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Vegetable oils are used in the industry of processed food, including deep-fat frying. This work determined data on the thermophysical properties of cotton, canola, sunflower, corn, and soybean oils. Thermal conductivity, heat capacity, density, and viscosity were measured within the temperature range of 299.15–433.15 K. The data showed that the temperature influenced the thermophysical properties of the oils studied. The developed correlations could be used to predict these properties within the range of temperatures studied.

Keywords: *Thermophysical properties, Vegetable oils, Viscosity, Modeling.*

INTRODUCTION

Oils and fat are esters of the three carbon trihydric alcohols, glycerin, and many straight chained monocarboxylic acids known as fatty acids.[1] The oils are classified according to their origin as vegetable or marine. Vegetable oils are more extensively studied due to their commercial characteristics. Vegetable oils are used in the industry of processed food, including deep-fat frying (French fries, potato chips, seafood, fried chicken, donuts, snacks, etc.). Deep frying temperatures induce oil degradation, producing changes in its physical-chemical properties.[1,2] Such properties are being currently used to identify and control the quality of oils and fats in the food industry.[3]

Thus, different researches evaluating the quality and physical-chemical stability of vegetable oils during the frying process due to temperature were reported.[4–7] Understanding the vegetable oils' thermophysical properties is important for: (i) oil production, transport, and packaging processes; (ii) fried food processing; (iii) apparatus and control system project for frying process control; and (iv) utilization of such oils as other sources of diesel fuel. According to McMinn and Magee,[8] experimental measurements of

thermophysical properties are also useful in the fitting of statistical models and development of empirical models for their prediction. Although many different theoretical correlations are available for predicting thermophysical properties, they are unsatisfactory and limited due to the physical chemical complexity of foods. This research evaluated and analyzed effect of the temperature on the thermophysical properties, thermal conductivity, heat capacity, density, and viscosity of cotton, canola, sunflower, corn, and soybean oils. The experimental data were used to develop empirical correlations.

MATERIALS AND METHODS

Materials

Cotton, canola, sunflower, corn, and soybean oils were acquired from Bunge Foods (Gaspar, Brazil). Fatty acid methyl esters (FAMEs) Myristic (C14:0), Palmitic (C16:0), Stearic (C18:0), Oleic (C18:1), Linoleic (C18:2), and Linolenic (C18:3) acids were purchased from Sigma (St Louis, MO, USA).

Statistical Analysis

The experiments were carried out in triplicates at 15 different temperatures ranging from 299.15 to 433.15 K. The SAS® statistical[9] package was used to analyze the data. The suitability of the models was evaluated by using the coefficient of determination (R^2), the level of significance (p), and residual analysis.

Fatty Acid Composition

The fatty acid composition of the oils was determined, after converting the triglycerides into their methyl esters on a Shimadzu GL-14A (Shimadzu, Kyoto, Japan) gas chromatograph with split injection 1:40, equipped with flame ionization detector and a fused silica capillary column of 50 m × 0.33 mm DB-17 0.25 μm film thickness (Shimadzu). Working temperatures of the injector and detector were 473.15 and 493.15 K, respectively, and in the column were 463.15 to 473.15 K; a gradient was used at 2 K/min. Nitrogen was used as a carrier gas. Flow rates of hydrogen and air were selected to attain the maximum flame ionization detector signal response. Volume samples (1μL) were injected into the column. FAMEs were identified comparing their retention time and equivalent chain length with respect to standard FAMEs. FAME samples were quantified according to their percentage area.

Dynamic Viscosity

For dynamic viscosity (μ), vegetable oil measurements were determined in triplicates, and a rotating concentric cylinder viscometer, Searle type (Rheotest 2.1, Ottendorf-Okrilla, Germany) was used. The apparatus was completed with a thermotized bath (Marconi MA-184, São Paulo, Brazil), capable of maintaining the temperature at an accuracy of ±0.6 K.

Density

Density was measured using the pycnometer method[10] in triplicate. The sample kept in a 25 mL standard volumetric pycnometer was weighed using an analytical balance with a given uncertainty of ±0.0001 g (Mettler AB204, Columbus, OH, USA).

Heat Capacity and Thermal Conductivity

Both heat capacity and thermal conductivity were determined using equipment composed of a water thermostatic bath with stability of ±0.05% (Marconi MA-184, São Paulo, Brazil) and a cylindrical cell, with the liquid being tested by filling the annular space between two concentric cylinders. The cell was immersed in a thermostatic bath and the cell calibration was performed using distilled water and glycerin. Some details of this method, cell calibration, and experimental tests can be found elsewhere.[11−15] Power input to heater resistance was supplied by a laboratory DC power (Minipa MPS-3006D, São Paulo, Brazil), that allowed to adjust the current with a stability of 0.05%. An HP data logger with data acquisition monitored the temperatures with an accuracy of ±0.6 K. Heat capacity was measured under unsteady state conditions and thermal conductivity was measured under steady state conditions.[12,13]

RESULTS AND DISCUSSION

Table 1 shows the composition of the fatty acids of the vegetable oils obtained by gas chromatography, whose values are close to those described in the literature.[1,16] These oils are fundamentally constituted by triglyceride of fatty acids of chains C:16 and C:18. Moretto and Fett[17] reported that at temperatures below 473 K, the vegetable oils do not present significant alterations in their fatty acid composition.

The experimental data on density, thermal conductivity, heat capacity, and viscosity of the five vegetable oils are presented, respectively, in Tables 2–5, at the different temperatures evaluated. Oil viscosity decreases both in function of the degree of unsaturation and temperature.[5−7] Viscosity of the oils studied decreases approximately in 3% for each elevation of one degree in the temperature. Vegetable oil viscosity is the thermal physical property preferentially used to evaluate the quality of the oils used in large-scale food frying.[5,6] The viscosity data were correlated using the equations no linear (1)–(3). Equation (1) is the Arrhenius model.[7,10] Equation (2) is the modified form of the WLF (Williams-Landel-Ferry).[18,19] To correlate the μ of each oil, this study proposes the use of Eq. (3):

Table 1 Composition of fatty acids (%) of vegetable oils.

Oils	Miristic C14:0	Palmitic C16:0	Estearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3
Cotton	1.0	24.0	2.85	16.12	53.73	—
Canola	0.061	4.0	1.62	58.53	25.26	10.20
Sunflower	—	7.0	3.32	15.32	73.34	—
Corn	—	10.5	3.21	25.61	57.70	0.83
Soybean	0.12	10.51	3.22	22.31	53.58	8.50

Table 2 Vegetable oil density.

										Temperature (K)							
Oil	293.15 $\frac{\rho}{kg \cdot m^{-3}}$	303.15 $\frac{\rho}{kg \cdot m^{-3}}$	313.15 $\frac{\rho}{kg \cdot m^{-3}}$	323.15 $\frac{\rho}{kg \cdot m^{-3}}$	333.15 $\frac{\rho}{kg \cdot m^{-3}}$	343.15 $\frac{\rho}{kg \cdot m^{-3}}$	353.15 $\frac{\rho}{kg \cdot m^{-3}}$	363.15 $\frac{\rho}{kg \cdot m^{-3}}$	373.15 $\frac{\rho}{kg \cdot m^{-3}}$	383.15 $\frac{\rho}{kg \cdot m^{-3}}$	393.15 $\frac{\rho}{kg \cdot m^{-3}}$	403.15 $\frac{\rho}{kg \cdot m^{-3}}$	413.15 $\frac{\rho}{kg \cdot m^{-3}}$	423.15 $\frac{\rho}{kg \cdot m^{-3}}$	433.15 $\frac{\rho}{kg \cdot m^{-3}}$
Cotton	926.6	927.1	922.9	925.4	921.3	919.3	923.2	921.2	914.1	918.2	911.1	912.5	905.4	912.1	911.4
Canola	920.2	918.3	915.2	914.0	910.7	908.2	907.3	904.7	900.8	900.0	895.9	894.3	890.3	890.2	888.0
Sunflower	919.6	916.7	916.4	917.8	913.3	913.0	914.3	910.7	909.6	910.1	905.3	905.0	901.6	904.7	901.9
Corn	931.6	928.6	925.7	926.3	921.7	920.0	919.6	916.4	914.4	913.6	908.8	907.7	904.9	904.6	901.7
Soybean	922.7	920.3	913.7	910.6	906.9	902.0	898.7	896.0	889.8	887.1	882.5	879.2	874.7	870.8	867.9

Table 3 Heat capacity of vegetable oils.

Oil	Temperature (K)														
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15	413.15	423.15	433.15
	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$	$\dfrac{C_p}{J \cdot g^{-1} \cdot K^{-1}}$
Cotton	1.950	2.016	2.007	2.066	2.108	2.131	2.185	2.249	2.248	2.314	2.338	2.393	2.426	2.464	2.529
Canola	1.837	1.904	1.938	2.010	2.052	2.099	2.181	2.235	2.249	2.336	2.355	2.426	2.440	2.544	2.607
Sunflower	2.124	2.153	2.179	2.268	2.266	2.314	2.388	2.410	2.453	2.520	2.509	2.570	2.598	2.675	2.700
Corn	1.956	2.008	1.985	2.029	2.057	2.066	2.105	2.154	2.140	2.190	2.201	2.241	2.259	2.283	2.332
Soybean	1.918	1.974	1.957	2.006	2.038	2.052	2.095	2.148	2.140	2.194	2.209	2.254	2.277	2.306	2.359

Table 4 Thermal conductivity of vegetable oil.

Oil	Temperature (K)														
	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15	413.15	423.15	433.15
	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$	k / $W \cdot m^{-1} \cdot K^{-1}$
Cotton	0.174	0.176	0.175	0.177	0.178	0.178	0.180	0.182	0.181	0.183	0.184	0.185	0.186	0.187	0.189
Canola	0.166	0.167	0.168	0.169	0.169	0.170	0.172	0.172	0.173	0.175	0.175	0.176	0.176	0.178	0.179
Sunflower	0.161	0.161	0.162	0.163	0.162	0.163	0.164	0.164	0.164	0.165	0.164	0.165	0.165	0.167	0.167
Corn	0.162	0.162	0.163	0.165	0.164	0.165	0.167	0.167	0.168	0.169	0.168	0.169	0.169	0.171	0.172
Soybean	0.153	0.154	0.154	0.155	0.155	0.156	0.157	0.158	0.158	0.159	0.159	0.160	0.160	0.161	0.162

Table 5 Dynamic viscosity of vegetable oil.

| | Temperature (K) | | | | | | | | | | | | | | |
| Oil | 293.15 | 303.15 | 313.15 | 323.15 | 333.15 | 343.15 | 353.15 | 363.15 | 373.15 | 383.15 | 393.15 | 403.15 | 413.15 | 423.15 | 433.15 |
	mPa.s	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*	*mPa.s*
Cotton	52.246	33.504	21.875	15.922	11.847	9.084	7.404	6.131	4.948	4.325	3.662	3.253	2.831	2.585	2.366
Canola	93.990	61.280	40.668	29.203	20.989	15.645	12.208	9.586	7.528	6.234	5.039	4.261	3.566	3.106	2.695
Sunflower	63.941	41.671	28.772	21.416	15.910	12.476	10.159	8.274	6.932	5.964	5.044	4.444	3.910	3.538	3.166
Corn	69.903	45.732	29.681	21.144	16.172	12.288	9.916	8.368	6.633	5.787	5.005	4.430	3.850	3.482	3.241
Soybean	60.598	40.494	28.001	20.576	14.997	11.436	9.135	7.198	5.729	4.818	3.905	3.337	2.783	2.494	2.167

$$\mu = \mu_0 \exp\left(E_a/RT\right), \tag{1}$$

where μ is the viscosity values (mPa.s), μ_0 is the pre-exponential factor, E_a is the molar energy of activation of the viscous flow (kcal/g mol), T is the temperature (K), and R is the constant of the gases (1.987×10^{-3} kcal/gmol·K).

$$Ln(\mu) = \frac{a \cdot T}{b + T}, \tag{2}$$

where a and b are constants to be determined from Eq. (2) for each oil.

$$\mu = \frac{a' + b' \cdot T}{1 + c' \cdot T}, \tag{3}$$

where a', b', and c' are constants to be determined from Eq. (3) for each oil. The relative average deviations (RAD) were used for comparisons of experimental and correlated results according to the following equation:

$$RAD = \left[\frac{1}{m} \sum_{i=1}^{m} \left(\frac{|\mu_{\exp,i} - \mu_{cal,i}|}{\mu_{\exp,i}} \right) \right], \tag{4}$$

where $\mu_{\exp,i}$ and $\mu_{cal,i}$ are the calculated and experimental values for the dynamic viscosities, respectively; m is the number of experimental points. In Table 6, we present the parameters of Eqs. (1) to (3) and values of RAD of viscosity. In Table 6 it can be observed that the considered model (Eq. 3) to describe the behavior of the viscosity of oils studied in function of the temperature, presented the lowest values of RAD if compared to the other employed models. It brought a good fit to the experimental data. In both cases the same behavior of the data as well as the good capacity of the employed model (Eq. 3) was observed to predict the behavior of the experimental data.

Density, thermal conductivity, and heat capacity were correlated by using a simple linear model, as shown in the following equation:

$$\delta = A + BT, \tag{5}$$

where δ is the thermal physical property, A and B are constants determined by regression for each oil. The A and B values for each oil are presented in Table 7. The values of R^2 and p

Table 6 Parameter values used in Eqs. (1) to (3).

μmPa.s	[1]μ_o	[1]Ea	[1]RAD	[2]a	[2]b	[2]RAD	[3]a'	[3]b'	[3]c'	[3]RAD
Cotton	0.0004	6.8847	0.125	0.6472	−245.5402	0.334	−8.499	0.017	0.0037	0.093
Canola	0.0004	7.1270	0.058	0.8694	−237.4607	0.511	−19.369	0.043	0.0037	0.152
Sunflower	0.0011	6.3794	0.153	0.7771	−238.7205	0.277	−11.325	0.023	0.0036	0.074
Corn	0.0005	6.8359	0.581	0.7705	−240.3424	0.290	−11.7826	0.0246	0.0036	0.102
Soybean	0.0007	6.5800	0.219	0.7442	−240.4647	0.483	−13.3486	0.0294	0.0036	0.115

[1]Eq. (1); [2]Eq. (2); [3]Eq. (3).

Table 7 Parameter values used in Eq. (5).

	δ	A	B	p	R^2
Cotton	ρ/kg.m^{-3}	967.067	-0.134	<0.0001	0.83
	Cp/J.g^{-1}.K^{-1}	0.768	0.0001	<0.0001	0.99
	κ/W.m^{-1}.K^{-1}	0.144	0.0001	<0.0001	0.98
Canola	ρ/kg.m^{-3}	990.070	-0.237	<0.0001	0.99
	Cp/J.g^{-1}.K^{-1}	0.287	0.0053	<0.0001	0.99
	κ/W.m^{-1}.K^{-1}	0.139	0.0001	<0.0001	0.99
Sunflower	ρ/kg.m^{-3}	956.786	-0.127	<0.0001	0.94
	Cp/J.g^{-1}.K^{-1}	0.894	0.004	<0.0001	0.98
	κ/W.m^{-1}.K^{-1}	0.149	0.0001	<0.0001	0.91
Corn	ρ/kg.m^{-3}	992.686	-0.210	<0.0001	0.99
	Cp/J.g^{-1}.K^{-1}	1.198	0.002	<0.0001	0.99
	κ/W.m^{-1}.K^{-1}	0.142	0.0001	<0.0001	0.92
Soybean	ρ/kg.m^{-3}	1039.225	-0.397	<0.0001	0.99
	Cp/J.g^{-1}.K^{-1}	1.024	0.003	<0.0001	0.99
	κ/W.m^{-1}.K^{-1}	0.134	0.0001	<0.0001	0.99

are presented in Table 7, and indicate a good fitting of the linear model to the experimental data.

Oil density is a function of its degrees of saponification, unsaturation, free fatty acid content, humidity content, and temperature.[6] Therefore, density decreases with the temperature increase.[16] In the data presented, the density values of the five oils show an inverse relation to temperature increase on an average of –0.16 Kg/m^3 per each temperature degree. Timms[6] found the same tendency in density values when analyzing sunflower, olive, soybean, palm, coconut, and olive oils at different temperatures.

Thermal conductivity and heat capacity of the vegetable oils studied present a direct increase of their values with temperature increase, on an average of 0.0039 (J.g^{-1}.K^{-1}) and 0.0001 (W.m^{-1}.K^{-1}), respectively, for each temperature degree. Such research presented the same linear tendency obtained by Miller et al.[4] and Timms[6] who studied thermal conductivity and heat capacity, respectively, of vegetable oils at different temperatures.

CONCLUSIONS

The thermophysical properties of cotton, canola, sunflower, corn, and soybean oils were affected by the temperature. The mathematical models were well adjusted to the observed data. The model applied to predict the data of viscosity presented R^2 values superior to 0.83, on all cases. The linear model used for the correlation of thermal conductivity, heat capacity, and density showed results of *RAD*, which were inferior to 0.152, an indication of a good fit to the experimental data, for all studied cases. In general, the temperature increase promotes an increase in the viscosity and density properties. The opposite behavior is exhibited for the heat capacity and thermal conductivity.

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