Densities and Viscosities of Vegetable Oils of Nutritional Value

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Densities and viscosities of five vegetable oils (Babassu oil, Buriti oil, Brazil nut oil, macadamia oil, and grape seed oil) and of three blends of Buriti oil and soybean oil were measured as a function of temperature and correlated by empirical equations. The estimation capability of two types of predictive methodologies was tested using the measured data. The first group of methods was based on the fatty acid composition of the oils, while the other was based on their triacylglycerol composition, as a multicomponent system. In general, the six models tested presented a good representation of the physical properties considered in this work. A simple method of calculation is also proposed to predict the dynamic viscosity of methyl and ethyl ester biodiesels, based on the fatty acid composition of the original oil. Data presented in this work and the developed model can be valuable for designing processes and equipment for the edible oil industry and for biodiesel production.

Introduction

Vegetable oils and fats are important in human nutrition as a source of energy, essential fatty acids, and fat-soluble vitamins (A, D, E, and K). Nowadays, they are also considered as a potential renewable source of energy. The interest in daily intake of nutritional constituents of edible oils and in the production of biodiesel on a worldwide scale has increased the demand for new renewable oil sources. The knowledge of their physical properties as a function of temperature and reliable predictive models is of great practical interest for food and chemical engineering, considering the demand of computational tools in the design and evaluation of processes.

The prediction of the behavior of liquid oils under processing conditions depends on measuring bulk properties (density and viscosity) and relating the experimental data by empirical equations. When no experimental data are available, group contribution methods are of interest for engineering applications.

In this work, three vegetable oils from the Amazon region (Babassu oil, Brazil nut oil, and Buriti oil) and also grape seed oil and macadamia oil were selected for investigation based on their nutritional value and also on their possible application as biodiesel fuel. Although Babassu oil (a lauric oil extracted from a palm tree named Babassu or *Orbignya ssp*) is characterized by a high level of short-chain and saturated fatty acids, it also contains an important concentration of unsaturated fatty acids,[1] in comparison with coconut oil (an important textural agent in the food industry). Brazil nut oil, Buriti oil (extracted from a palm tree named Buriti or *Mauritia flexuosa*), grape seed oil, and macadamia oil exhibit very high content of unsaturated fatty acids (oleic acid and/or linoleic acid),[1,2] which gives them credit as high-quality nutritional oils in terms of prevention of cardiovascular diseases, due to their blood cholesterol-lowering properties. Buriti oil is also characterized by an exceptional high concentration of carotenes,[2] and its blend with other oil could be interesting for culinary use.

Vegetable oils are formed mainly by triacylglycerols, in addition to a variety of minor compounds. Variations in the quantity and type of these triacylglycerols are responsible for the wide range of oils found in nature and for the differences in their physical properties. Besides measuring new data for density and viscosity of vegetable oils, relating them mathematically with oil composition is important for design and optimization of edible oil refining and biodiesel processes. Allen et al.[3] and more recently Shu et al.[4] developed methods capable of predicting the viscosity of biodiesel based only on their fatty acid ester composition. In the case of the work of Shu et al.,[4] the authors applied a novel topological index, correlating it to viscosity by linear equations.

To expand the available databank for density and viscosity of vegetable oils in the literature, the present work reports viscosity data for five different oils, and also blends of Buriti oil/soybean oil (1 to 1, 1 to 2, and 1 to 3 of volume fractions), as a function of temperature. Following previous works,[5,6] predictive methods from the literature were also tested for densities and viscosities of the oils and blends, and the results were compared with the experimental data. Two approaches were adopted: the first one was a group of methods that considered the fatty acid composition of the oil or blend as inputs;[5,7,8] the second one considered the oil or blend as a multicomponent mixture of triacylglyerols.[9–11] Except for grape seed oil, no previous work reported or predicted density or viscosity of the selected oils (or blends).

Experimental Section

Materials. Babassu oil was kindly supplied by Oleama (Maranhão, Brazil). Buriti oil was bought in the region of the Araguaia River (Tocantins, Brazil). Maranhão is a state of northern Brazil, situated south of the Equator and to the southeast of the Amazon River basin. Tocantins is an inland

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Table 1. Densities ρ of Oils and Blends as a Function of Temperature t

	vegetable oils					blends of Buriti oil/soybean oil (volume fractions)		
t/°C	Babassu	Brazil nut	Buriti	grape seed	macadamia	1 to 1	1 to 2	1 to 3
					ρ/g·cm^{-3}			
20	−	0.91462	0.91254	0.92060	0.91249	0.91661	0.91681	0.91977
30	0.91347	0.90730	0.90513	0.91398	0.90534	0.90923	0.90906	0.91240
40	0.90637	0.90035	0.89831	0.90683	0.89895	0.90231	0.90253	0.90547
50	0.89923	0.89355	0.89155	0.90012	0.89172	0.89554	0.89579	0.89880
60	0.89307	0.88642	0.88441	0.89311	0.88427	0.88843	0.88865	0.89164
70	0.88487	0.87969	0.87775	0.88632	0.87698	0.88175	0.88203	0.88496

Table 2. Dynamic Viscosities η of Oils and Blends as a Function of Temperature t

	vegetable oils					blends of Buriti oil/soybean oil (volume fractions)		
t/°C	Babassu	Brazil nut	Buriti	grape seed	macadamia	1 to 1	1 to 2	1 to 3
					η/mPa·s			
20	−	70.83	75.04	60.04	80.39	71.79	71.48	63.46
30	39.15	46.72	53.24	40.80	52.76	48.66	48.04	42.09
40	26.36	31.86	35.77	28.43	35.26	34.12	32.76	28.99
50	18.69	22.59	25.14	20.74	24.72	23.56	22.68	21.03
60	13.70	16.58	18.24	15.53	17.95	16.85	16.65	15.71
70	10.58	12.87	14.17	12.15	13.86	13.10	12.80	12.14
80	8.13	9.86	10.83	9.58	10.55	10.11	10.02	9.60
90	6.50	7.87	8.65	7.78	8.58	8.12	8.07	7.74

state of north-central Brazil, forming the boundary between the Amazon Rainforest and the coastal savanna. Commercial samples of Brazil nut oil, grape seed oil, and soybean oil were bought from a local supplier in the city of Campinas (São Paulo, Brazil). The oil from macadamia nuts was extracted from broken nuts by cold pressing at 60 t in a manual control hydraulic press (Charlott Hydraulic Press, U.S.A.). Oils were analyzed by gas chromatography for the fatty acid methyl esters to determine the fatty acid composition, according to the official method (1-62) of the AOCS.[12] The fatty acid samples were prepared in the form of fatty acid methyl esters according to the official method (2-66) of the AOCS.[12] Analytical conditions: chromatograph, CGC Agilent 6850 GC System; column, DB-23, Agilent (50 % Cyanopropyl−methylpolysiloxane), 60 m × 0.25 mm × 0.25 μm; helium as the carrier gas at a rate of 1.0 mL·min^{-1}; injection temperature of 250 °C; column temperature of 110 °C for 5 min, 110 to 215 °C (rate of 5 °C·min^{-1}), 215 °C for 24 min; detection temperature of 280 °C. The fatty acid methyl esters were identified by comparison with external standards purchased from Nu Check Inc. (Elysian, IL). The quantification was accomplished by internal normalization. The acidity values, expressed as mass fraction of oleic acid, for Babassu oil, Brazil nut oil, Buriti oil, grape seed oil, macadamia oil, and soybean oil, were 0.10 %, 0.03 %, 2.60 %, 0.08 %, 0.20 %, and 0.11 %, respectively. Unsuitable handling of Buriti fruit previous to the oil extraction was probably the cause of its higher content of acidity. Blends of Buriti oil and soybean oil with volume fractions of 1 to 1, 1 to 2, and 1 to 3 were prepared by means of volumetric Pyrex glass flasks of (25 and 50) mL. Buriti oil had 1296 mg·kg^{-1} of total carotenes, which were measured by the method of PORIM.[13] Samples of macadamia oil and Babassu oil used in this work were provided by co-workers. In this way, their fatty acid compositions were already set and can be reached referring to Rodrigues et al.[14] for macadamia oil and to Reipert[15] for Babassu oil.

Apparatus and Procedure. Densities, ρ, of the oils and blends were determined at different temperatures with an Anton Paar DMA-58 vibrating tube densimeter for which the temperature was controlled within ± 0.01 K. The standard deviations of the measurements in the densimeter after proper calibration were $\leq 4 \cdot 10^{-5}$ g·cm^{-3}. The variation coefficients (calculated by the ratio of the standard deviation to the mean density value) changed within the range of 0.0006 % and 0.0029 % so that the uncertainty of the experimental measurements can be estimated as being not higher than 0.003 %. The experimental data were measured at temperatures from 20 °C to 70 °C at 10 °C intervals, except for Babassu oil, which had a melting point of ≈ 30 °C. Each measurement was replicated three times. Apparatus calibration was made at each temperature, using distilled water, air, and a standardized mineral oil, in accordance with the user manual. Dynamic viscosity data, η, were determined at different temperatures in an automatic viscosimeter AMV 200 (Anton Paar), connected to a thermostatic bath (Paar Physica model Viscotherm VT2). The principle of the measuring is the efflux time of a ball immersed in the sample inside a glass capillary for different inclination angles. The experimental data were measured at temperatures from 20 °C to 90 °C at 10 °C intervals, except for Babassu oil, which had a melting point of ≈ 30 °C. Each record was replicated at least four times with nine different inclination angles (30° to 70°). The standard deviations of the determinations in the Anton Paar viscosimeter varied within the range of 0.024 mPa·s (Babassu oil at 90 °C) and 1.729 mPa·s (blend 1 to 2 of volume fractions at 20 °C), being more important at lower temperatures. The variation coefficient ranged from 0.0006 % to 2.882 %, so that the uncertainty of the experimental measurements, especially at low temperatures, can be estimated as being not higher than 2.9 %. Apparatus calibration (measuring systems 1.8 and 3.0) was made periodically, using a standardized mineral oil, in accordance with the user instructions.

Prediction. The capabilities of two types of predictive models were tested in this work. The first type was a group of methods that considered the fatty acid composition of the oil as inputs, i.e., the model of Halvorsen et al.[7] for estimating density of oils and the recent models suggested by Fasina et al.[8] and Ceriani et al.[5] for estimating viscosity of oils. The second type was a group of methods that considered the oil or blend of oils as a multicomponent mixture of triacylglycerols. To estimate the triacylglycerol composition of the five oils selected in this work, the statistical methodology suggested by Antoniossi Filho et al.,[16] extensively applied in previous works of this research group, was used. Probable triacylglycerol compositions of macadamia oil and Babassu oil were taken from Rodrigues et al.[14] and Reipert,[15] respectively. Initially, it was necessary to

predict density and viscosity for each triacylglycerol of the oil/blend using the methods of Halvorsen et al.[7] and Ceriani et al.,[5] respectively, and then use one of the following methods to estimate the viscosity of the oil (multicomponent mixture): the modified Kay's rule,[9] the Kendall and Moore model,[10] and the GC-UNIMOD.[11] The modified Kay's rule and the Kendall and Moore model are presented in eqs 1 and 2, respectively.

$$\ln\left(\frac{\eta_{oil}}{\rho_{oil}}\right) = \sum_{i=1}^{n} x_i \cdot \ln\left(\frac{\eta_i}{\rho_i}\right) \quad (1)$$

$$\left(\frac{\eta_{oil}}{\rho_{oil}}\right)^{1/3} = \sum_{i=1}^{n}\left[x_i \cdot \left(\frac{\eta_i}{\rho_i}\right)^{1/3}\right] \quad (2)$$

where x_i is the mole fraction of triacylglycerol i; η_i is the dynamic viscosity of the triacylglycerol i; ρ_i is the density of the triacylglycerol i; and n is the number of triacylglycerols of the oil (or blend).

The group-contribution thermodynamics viscosity model (GC-UNIMOD) is similar to the UNIFAC method proposed for phase equilibrium prediction. It takes into account two contributions for the mixture kinematic viscosity (ν_{oil}): *combinatorial* and *residual part*, as follows

$$\ln(\nu_{oil}) = \sum_{i=1}^{n}\left[\xi_i^C + \xi_i^R\right] \quad (3)$$

The combinatorial part, ξ_i^C, is related to the differences in size of the molecules present in the mixture, so that only properties for pure substances are considered in this contribution. The residual part, ξ_i^R, takes into consideration the energy of interaction between the different groups present in the mixture.

The modified Kay's rule and the Kendall and Moore model are much easier to use than the GC-UNIMOD, but the last one is supposed to be capable of describing differences between molecules in a mixture in a better way, given that it considers differences in size of the molecules and the interaction between the different groups in the mixture. These three methods were already tested for binary, ternary, and quaternary mixtures of fatty compounds by Gonçalves et al.[6] satisfactorily.

To evaluate the predictive capability of the tested models, the average relative deviation (ARD) was calculated according to the relation below

$$\mathrm{ARD} = \frac{\sum_{n}\dfrac{\left|P_{exptl} - P_{calcd}\right|}{P_{exptl}}}{N} \quad (4)$$

where N is the number of experimental data for each oil and P is the physical property considered (density or viscosity).

Dynamic viscosities were converted into kinematic viscosities by means of the following equation

$$\nu = \frac{\eta}{\rho} \quad (5)$$

where ρ is the density.

Results

Table 1 presents the densities of oils and blends of oils as a function of temperature. The experimental values of dynamic viscosities measured in this work are given in Table 2. Linear correlations of ρ/g·cm^{-3} vs t/°C and of ln(η/mPa·s) vs t/°C were adjusted using the toolbox *curve fitting* from MatLab (Mathworks 7.1) for the temperature ranges of (20 to 70) °C for density and of (20 to 90) °C for viscosity. Tables 3 and 4 give the coefficients.

Table 3. Linear Coefficients for the Correlation of ρ vs t[a]

vegetable oil	temperature range t/°C	a	b	R^2
Babassu	30 to 70	0.9342	−0.0006937	0.9989
Brazil nut	20 to 70	0.9284	−0.0006983	0.99990
Buriti		0.9262	−0.0006932	0.9998
grape seed		0.9343	−0.0006860	0.9999
macadamia		0.9269	−0.0007111	0.9991
blends of Buriti oil/soybean oil (volume fractions)				
1 to 1	20 to 70	0.9303	−0.0006958	0.9998
1 to 2		0.9301	−0.0006887	0.9991
1 to 3		0.9334	−0.0006946	0.9998

[a] Linear equation: ρ/g·cm^{-3} = a + b·t/°C.

Table 4. Linear Coefficients for the Correlation of ln η vs t[a]

vegetable oil	temperature range t/°C	a	b	c	R^2
Babassu	30 to 90	−2.467	894.3	115.9	0.99990
Brazil nut	20 to 90	−3.209	1248.0	147.1	0.9996
Buriti		−4.339	1793.0	186.6	0.9997
grape seed		−2.731	1109.0	142.4	0.9993
macadamia		−3.263	1267.0	145.5	0.9993
blends of Buriti oil/soybean oil (volume fractions)					
1 to 1	20 to 90	−5.945	2551.0	229.5	0.9989
1 to 2		−4.247	1678.0	176.9	0.9988
1 to 3		−2.491	1000.0	130.5	0.9992

[a] Linear equation: ln(η/mPa·s) = a + b/(t/°C + c).

To apply the two types of predictive methods and compare them with the experimental data shown in Tables 1 and 2, it was first necessary to obtain the fatty acid composition of the oils selected (Table 5). Table 6 gives their probable (estimated) composition in terms of triacylglycerols. Tables 5 and 6 also show the composition of the three blends of Buriti and soybean oil. Considering that our goal in this case was to test the capability of the selected methods in handling mixtures of oils as a solution of groups (group contribution concept), their compositions in terms of fatty acids and triacylglycerols were calculated as a function of the compositions of the original oils (soybean oil and Buriti oil) and their respective mole fractions in the blends. Note that the compositions of the blends had interesting proportions between oleic and linoleic fatty acids, besides its concentration of carotenes, being very attractive in terms of their nutritional value.

The predictive method described by Halvorsen et al.[7] was tested for densities of each oil and blends of oils over the temperature range studied, and the ARDs were calculated (Table 7). As one can see, the method was capable of predicting, with the same range of accuracy, the density of blends of oils, using their calculated fatty acid composition and the volumes of each fraction in the blends. To convert volumes into mole fractions, it was also necessary to use the calculated molecular weight (MW) of Buriti oil and soybean oil (870.94 g·gmol^{-1}and 872.14 g·gmol^{-1}, respectively) and their experimental density values at 25 °C (0.90887 g·cm^{-3} and 0.91835 g·cm^{-3}). According to Halvorsen et al.,[7] the molecular weight can be calculated by the following expression

$$\mathrm{MW}_{oil} = 3 \cdot \sum_i \mathrm{MW}_i \cdot x_i + 38.0488 \quad (6)$$

where x_i is the mole fraction of component i in the fatty acid composition of the oil.

Table 5. Fatty Acid Composition of Oils (Mole Fraction)[a]

fatty acid		vegetable oils				blends (volume fractions)		
formula[b]	trivial name (abbreviation)	Brazil nut	Buriti	grape seed	soybean	1 to 1[c]	1 to 2[d]	1 to 3[e]
14:0	miristic (M)	0.11	0.10	0.06	0.11	0.10	0.10	0.11
16:0	palmitic (P)	17.23	18.00	7.4	12.51	15.25	14.33	13.88
16:1	palmitoleic (Po)	0.38	0.45	0.15	0.09	0.27	0.21	0.18
18:0	stearic (S)	10.11	1.18	3.17	2.91	2.05	2.34	2.48
18:1	oleic (O)	37.08	77.34	20.08	22.55	49.82	40.70	36.15
18:2	linoleic (Li)	34.56	1.39	68.6	55.53	28.58	37.59	42.08
18:3	linolenic (Ln)	0.05	1.25	0.21	5.81	3.54	4.30	4.68
20:0	arachidic (A)	0.36	0.08	0.09	0.22	0.15	0.18	0.19
20:1	gadoleic (G)	0.05	0.21	0.17	0.09	0.16	0.13	0.12
22:0	behenic (Be)	0.07	−−	0.07	0.18	0.09	0.10	0.13
IV[f]		92.28	72.79	136.91	130.92	101.99	111.66	116.49

[a] Fatty acid composition of macadamia oil and Babassu oil can be reached referring to Rodrigues et al.[14] and Reipert,[15] respectively. [b] NC (number of carbon atoms):ND (number of double bounds). [c] 25 mL of Buriti oil + 25 mL of soybean oil (x_{Buriti} = 0.4977 and $x_{soybean}$ = 0.5023). [d] 25 mL of Buriti oil + 50 mL of soybean oil (x_{Buriti} = 0.3313 and $x_{soybean}$ = 0.6687). [e] 25 mL of Buriti oil + 75 mL of soybean oil (x_{Buriti} = 0.2483 and $x_{soybean}$ = 0.7517). [f] Iodine value (IV) is the number of grams of iodine that will react with the double bonds in 100 g of oil; i.e., high IV oil contains a greater number of double bonds than low IV oil. This value can be calculated from the fatty acid composition according to the method Cd 1c-85.[12]

Table 6. Estimated Compositions of Oils[a]

			vegetable oils				blends of Buriti oil/soybean oil (volume fractions)		
triacylglycerol[b]	NC[c]	ND[d]	Brazil nut	Buriti	grape seed	soybean	1 to 1[e]	1 to 2[f]	1 to 3[g]
					100*x*				
MSO/POP	50	1	3.56	7.08	−	0.98	4.02	3.00	2.49
POS	52	1	4.12	0.95	−	−	0.47	0.31	0.24
SOS/POA	54	1	1.36	−	−	−	−	−	−
PLiP/PPoO	50	2	3.50	0.73	1.00	2.45	1.59	1.88	2.02
POO	52	2	12.00	35.70	1.80	3.24	19.40	14.00	11.30
SOO	54	2	6.03	2.53	0.63	0.73	1.63	1.33	1.18
PLiO/PoOO	52	3	15.31	2.07	6.64	10.59	6.35	7.77	8.47
OOO/SOLi	54	3	13.55	45.01	3.69	3.65	24.23	17.35	13.92
PLiLi/POLn/PoOLi	52	4	7.31	1.20	11.41	14.02	7.64	9.77	10.84
PLiLn	52	5	−	−	−	2.78	1.40	1.86	2.09
OOLi	54	4	17.22	2.50	13.24	11.78	7.16	8.71	9.48
OLiLi/OOLn	54	5	12.22	2.23	28.75	22.50	12.41	15.78	17.46
LiLiLi	54	6	3.82	−	32.84	21.64	10.87	14.47	16.27
LiLiLn	54	7	−	−	−	5.64	2.83	3.77	4.24

[a] Probable triacylglycerol composition of macadamia oil and Babassu oil can be reached referring to Rodrigues et al.[14] and Reipert,[15] respectively. [b] Abbreviation of the three fatty acids attached in the triacylglycerol. For example, OOO stands for triolein or glyceryl trioleate. See Table 5 for usual abbreviations of trivial names of fatty acids. [c] NC = number of carbons (except glycerol carbons). [d] ND = number of double bonds. [e] 25 mL of Buriti oil + 25 mL of soybean oil (x_{Buriti} = 0.4977 and $x_{soybean}$ = 0.5023). [f] 25 mL of Buriti oil + 50 mL of soybean oil (x_{Buriti} = 0.3313 and $x_{soybean}$ = 0.6687). [g] 25 mL of Buriti oil + 75 mL of soybean oil (x_{Buriti} = 0.2483 and $x_{soybean}$ = 0.7517).

Table 7. ARD for the Prediction of Densities of Vegetable Oils/Blends Using the Method of Halvorsen et al[7]

vegetable oil	temperature range *t*/°C	100ARD (min. value − max. value)[a]
Babassu	30 to 70	0.288 (0.177 – 0.548)
Brazil nut	20 to 70	0.200 (0.041 – 0.309)
Buriti		0.137 (0.029 – 0.225)
grape seed		0.122 (0.025 – 0.212)
macadamia		0.146 (0.003 – 0.330)
blends of Buriti oil/soybean oil (volume fractions)		
1 to 1	20 to 70	0.122 (0.052 – 0.203)
1 to 2		0.229 (0.067 – 0.316)
1 to 3		0.071 (0.017 – 0.184)

[a] 100ARD calculated by eq 4 over *N* experimental points for each oil. Minimum and maximum values of the relative deviations, $100|\rho_{calcd} - \rho_{exptl}|/\rho_{exptl}$, for each oil are also shown.

Figure 1 shows dynamic viscosities of Buriti oil, soybean oil, and its blends (1 to 1, 1 to 2, and 1 to 3 of volume fractions) as a function of temperature. As one can see, the differences among viscosity values of Buriti oil, soybean oil, and their blends decrease with temperature and with the volume fraction of soybean in the blend.

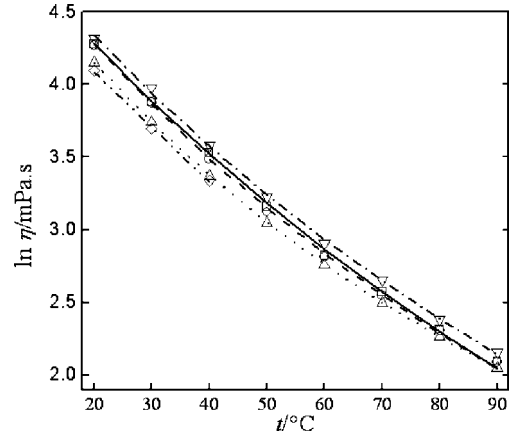

Figure 1. Dynamic viscosities of vegetable oils as a function of temperature: ▽, buriti oil; ◇, soybean oil; □, blend 1 to 1 of volume fractions; ○, blend 1 to 2 of volume fractions; △, blend 1 to 3 of volume fractions. Lines represent equations shown in Table 4. For soybean oil, $\ln(\eta/\text{mPa·s}) = -5.111 + 2045/(t/°\text{C} + 202.2)$.

To apply the predictive methods suggested by Fasina et al.[8] and Ceriani et al.[5] for estimating viscosity of oils, the values of the parameters p and p', for the method of Ceriani et al.,[5] and

Table 8. Calculated Parameters

	vegetable oils					blends of Buriti oil/soybean oil (volume fractions)		
parameters	Babassu[a]	Brazil nut	Buriti	grape seed	macadamia[a]	1 to 1	1 to 2	1 to 3
MUFA[b]	13.52	38.16	79.33	20.61	81.51	51.10	41.72	37.05
PUFA[b]	2.48	34.98	2.66	69.13	2.17	32.36	42.23	47.14
p[c]	11	14	14	13	14	13	13	13
p'[c]	0	1	1	2	1	1	1	1

[a] Parameters calculated from the fatty acid composition given by Rodrigues et al.[14] and Reipert.[15] [b] MUFA (monounsaturated fatty acid mass fraction) and PUFA (polyunsaturated fatty mass fraction) are values used in the model suggested by Fasina et al.[8] [c] p (number of CH_2 groups in a representative or equivalent fatty acid) and p' (number of CH═CH groups in a representative or equivalent fatty acid) are related to the model developed by Ceriani et al.[5]

Table 9. ARD for the Prediction of Viscosities of Vegetable Oils/Blends

		100ARD (min. value − max. value)[a]					
		fatty acid composition			multicomponent mixture		
			Fasina et al.[8]				
vegetable oil	temp range t/°C	Ceriani et al.[5]	MUFA	PUFA	Kay's rule[9]	Kendall and Moore[10]	GC-UNIMOD[11]
Babassu	30 to 90	11.51 (7.71 − 16.46)	11.80 (1.94 − 23.41)	28.45 (9.68 − 40.42)	1.67 (0.81 − 2.66)	1.98 (0.90 − 3.15)	2.38 (0.32 − 3.74)
Brazil nut	20 to 90	6.56 (0.39 − 14.94)	10.27 (0.88 − 19.29)	11.06 (0.11 − 18.78)	5.04 (1.32 − 11.95)	4.61 (0.95 − 11.32)	5.51 (1.80 − 12.42)
Buriti		6.29 (0.81 − 12.59)	4.58 (0.28 − 7.00)	7.33 (1.09 − 17.56)	5.29 (1.91 − 6.33)	5.18 (1.83 − 9.40)	5.46 (2.08 − 9.71)
grape seed		14.42 (5.07 − 23.99)	16.05 (2.51 − 30.96)	21.99 (0.24 − 40.70)	15.39 (11.60 − 20.41)	15.09 (11.32 − 20.18)	15.61 (11.83 − 20.60)
macadamia		6.89 (0.63 − 16.21)	3.50 (0.87 − 5.83)	6.24 (0.49 − 16.95)	7.12 (4.12 − 14.88)	6.96 (2.64 − 14.66)	7.08 (2.75 − 14.85)
		blends of Buriti oil/soybean oil (volume fractions)					
1 to 1	20 to 90	11.86 (7.05 − 16.55)	8.49 (2.76 − 13.04)	8.91 (1.53 − 17.16)	14.38 (9.25 − 20.25)	13.64 (8.57 − 19.20)	14.56 (9.45 − 20.43)
1 to 2		10.22 (5.93 − 16.18)	10.08 (2.91 − 18.95)	10.57 (0.76 − 17.81)	17.61 (12.92 − 25.32)	16.86 (12.24 − 24.28)	17.80 (13.13 − 25.50)
1 to 3		3.20 (0.30 − 8.05)	10.72 (1.73 − 18.83)	18.99 (2.09 − 32.77)	12.97 (9.26 − 18.49)	12.19 (8.51 − 17.37)	13.18 (9.48 − 18.69)

[a] 100ARD calculated by eq 4 over N experimental points for each oil and each method. Minimum and maximum values of the relative deviations $|\eta_{calcd} - \eta_{exptl}|/\eta_{exptl}$ for each oil and each method are also shown.

the monounsaturated fatty acid mass fraction (MUFA) and the polyunsaturated fatty acid mass fraction (PUFA), for the method of Fasina et al.,[8] were calculated for the oils and blends of oils using the fatty acid composition given in Table 5. Table 8 gives the calculated parameters. The ARD values and the minimum and the maximum values of the relative deviations $|\eta_{calcd} - \eta_{exptl}|/\eta_{exptl}$ are given in Table 9 for the six predictive models tested. As one can see, the methods based on the triacylglycerol composition (Kay's rule,[9] the method of Kendall and Moore,[10] and GC-UNIMOD[11]) predicted the viscosities of Babassu oil and Brazil nut oil much better than the methods of Fasina et al.[8] and Ceriani et al.[5] The method of Ceriani et al.[5] gave the lower value of ARD (8.8 %) considering the experimental databank as a whole (63 values of viscosity). The method of Kendall and Moore[10] predicted the values of viscosities of oils with a slightly better ARD value (6.9 %) than Kay's rule[9] (7.0 %) and GC-UNIMOD[11] (7.3 %) but much better than the methods of Fasina et al.[8] (9.2 % for MUFA and 14.7 % for PUFA) and Ceriani et al.[5] (9.1 %).

It is interesting to note that the methods of Ceriani et al.[5] and Fasina et al.[8] were capable of describing the viscosity values for the blends of Buriti oil and soybean oil much better than the methods based on their triacylglycerol composition. This fact could be an indication that the arrangement of the fatty acids in the triacylglycerols in these cases could be different than the estimated compositions given by the method of Antoniossi Filho et al.[16] based on the calculated fatty acid composition.

Figure 2 brings the relative deviations $\Delta\eta/\eta = (\eta_{calcd} - \eta_{exptl})/\eta_{exptl}$ of predicted and experimental dynamic viscosity of vegetable oils and blends of oils studied, as a function of temperature, using the three models based on the fatty acid composition of oils/blends.[5,8] Additionally, Figure 3 shows the relative deviations $\Delta\eta/\eta$ calculated using the three models based on the triacylglycerol composition of oils/blends.[9–11] In most of the cases, the PUFA model[8] estimated higher values of viscosity in comparison to experimental data. In contrast, Kay's rule,[9] the method of Kendall and Moore,[10] and GC-UNIMOD[11] always predicted values lower than experiment, except for Buriti oil. No systematic deviations arose from the models investigated.

To finalize this work and extend its applicability, a simple method of calculation was proposed to predict the dynamic viscosity of biodiesel fuels based on the fatty acid composition of the original oils, following the main ideas of the group contribution procedure developed by Ceriani et al.[5] for vegetable oils. In the previous work, the authors estimated the viscosity of vegetable oils by establishing an equivalent triacylglycerol to represent the multicomponent mixture of triacylglycerols, and then they used their group contribution model for prediction.

Biodiesel is also a multicomponent mixture, composed of a variety of methyl or ethyl esters. So, the idea is to represent it by an equivalent ester. Considering that the viscosity of the biodiesel depends on its fatty acid composition,[3,4] it was first necessary to compute an equivalent fatty acid (eqFA) to represent it and then calculate an equivalent fatty ester. Following the group contribution concept, $\eta_{methylE}$ (dynamic viscosity of methyl ester biodiesel) or η_{ethylE} (dynamic viscosity of ethyl ester biodiesel) could be computed as the sum of the contributions, $[\eta]$, of groups CH_3, CH_2, CH═, and COO, explicitly.

For methyl ester biodiesel:

$$\eta_{methylE} = \eta_{eqFA} + [\eta]_{COO} + [\eta]_{CH_3} - [\eta]_{COOH} \quad (7)$$

For ethyl ester biodiesel:

$$\eta_{ethylE} = \eta_{eqFA} + [\eta]_{COO} + [\eta]_{CH_3} + [\eta]_{CH_2} - [\eta]_{COOH} \quad (8)$$

Assuming that

$$\eta_{eqFA} = [\eta]_{CH_3} + p \cdot [\eta]_{CH_2} + 2 \cdot p' \cdot [\eta]_{CH=} + [\eta]_{COOH} \quad (9)$$

the dynamic viscosities of the methyl and ethyl ester biodiesel could be calculated, respectively, considering the following equations

$$\eta_{methylE} = [\eta]_{COO} + 2 \cdot [\eta]_{CH_3} + p \cdot [\eta]_{CH_2} + 2 \cdot p' \cdot [\eta]_{CH=} \quad (10)$$

$$\eta_{ethylE} = [\eta]_{COO} + 2 \cdot [\eta]_{CH_3} + (p+1) \cdot [\eta]_{CH_2} + 2 \cdot p' \cdot [\eta]_{CH=} \quad (11)$$

where $[\eta]$ is the contribution of a group to the dynamic viscosity of a compound. The group contribution method suggested by Ceriani et al.[5] should be used in this case to calculate the contribution of each group in the viscosity of biodiesel.

To calculate p, the number of CH_2 groups in the equivalent fatty acid, and p', the number of CH═CH groups in the equivalent fatty acid, the fatty acid composition of the oil is used (see Ceriani et al.[5] for an example of calculation)

$$p = \sum_j x_j \cdot (NC_j - 2 - 2 \cdot ND_j) \quad (12)$$

$$p' = \sum_j x_j \cdot ND_j \quad (13)$$

where NC is the number of carbons and ND is the number of double bounds in the fatty acid of type j. Note that p and p' are necessarily integers to have a physical meaning. In this way, the values calculated with eq 12 and eq 13 should be rounded to the closest integer.

The methods outlined above were compared with the mixture topological index method proposed by Shu et al.[4] The authors generated two linear regression equations that use the topological index values of the fatty acid methyl ester mixture, calculated from the fatty acid composition of the original oil. Using the fatty acid composition of the biodiesels cited by Shu et al.,[4] the equivalent fatty esters were computed (eqs 12 and 13). Equation 10 was applied for estimating the viscosities of the methyl ester biodiesels of Shu et al.[4] at 40 °C. Table 10 gives the ARD values obtained in this work and the values reported by Shu et al.,[4] together with the calculated values of p and p', after rounding them, as mentioned above. As one can see, each model generated two lower ARD values in comparison to the other models, i.e., 1.1 % of biodiesel from canola oil and 7.4 % for soybean oil (this work), 0.46 % for biodiesel from coconut oil and 1.1 % for rapeseed oil (eq 6 from Shu et al.[4]), and 0.04 % for biodiesel from peanut oil and 4.8 % for palm oil (eq 7 from Shu et al.[4]). The model generated in this work gave a mean ARD value of 7.2 %, which was between the mean ARD values calculated from the results of Shu et al.[4] (3.8 % for eq 6 and 10.1 % for eq 7).

With data presented in Table 5 and the method suggested in this work and/or the methods from Allen et al.[3] and Shu et al.,[4] one can predict the dynamic viscosity of the methyl ester or ethyl ester biodiesels generated from the studied vegetable oils; besides, these data have not been determined experimentally. Note that the method proposed here is advantageous in relation to the ones from Allen et al.[3] and Shu et al.,[4] considering that it could be applied for a range of temperatures, not only at 40

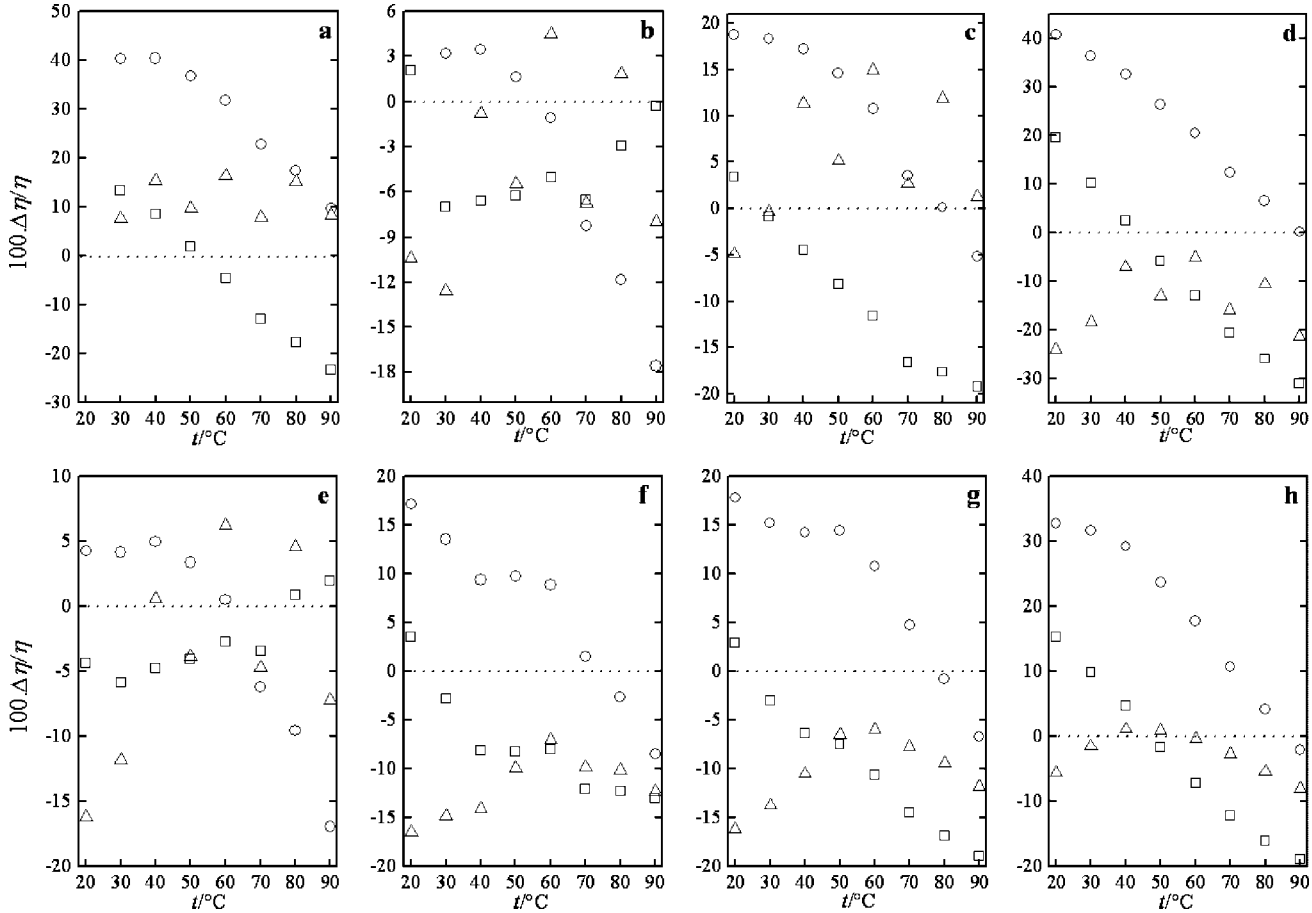

Figure 2. Relative deviations $\Delta\eta/\eta = (\eta_{calcd} - \eta_{exptl})/\eta_{exptl}$ between the predicted and experimental dynamic viscosity of vegetable oils: a, Babassu oil; b, Buriti oil; c, Brazil nut oil; d, grape seed oil; e, macadamia oil; f, blend 1 to 1 of volume fractions; g, blend 1 to 2 of volume fractions; h, blend 1 to 3 of volume fractions; □, MUFA;[8] ○, PUFA;[8] Δ, Ceriani et al.[5]

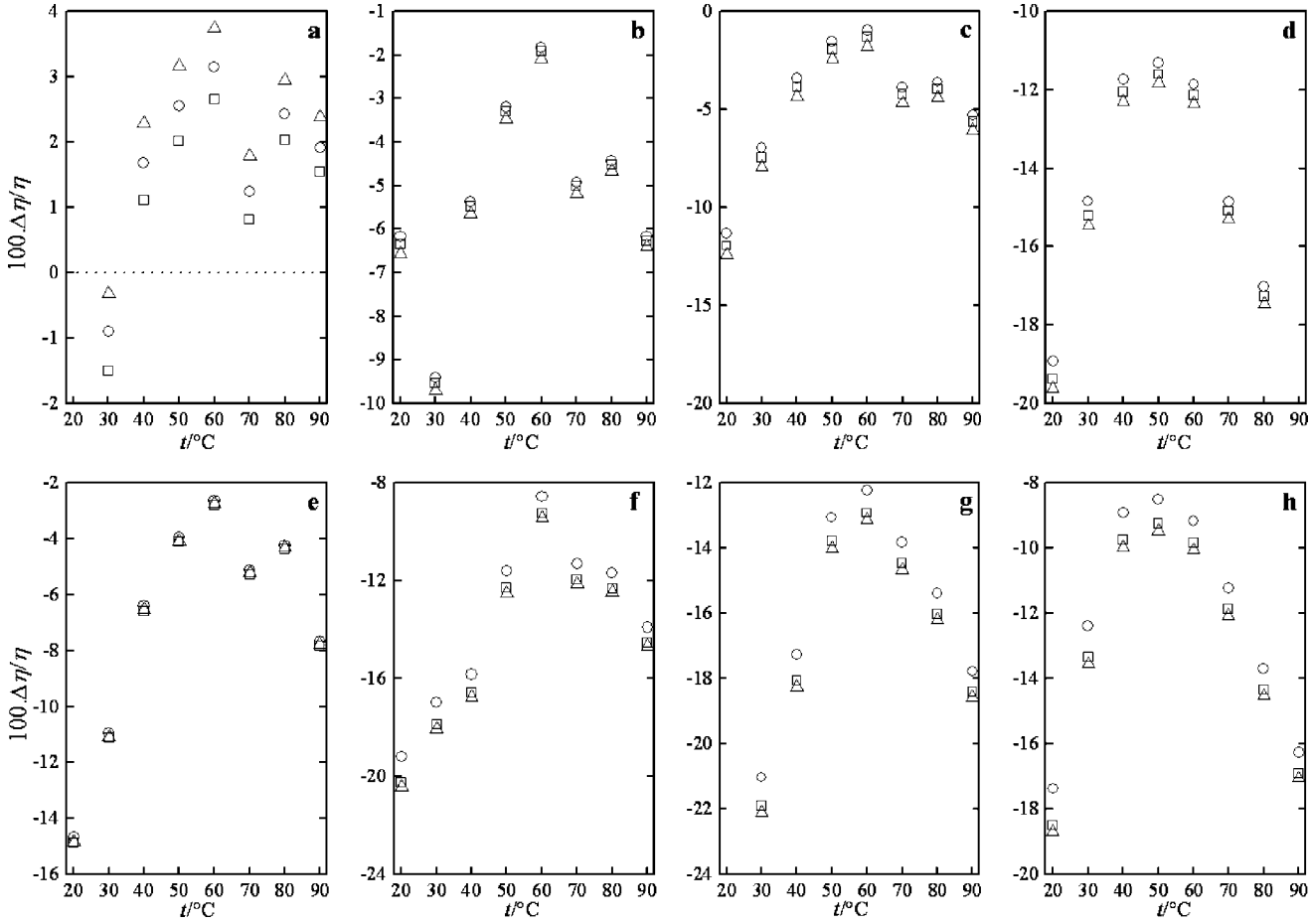

Figure 3. Relative deviations $\Delta\eta/\eta = (\eta_{calcd} - \eta_{exptl})/\eta_{exptl}$ between the predicted and experimental dynamic viscosity of vegetable oils: a, Buriti oil; b, Babassu oil; c, Brazil nut oil; d, grape seed oil; e, macadamia oil; f, blend 1 to 1 of volume fractions; g, blend 1 to 2 of volume fractions; h, blend 1 to 3 of volume fractions; □, Kay's rule; [9] ○, Kendall and Moore model; [10] Δ, UNIMOD.[11]

Table 10. ARD for Viscosities of Methyl Ester Biodiesel

				η_{calcd}/mPa·s (100ARD)		
					Shu et al.[4]	
original oil	p^a	p'^a	η_{exptl}/mPa·s[3]	this work	eq 6[b]	eq 7[c]
canola	13	1	3.45	3.41 (1.1 %)	3.55 (2.9 %)	4.23 (22.6 %)
coconut	10	0	2.15	2.02 (6.2 %)	2.16 (0.5 %)	2.09 (2.6 %)
palm	14	1	3.59	4.03 (12.3 %)	3.29 (8.3 %)	3.42 (4.8 %)
peanut	14	1	3.51	4.03 (14.9 %)	3.53 (0.6 %)	3.50 (0.04 %)
rapeseed	15	1	4.70	4.75 (1.2 %)	4.65 (1.1 %)	3.79 (19.3 %)
soybean	13	2	3.26	3.50 (7.4 %)	3.56 (9.2 %)	3.63 (11.3 %)
mean value				7.2 %	3.8 %	10.1 %

[a] Parameters calculated using the fatty acid composition of vegetable oils as cited by Shu et al.[4] [b] Results reported by Shu et al.[4] using eq 6 of their article (η/mPa·s = 5.96249·χ_m − 10.08814), where χ_m is the mean mixture topological index of biodiesel (see Shu et al.[4] for a detailed explanation). [c] Results reported by Shu et al.[4] using eq 7 of their article (η/mPa·s = χ_m + 0.038).

°C, since data used in the regression done by Ceriani et al.[5] were wide [(10 to 100) °C for fatty esters].

Conclusion

This work presented experimental data of density and viscosity of vegetable oils of nutritional value as a function of temperature. Two types of predictive models were tested using the measured databank, one based on the fatty acid composition of the oils and the other based on their triacylglycerol composition. In general, the models tested in this work were capable of predicting densities and viscosities satisfactorily. Besides the difference in their complexity, no relevant distinction about their predictive capability arose from the results. A calculation procedure was developed to estimate the viscosity of biodiesel with accuracy sufficient for engineering applications, comparable to previous works in the literature.[3,4]

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