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Thermodynamic properties of palm oil (*Elaeis guineensis*) and evening primrose seed oil (*Oenothera biennis*) as a function of temperature

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Abstract
This paper contains the results of a new experimental study of the effect of temperature on density and ultrasonic velocity for palm oil (*Elaeis guineensis*) and evening primrose seed oil (*Oenothera biennis*), due to their worldwide economic importance and potential for intensive farming in arid areas or regions with irregular rainfall/low water resources. Current processes design is strongly computer oriented then, consideration was also given to how accurate different theoretical prediction methods work. The Halvorsen's model and Collision Factor Theory were selected for prediction, attending to ease of use, accuracy and range of application, a good response at the studied conditions being observed, despite of geometrical simplifications and the use of estimated critical magnitudes by molecular group contribution approach.

Keywords: Thermodynamic properties, Vegetable oil, Temperature, modeling

1. Introduction

Thermodynamic properties are the most important parameters required in the design of equipments and processes. They are of practical interest into industrial manufacture of oils since applied thermal and mechanical procedures are close related on their temperature and pressure trend. In the last few years a considerable effort has been developed on physico-chemical properties of organic chemicals but no systematic analogous projects have been developed for food technology, a relative scarce of data being encountered in oils and fats, despite their economical importance.

Continuing our scientific work investigating physical properties related to equipment design of oil industries, we present the temperature dependence (288.15-333.15 K) of density and ultrasonic velocity for palm oil (*Elaeis guineensis*) and evening primrose seed oil (*Oenothera biennis*), due to their worldwide economic importance. From the experimental data, temperature dependent polynomials were fitted, the corresponding parameters being gathered.

Current processes design is strongly computer oriented then, consideration was also given to how accurate different prediction methods work. An enormous quantity of chemicals may be found in vegetable oils (free fatty acids, phenols, peroxide, monoacylglycerols, diacylglycerols, flavonoid polyphenols, polycyclic aromatic hydrocarbons and many other complex substances). The triacylglycerol molecule is often considered the main chemical structure to develop estimative studies on thermophysical properties [1]. The Rackett equation described by Halvorsen et al. [2-4] was tested for density estimation. This method requires the critical properties of the fatty acids and considers their composition as input. The Collision Factor Theory [5] was applied for ultrasonic velocity estimation. Accurate results were obtained despite of geometrical simplifications and use of estimated critical magnitudes by group contribution method.

2. Materials and methods

The oils, supplied by usual local providers, were stored in sun light protected form and constant humidity and temperature in our laboratory. They were analysed to determine their fatty acids compositions, the procedure being described earlier [6]. The average molar mass was computed as follows:

$$M_{oil} = 3\cdot\left(\sum_{i=1}^{N} x_i . M_i\right) + 2.M_{CH_2} + M_{CH} \quad (1)$$

being x_i the molar fraction and M_i the molar mass of each fatty acid without a proton, N the number of fatty acid found by analysis and M_{CH2} and M_{CH} are the molar mass contributions of glyceride molecule residue. Densities and ultrasonic velocities were measured with an Anton Paar DSA-48 vibrational tube densimeter and sound analyser, with a resolution of 10^{-5} gcm^{-3} and 1 ms^{-1}. Apparatus calibration was performed periodically in accordance with vendor instructions using Millipore quality water and ambient air at each temperature. Accuracy in the measurement temperature was better than $\pm 10^{-2}$ K. The molar mass, experimental and literature data of oils at 298.15 K [7-8] are gathered in Table 1.

3. Results and discussion

3.1. Data Treatment

The density and ultrasonic velocity were correlated as a function of temperature using Eq. 2:

$$P = \sum_{i=0}^{N} A_i T^i \quad (2)$$

where P is density (gcm^{-3}) or ultrasonic velocity (ms^{-1}), T is absolute temperature in Kelvin degrees and A_i are fitting parameters. N stands for the extension of the mathematical serie, optimised by means of the Bevington test. These properties are given as supplementary material. The fitting parameters were obtained by the unweighted least squared method applying a fitting Marquardt algorithm. The root mean square deviations were computed using Eq. 3, where z is the value of the property, and n_{DAT} is the number of experimental data.

$$\sigma = \left(\frac{\sum_{i=1}^{n_{DAT}} \left(z_{exp} - z_{pred}\right)^2}{n_{DAT}} \right)^{1/2} \quad (3)$$

Fitting parameters and deviations are gathered in Table 2. In Figures 1-3, the temperature trend of density, ultrasonic velocity and isentropic compressibility (computed by the Newton-Laplace equation) are gathered. These figures show a diminution of density and ultrasonic velocity when temperature rises, due to a strong diminution of the packing efficiency of the triacylglycerol by molecules kinetics.

3.2. Prediction of densities

The physical property packages used in chemical simulators typically rely on generalized equations for predicting properties as a function of temperature, pressure, etc. Despite the success developing several procedures of density estimation for pure compounds or mixtures, only a few of them may be of real application for fats and oils. One proposed correlation that holds promise for application to oils is the Rackett equation of state [2,3]. The modification of this equation by Halvorsen et al. [4] has demonstrated to be accurate, only requiring critical magnitudes for the enclosed fatty acids. If these magnitudes are not known, they must be estimated. Previous works show that the molecular group contribution method of Constantinou and Gani [9] provides accurate predictions for organic molecules as fatty acids (Table 3). The method of Halvorsen [2-4] is described as follows:

$$\rho = \frac{\sum x_i . M_i}{R.\left(\frac{\sum x_i T_{ci}}{P_{ci}}\right).\left(\sum x_i . \beta_i\right)^{[1+(1-T_r)^{2/7}]}} + F_c \quad (4)$$

where ρ is the oil density, x_i is the mole fraction of fatty acid, M_i is the molar mass of each fatty acid, R is the universal constant of gases, P_{ci} is the critical pressure, T_r is the reduced temperature and b is the compressibility factor, Z_c, or an acentric factor dependent parameter [3]. The mixing rule to compute the pseudocritical temperature of the oil is described as follows

$$T_r = \frac{T}{\sum x_i T_{ci}} \quad (5)$$

F_c is a correction factor proposed by Halvorsen which depends on the oil structure backbone. The correction factor equation for the studied is:

$$F_c = 0.0236 + 0.000082 \cdot (875 - M_{oil}) \quad (6)$$

The Figure 4 shows the flowchart to calculate the density of each oil. In Table 4 shows the root square deviations for predictive density values by Halvorsen's model (HM) versus experimental data.

3.3. Prediction of ultrasonic velocities

In the last few years an increasingly interest for the application of low/high frequency ultrasound techniques for thermodynamic applications has occurred, caused by their versatile uses as computation of heat capacity, compressibility studies or concentration measurements. Ultrasonic velocity has been systematically measured but this kind of data is scarce yet. We compare our experimental data with the values determined by the Collision Factor Theory (CFT) [5], which is dependent on the collision factors among molecules as a function of temperature:

$$u = \frac{u_\infty . \left(\sum x_i S_i\right) . \left(\sum x_i B_i\right)}{V} \quad (7)$$

where u_∞ is 1600 m/s, S_i is the collision factor of each fatty acid, B_i is the molecular volume of each fatty acid (calculated by Bondi's method) and V is the molar volume considering the oil a mixture of fatty acids. The collision factors (S) were estimated by Eq. 8, using open literature for density [10] and Wada method for estimation of ultrasonic velocity of each fatty acid [11]. The deviations for CFT method are gathered in Table 4.

4. Conclusions

In this work, the densities and ultrasonic velocities of the triacylglycerol vegetable oils palm oil (*Elaeis guineensis*) and evening primrose seed oil (*Oenothera biennis*) were studied at the range of temperature 288.15-333.15 K and atmospheric pressure. These data were correlated by polynomial expressions which fitted the data well. The systems exhibited a strong expansive tendency attending to rising temperatures due to the huge molecular volume of triacylglycerol molecules. It is known that certain properties of the enclosed fatty acid residues have significant effects on the fluidity and, in general, thermodynamics of the vegetable oils. Most of the bonds in the hydrocarbon chains of fatty acids are single bonds, but the relative abundance of unsaturated bonds modifies the electronic density into chains and then, intermolecular interaction into the same molecule or dislike molecules. This trend is strong dependent of temperature, the presence of double bonds (unsaturated bonds), which in fatty acid residues exist in cis configurational form, produces folds in the geometry of the molecules, resulting in close intermolecular contacts, and relative increase of density, ultrasonic velocity and decrement of isentropic compressibility (Figures 1-3), as our experimental data confirm.

In what is referred to theoretical estimation, the tested models offer relative accurate results at the studied temperatures. A slight underestimation was observed for the Halvorsen´s method (deviation of 1.56% for palm oil and 3.69% for evening primrose seed oil) and for Collision Factor Theory (deviation of 18.60% palm oil and 23.42% for evening primrose seed oil). Deviations yielded for these magnitudes should be considered as a satisfactory result for industrial uses, supporting their validity as predictive tools, having in mind the high non-ideality of these compounds.

Table 1: Comparison of experimental and literature data for vegetable oils at 298.15 K

Compound	Provider	Molar Mass ($gmol^{-1}$)	Fatty acid Mass comp. %	Exp. Density (gcm^{-3})	Lit. Density (gcm^{-3})	Exp. Ultrasonic Velocity (ms^{-1})	Lit. Ultrasonic Velocity (ms^{-1})
Palm oil	Master foods	851.08	Myristic (14:0) 1.3 Palmitic (16:0) 41.8 Stearic (18:0) 3.4 Oleic (18:1) 41.9 Linoleic (18:2) 11.6	0.908973	0.91414[a]	1443.10	na
Evening primrose seed oil	Inkanat-terra amazonas	877.37	Palmitic (16:0) 6.6 Stearic (18:0) 1.8 Oleic (18:1) 7.8 Linoleic (18:2) 75.2 Linolenic (18:3) 8.6	0.922074	0.9283[b]	1455.14	na

[a]Narvaez et al., 2008 [1]
[b]Budavari, 1996 [2]
na, not available

Table 2: Parameters of Eq. 2 for 288.15–333.15 K and root mean square deviations (σ) (Eq. 3)

			$\rho/(gcm^{-3})$		
	A_0	A_1	A_2	A_3	σ
Palm oil	1.185277	-1.336622 E-3	1.945689 E-6	-1.914860 E-9	0.393 E-9
Evening primrose seed oil	1.139240	-7.855917 E-4	2.195822 E-7	-9.287043 E-11	0.172 E-10
			$u/(ms^{-1})$		
	A_0	A_1	A_2	A_3	σ
Palm oil	3080.009102	-8.269506	0.011646	-7.795308 E-6	1.047 E-2
Evening primrose seed oil	3734.931811	-14.586633	0.032279	-3.019106 E-5	6.291 E-3

Table 3: Estimated critical values by Constantinou and Gani method's [9] for the fatty acids enclosed into the vegetable oils

Fatty acid	P_c(MPa)	T_c(K)	Z_c	ω
Palmitic	1.4307	780.38	0.2076	0.8007
Oleic	1.2802	797.50	0.1999	0.8699
Linoleic	1.3059	798.36	0.2006	0.8585
Linolenic	1.3325	799.20	0.2013	0.8470
Stearic	1.2553	796.65	0.1993	0.8813
Myristic	1.6510	762.51	0.2165	0.7184

Table 4: Root mean square deviations (Eq. 3) for predictive density values by Halvorsen's Model [2-4] (HM) and ultrasonic velocities by Collision Factor Theory [5] (CFT) at 298.15 K

	HM	CFT
Palm oil	1.56	18.60
Evening primrose seed oil	3.69	23.42

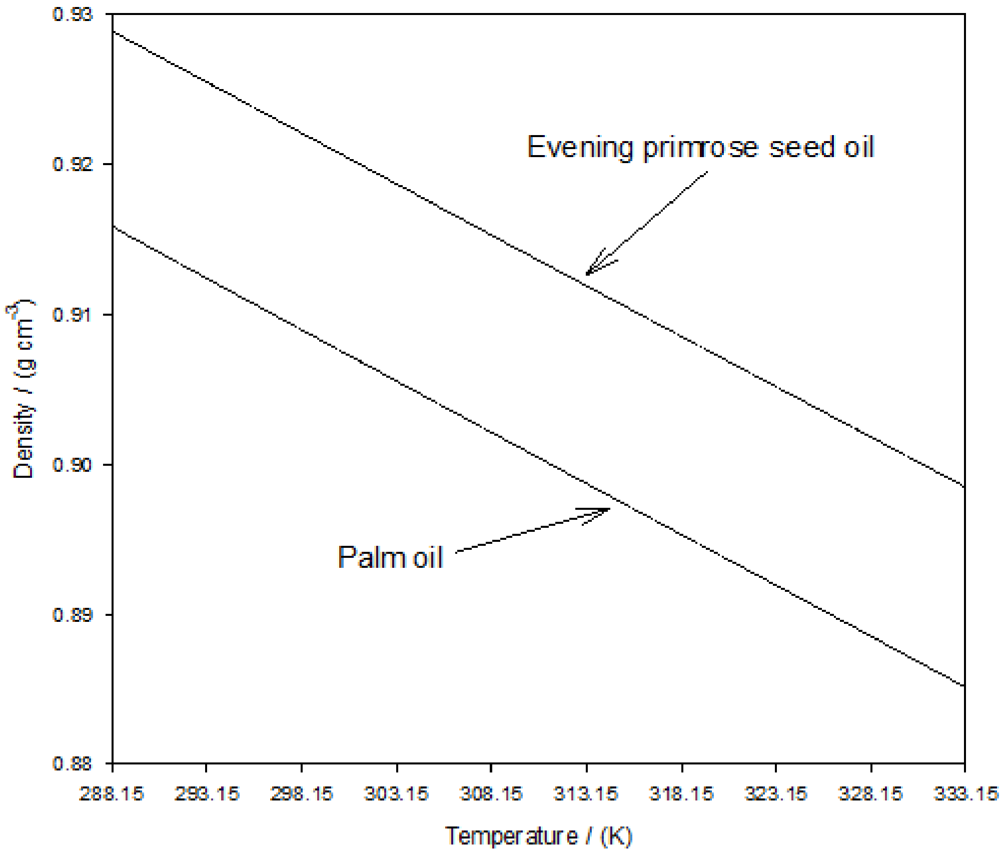

Fig. 1 Temperature dependence of density for the studied vegetable oils

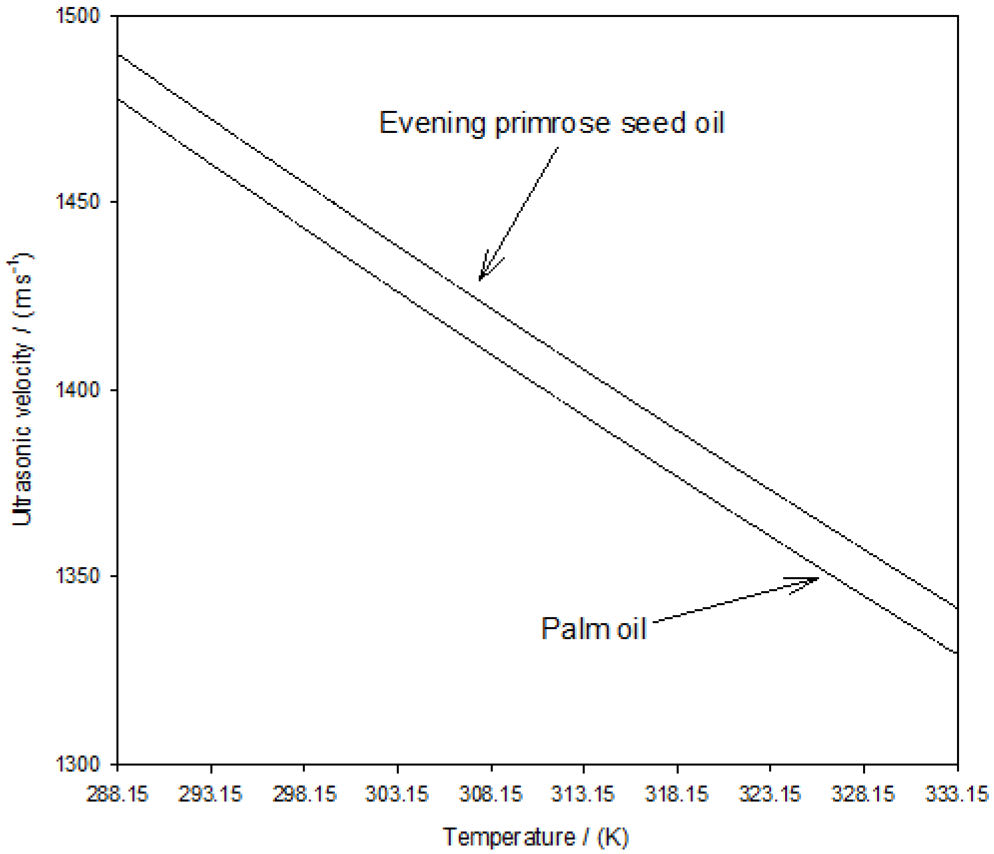

Fig. 2 Temperature dependence of ultrasonic velocity for the studied vegetable oils

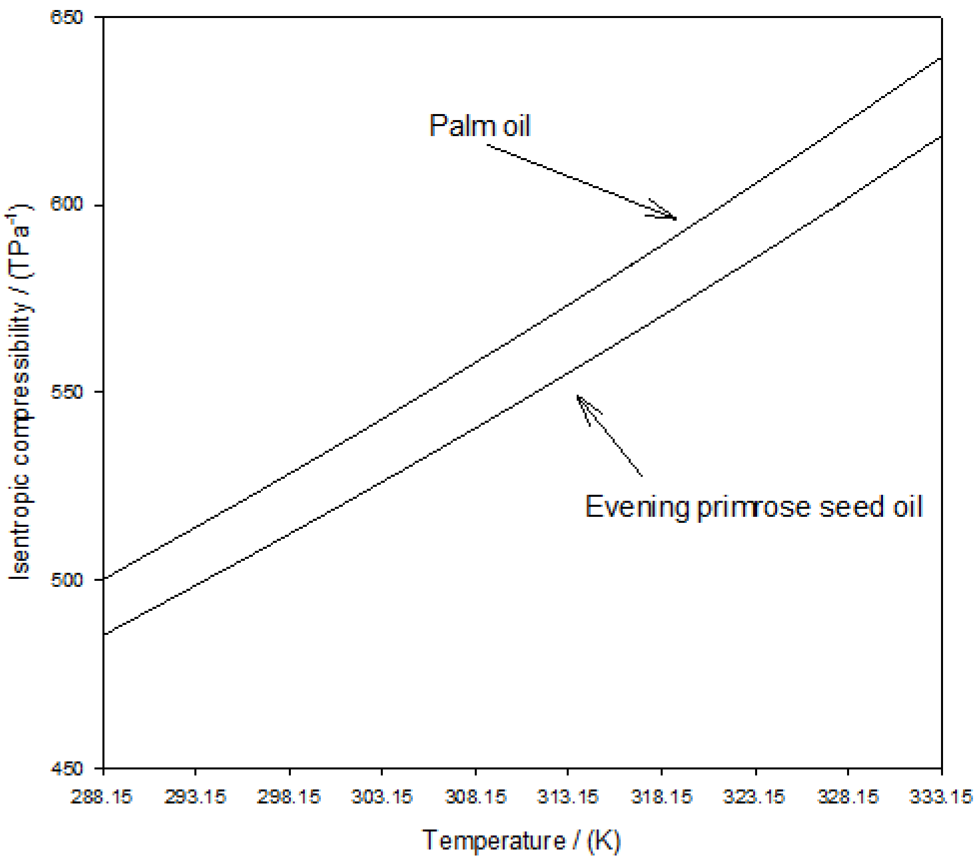

Fig. 3 Temperature dependence of isentropic compressibility for the studied vegetable oils

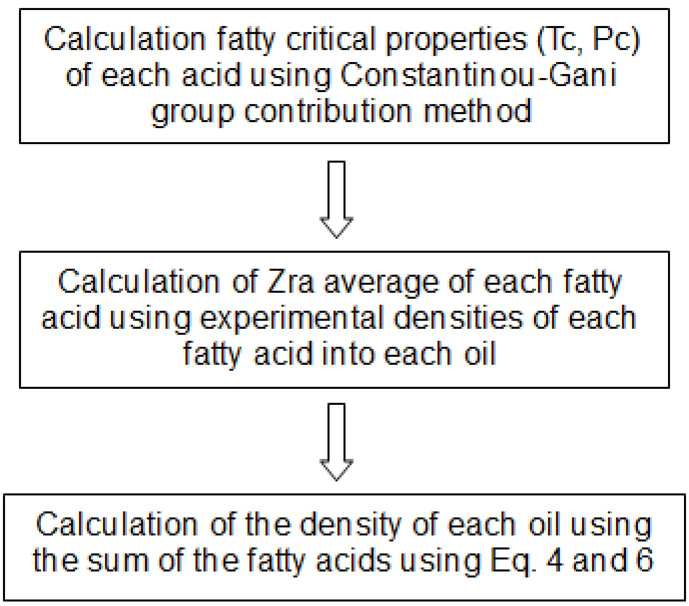

Fig. 4 Flowchart to calculate the density of each oil by Halvorsen´s method

5. Appendix

Supplementary data should be found in the online version

6. Acknowledgments

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