear rate (s^{-1}) and μ is viscosity (mPa s). As expected, the viscosities of the oil decreased in an exponential manner with increase in temperature (Table 2). The viscosity at 35°C was about 10-to 15-fold of the viscosity at 180°C. This will have significant effects on the energy required to pump the oil and on the rate of heat transfer at elevated temperatures. In addition, the viscosity values obtained in this study were within 12% of the viscosity values reported in literature for soybean, corn and sunflower oil.[9, 13, 20, 21, 22]

The dependence of the oil viscosities to temperature was modeled using Eqs. 2–4. Eq. 2 is the Arrhenius model that is commonly used to model temperature dependence of a property.[9, 23] Eqs. 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.[23,24,26,27,28]

Arrhenius Model

$$\mu = A\exp\left(\frac{E_a}{RT}\right), \tag{2}$$

Table 1 Viscosity* (mPa s) of vegetable oil at different temperatures.

	Sample temperature (°C)									
Oil Source	35	50	65	80	95	110	120	140	160	180
Almond	43.98	26.89	17.62	12.42	9.15	7.51	6.54	5.01	4.02	3.62
Canola	42.49	25.79	17.21	12.14	9.01	7.77	6.62	5.01	4.29	4.65
Corn	37.92	23.26	15.61	10.98	8.56	6.83	6.21	4.95	3.96	3.33
Grape Seed	41.46	25.27	16.87	11.98	9.00	10.37	9.18	7.50	6.10	4.78
Hazlenut	45.55	27.40	17.83	12.49	9.23	7.56	6.69	5.25	4.12	3.48
Olive	46.29	27.18	18.07	12.57	9.45	7.43	6.49	5.29	4.13	3.44
Peanut	45.59	27.45	17.93	12.66	9.40	7.47	6.47	5.14	3.75	3.26
Safflower	35.27	22.32	14.87	11.17	8.44	6.73	6.22	4.77	4.11	3.44
Sesame	41.14	24.83	16.80	11.91	8.91	7.19	6.25	4.95	4.16	3.43
Soybean	38.63	23.58	15.73	11.53	8.68	7.17	6.12	4.58	3.86	3.31
Sunflower	41.55	25.02	16.90	11.99	8.79	7.38	6.57	4.99	4.01	3.52
Walnut	33.72	21.20	14.59	10.51	8.21	6.71	5.76	4.80	3.99	3.46

*The viscosity values were obtained from slope of the fit of experimental shear stress—the shear rate data for the Newton's law of viscosity equation (Eq. 1).

Table 2 Values of constant 'A' and activation energy (E_a) obtained from Arrhenius equation (Eqn. 2) for the various samples of vegetable oil.

Source of oil	(mPa s) $\times 10^3$	Ea (MJ/kg mol k)	SEE*
Almond	3.82	23.90	1.072
Canola	4.82	23.20	1.369
Corn	4.99	22.82	1.074
Grapeseed	1.41	20.31	2.349
Halzenut	3.31	24.35	1.192
Olive	3.02	24.63	1.250
Peanut	3.19	24.45	1.045
Safflower	7.15	21.76	0.963
Sesame	4.36	23.38	1.093
Soybean	4.84	22.95	1.015
Sunflower	4.37	23.40	1.140
Walnut	7.51	21.47	0.951

*SEE is the standard error of estimate.

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).

Modified WLF Model

$$Ln(\mu) = \frac{aT}{b+T}, \tag{3}$$

where a and b are constants to be determined from Eq. 3.

Power Law Model

$$\mu = k(T - T_{ref})^n, \tag{4}$$

where k and n are constants. T_{ref} is reference temperature of 273.15 K. Constants A, a, b, k, and n in Eqs. 2–4 were estimated by using the non-linear regression procedure NLIN in SAS statistical package.[29] The standard error of estimate (SEE) was computed and used to compare the goodness of fit (an equation with lower SEE value gives a better fit to experimental data compared to an equation with higher SEE value) of the equations to experimental data.[30, 31] The lower the estimated SEE for an equation, the better the fit of that equation to experimental data. The values of the estimated constants for Eqs. 2 to 5 are given in Tables 3–5, respectively. For all the models and vegetable oil samples, the correlation coefficient obtained from the non-linear regression procedure was greater than 0.99. However, comparisons of the calculated standard error of estimate (Eq. 5) indicate that the temperature-dependence of viscosity for the vegetable oil samples was best described by the modified WLF model. The Arrhenius equation gave the worst fit to the viscosity data. Similar result was obtained by Sopade et al.[25] for the viscosities of

Table 3 Values of constants ‘a’ and ‘b’ obtained from the modified WLF model (Eqn. 3) for the various samples of vegetable oil.

Source of oil	a	b	SEE*
Almond	0.658	–255.5	0.169
Canola	0.671	–253.9	0.136
Corn	0.649	–254.4	0.145
Grapeseed	0.804	–241.5	0.119
Halzenut	0.664	–255.4	0.159
Olive	0.662	–255.8	0.164
Peanut	0.647	–257.0	0.204
Safflower	0.654	–252.4	0.121
Sesame	0.656	–254.6	0.145
Soybean	0.639	–255.2	0.158
Sunflower	0.656	–254.8	0.159
Walnut	0.636	–253.3	0.132

*SEE is the standard error of estimate.

Table 4 Values of constants ‘k’ and ‘n’ obtained from the power law model (Eqn. 5) for the various samples of vegetable oil (Eq. 5).

Source of oil	k	n	SEE*
Almond	10.33×10^3	–1.535	0.430
Canola	9.00×10^3	–1.5060	0.373
Corn	7.00×10^3	–1.467	0.224
Grapeseed	5.48×10^3	–1.375	1.445
Halzenut	11.62×10^3	–1.558	0.356
Olive	12.19×10^3	–1.597	0.363
Peanut	11.93×10^3	–1.565	0.464
Safflower	5.36×10^3	–1.413	0.134
Sesame	8.55×10^3	–1.500	0.379
Soybean	7.59×10^3	–1.485	0.223
Sunflower	8.80×10^3	–1.506	0.420
Walnut	4.90×10^3	–1.400	0.285

*SEE is the standard error of estimate.

Table 5 Values of constants ‘m’ and ‘b’ in Eq. 6.

Source of oil	$m \times 10^3$	b	R^2
Almond	3.314	2.143	0.996
Canola	3.003	2.086	0.998
Corn	3.162	1.963	0.997
Grapeseed	2.920	2.037	0.993
Halzenut	2.492	1.807	0.996
Olive	1.715	2.025	0.998
Peanut	3.677	2.449	0.985
Safflower	2.832	2.181	0.998
Sesame	3.043	2.446	0.997
Soybean	2.792	1.956	0.996
Sunflower	3.477	2.566	0.998
Walnut	2.835	2.165	0.962

Australian honeys when the goodness of fit of the WLF model was compared to three other models (including Arrhenius equation and power law model).

Specific Heat

Specific heat of all the vegetable oil samples tested in the study increased linearly with increase in temperature from 35–180°C (Table 6 and Figure 2). The percent increase in specific heat was about 17% within this temperature range. Therefore, more heat will be required for a unit change in temperature per unit mass of a food that is cooked or fried with oil. It has been postulated that the increase in specific heat of materials with increase in temperature is because of expansion of a substance during heating.[32] Some of the heat being provided is therefore used to furnish the work required for the expansion of that material against the surroundings.[32] Similar increase in specific heat with increase in temperature has been obtained for various food and biological materials.[19,33,34,35]

The trendline function in Microsoft Excel was used to fit linear equation (Eq. 6) to the specific heat versus temperature.

$$c = m(T - T_{ref}) + b, \tag{5}$$

where T_{ref} is the reference temperature of 273.15 K and T is sample temperature in degrees Kelvin. The values of the slope (m) and intercept (b) of Eq. 6 for the various oil samples is given in Table 5. A good fit of the experimental data to Eq. 6 was obtained as evident by the values of regression coefficients (R^2) that were greater than 0.960. The linear equation will enable researchers and food processors to be able to predict the specific heat of these vegetable oils at temperatures between 35–180°C for quality control, and selection and design of equipment and processes that are needed to store, handle, and utilize vegetable oils.

CONCLUSIONS

It can be concluded from this study that temperature affects the viscosity and specific heat of vegetable oils at temperatures between 35–180°C with viscosity decreasing

Table 6 Specific heat (kJ/kg K) of the various oil samples at temperatures of 35 to 180°C.

T (°C)	Almond	Canola	Corn	Grapeseed	Halzenut	Olive	Peanut	Safflower	Sesame	Soybean	Sunflower	Walnut
35	2.354	2.208	1.673	1.572	1.726	1.746	2.045	2.076	2.117	1.675	2.244	2.034
40	2.368	2.223	1.684	1.576	1.731	1.742	2.055	2.090	2.131	1.692	2.257	2.046
45	2.375	2.231	1.692	1.579	1.734	1.738	2.060	2.098	2.137	1.702	2.263	2.054
50	2.388	2.245	1.702	1.586	1.742	1.742	2.071	2.110	2.148	1.715	2.276	2.068
55	2.400	2.257	1.714	1.595	1.750	1.747	2.081	2.122	2.158	1.728	2.287	2.082
60	2.417	2.274	1.728	1.606	1.761	1.756	2.095	2.137	2.172	1.741	2.302	2.095
65	2.427	2.283	1.738	1.615	1.767	1.760	2.102	2.147	2.180	1.751	2.311	2.105
70	2.444	2.300	1.754	1.630	1.780	1.769	2.117	2.164	2.195	1.765	2.328	2.121
75	2.462	2.317	1.769	1.642	1.792	1.777	2.133	2.180	2.210	1.779	2.345	2.136
80	2.477	2.333	1.783	1.654	1.803	1.783	2.147	2.195	2.224	1.798	2.359	2.150
85	2.492	2.348	1.800	1.667	1.814	1.787	2.159	2.210	2.239	1.809	2.374	2.164
90	2.508	2.365	1.817	1.679	1.826	1.790	2.172	2.224	2.254	1.822	2.388	2.179
95	2.523	2.379	1.837	1.691	1.837	1.791	2.184	2.239	2.269	1.836	2.403	2.193
100	2.541	2.397	1.847	1.706	1.850	1.794	2.198	2.257	2.286	1.853	2.421	2.210
105	2.558	2.413	1.867	1.719	1.863	1.794	2.212	2.277	2.301	1.920	2.437	2.226
110	2.576	2.430	1.886	1.735	1.876	1.796	2.226	2.292	2.317	1.906	2.455	2.243
115	2.593	2.446	1.903	1.751	1.890	1.798	2.239	2.307	2.334	1.906	2.473	2.258
120	2.610	2.463	1.918	1.766	1.902	1.800	2.252	2.323	2.349	1.915	2.491	2.272
125	2.627	2.480	1.934	1.782	1.915	1.801	2.265	2.339	2.364	1.929	2.508	2.285
130	2.642	2.495	1.948	1.797	1.926	1.803	2.280	2.361	2.378	1.943	2.523	2.297
135	2.658	2.511	1.962	1.812	1.939	1.803	2.290	2.371	2.392	1.958	2.539	2.308
140	2.676	2.528	1.975	1.831	1.953	1.804	2.300	2.384	2.409	1.973	2.558	2.321
145	2.695	2.543	1.987	1.847	1.965	1.804	2.312	2.399	2.424	1.987	2.574	2.331
150	2.715	2.559	1.999	1.862	1.978	1.803	2.322	2.413	2.440	2.003	2.592	2.345
155	2.733	2.574	2.010	1.878	1.990	1.803	2.333	2.425	2.472	2.016	2.608	2.353
160	2.752	2.588	2.021	1.893	2.003	1.803	2.341	2.436	2.485	2.045	2.625	2.361
165	2.766	2.600	2.028	1.905	2.012	1.799	2.342	2.447	2.492	2.053	2.636	2.367
170	2.786	2.615	2.037	1.919	2.025	1.794	2.341	2.458	2.504	2.064	2.650	2.376
175	2.804	2.629	2.043	1.934	2.036	1.788	2.337	2.466	2.516	2.072	2.662	2.379
180	2.823	2.640	2.045	1.949	2.045	1.787	2.328	2.469	2.528	2.079	2.672	2.377

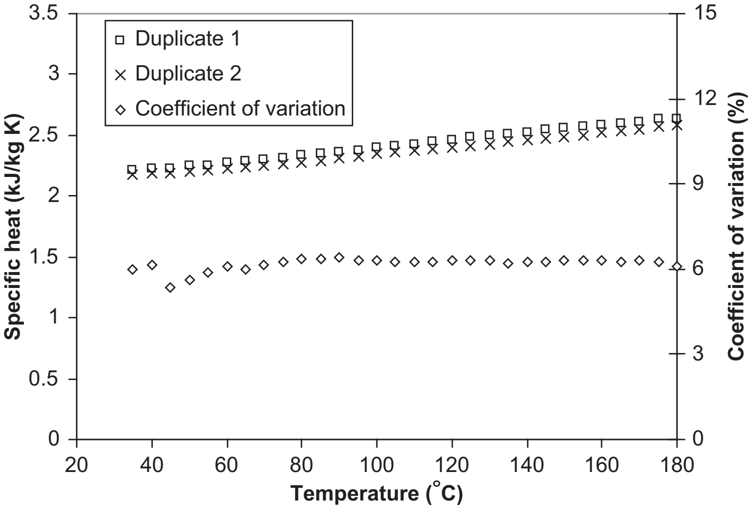

Figure 2 Closeness of duplicate specific heat values for canola oil at temperatures of 35ºC to 180ºC.

exponentially and specific heat increasing linearly with increase in temperature. The viscosity at 35°C was about 10-to 15-fold of the viscosity at 180°C while the percent increase in specific heat from 35–180°C was about 17%.

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