

Measurement and Prediction of Densities of Vegetable Oils at Pressures up to 45 MPa

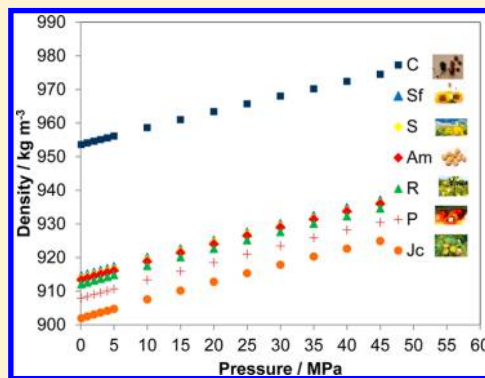
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ABSTRACT: This work addresses the measurement and modeling of the densities of seven vegetable oils (soybean, rapeseed, castor, palm, sunflower, *Aleurites moluccana*, and *Jatropha curcas* oils) at temperatures from (283.15 to 363.15) K and pressures from (0.1 to 45) MPa. The data measured here was correlated using the modified Tait-Tammann equation, and the data was used to evaluate the predictive abilities of the Halvorsen model, the fragment-based approach, and the revised GCVOL group contribution method. The results show that the models studied described well the experimental data, presenting not only stable deviations over the temperature range but also overall average relative deviations (OARD) of only (1.2, 0.34, and 1.1) %, respectively. An extension of the models here studied to high pressure is proposed. The models of Halvorsen, Zong, and revised GCVOL provide very good predictions of high-pressure densities with OARDs of (0.75, 1.04, and 0.41) %, respectively, with the deviations presenting just a slightly pressure-dependent with maximum deviations of less than 2.0 %.



1. INTRODUCTION

High pressure technology, commonly coupled with thermal processing, has been used in many engineering applications such as in food processing to achieve stable food products, additive free and microbiologically safe, as the constituents, and the contaminants of food can be controlled under this condition,^{1–5} and in the fuel industry to achieve low pollutant levels and lower fuel consumption through the enhancement of combustion process using of the common rail fuel injection system.^{6–8} High pressures in the processing of vegetable oils are used for their extraction from the corresponding seeds, the fractionation of their constituents with supercritical fluids^{9–11} and the production of biodiesels at near or supercritical conditions.^{12,13}

The supercritical fluid extraction of oil from seeds is already considered to be more beneficial than the conventional technology as it does not require the distillation and the solvent removal processes normally involved in conventional extraction.¹⁴ Moreover, the efficiency of the extraction is simply controlled by the pressure and/or the temperature of operation, the contact time, and the solubility of the oil in the extracting fluids.¹⁵ This feature can be also applied for the extraction of oil constituents with supercritical fluids as already addressed elsewhere in the literature.^{16,17}

Regarding biodiesel production, it has been shown that the transesterification with supercritical alcohol constitutes a better technical approach to the conventional catalytic transesterification of low quality feedstocks.¹⁸ It is known that the alkaline catalyzed transesterification is very sensitive to the purity of the reactants. It can only work with refined oils with less than 0.5 % of free fatty acids.¹⁹

Density is always important for any process as it gives enough information about the amount of material being processed and correlates with many other transport and acoustic properties such as viscosity, surface tension, volatility, and speed of sound, among others that are necessary for an efficient design, control, and optimization of operation conditions. For this reason, the knowledge of high-pressure density is required for the adequate performance of high-pressure technology. Although many works have addressed the solubility and provided correlations to predict this parameter,^{20,21} there is little information concerning the measurement of high-pressure density for vegetable oils and few models to predict their behavior. The experimental data are very scant, and those available are mostly measured at atmospheric pressure.

This work aims to provide the experimental densities of seven different vegetable oils at temperatures from (283.15 to 363.15) K and pressures from (0.1 to 45) MPa, correlating them using the modified Tait-Tammann equation and using them to evaluate the predictive ability of the revised GCVOL group contribution method, Halvorsen's model, and the Zong's fragment-based approach model. The development of a high pressure extension of these models is also here proposed.

2. EXPERIMENTAL DETAILS

2.1. Samples. Oils of soybean (S), rapeseed (R), sunflower (Sf), castor (C), palm (P), *Aleurites moluccana* (Am), and

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Table 1. Fatty Esters Profile of the Vegetable Oils (wt %)

FAME	S	R	P	Sf	C	Jc	Am
C10:0	0.00	0.01	0.03	0.00	0.00	0.00	0.03
C12:0	0.00	0.04	0.24	0.02	0.34	0.04	0.10
C14:0	0.07	0.07	0.57	0.07	0.00	0.11	0.10
C16:0	10.76	5.22	42.45	6.40	2.68	17.57	8.55
C16:1	0.07	0.20	0.13	0.09	0.00	0.00	0.00
C18:0	3.94	1.62	4.02	4.22	0.65	3.88	2.47
C18:1	22.96	62.11	41.92	23.90	3.29	36.67	24.04
C18:2	53.53	21.07	9.80	64.16	8.31	41.65	43.79
C18:3	7.02	6.95	0.09	0.12	0.82	0.09	20.91
C20:0	0.38	0.60	0.36	0.03	0.00	0.00	0.00
C20:1	0.23	1.35	0.15	0.15	0.00	0.00	0.00
C22:0	0.80	0.35	0.09	0.76	0.00	0.00	0.00
C22:1	0.24	0.19	0.00	0.08	0.00	0.00	0.00
C24:0	0.00	0.22	0.15	0.00	0.00	0.00	0.00
C18:1OH	0.00	0.00	0.00	0.00	83.91	0.00	0.00

Jatropha curcas (*Jc*) were here used. The first five oils were obtained from Portuguese companies (S from Bunge Ibérica Portugal SA; Sf, P, and R from Sovena; and C from José M. Vaz Pereira SA) while the last two nonedible oils were obtained by solid–liquid extraction of the corresponding seeds in a Soxhlet with n-hexane. The composition of fatty acids in these oils was measured by conversion of the oil into fatty esters. The fatty acid profile of the oils of S, P, Sf, and R were previously reported by Pratas et al.,²² whereas those of the two nonedible oils (*Am* and *Jc*) and C were here measured using the methodology of Ghadge et al.²³ for the esterifications, suitable for oils with high percentages of free fatty acids (FFA) as it includes a pretreatment process to reduce the FFA level in the oil. According to Ghadge et al.,²³ the esterification of these oils was carried in three separate steps. The first two steps were esterification reactions and occurred at 333.15 K using 1 % in volume fraction of H₂SO₄ and 45 % of methanol. Each esterification step was extended for 2 h to guarantee that the FFA level of the treated oil was successfully reduced to the desired value for the transesterification reaction. After each esterification reaction, the reaction was interrupted, and the upper phase containing the remaining methanol, glycerol, and catalyst was removed from the mixture in a separating funnel. The lower phase was used to perform the next reaction that could be another step of esterification or a transesterification reaction.

The transesterification reaction also occurred at 333.15 K using 1 % w/v of sodium methoxide and 35 % v/v of methanol during 24 h under methanol reflux. The reaction time chosen was adopted for convenience and to guarantee a complete reaction conversion. After this period, the reaction was quenched by adding 1 % v/v of phosphoric acid 85 %. The final mixture was then separated in two phases in a separating funnel. The upper phase (biodiesel) was then purified by washing with hot distilled water until a neutral pH was achieved and then dried in the oven for 2 h. This procedure was also applied for the production of biodiesel from C.

The composition of the fatty esters in these biodiesels was analyzed using a gas chromatography flame ionization detector (GC-FID). This equipment is a Varian CP-3800 with a FID in a split injection system with a Varian GC column CP9080 select biodiesel for FAME column (30 m × 0.32 mm × 0.25 μm). The column temperature was set at 393.15 K and then programmed to increase up to 523.15 at 4 K·min⁻¹. The detector and injector were set at 523.15 K. The carrier gas was helium with a flow rate of 2 cm³·min⁻¹.

The composition of fatty acid esters in the biodiesels of the corresponding oils is presented in Table 1.

2.2. Density Measurement. The experimental procedure of density measurement is already described elsewhere.^{24–26} An Anton Paar 512P vibrating tube densimeter, connected to an Anton Paar DMA 4500 data acquisition unit was used for this purpose. Temperature stability was ensured with a PolyScience 9510 circulating fluid bath, and the temperature value was determined with a CKT100 platinum probe placed in the immediacy of the density measuring cell, with an uncertainty that has been determined to be lower than 5 × 10⁻² K. The pressure was generated and controlled using a Ruska 7610 pressure controller, whose pressure stability is 2 × 10⁻³ MPa. This device determines the vibration period of a metallic U-shape cell filled with the studied fluid, which is directly linked to the sample fluid density. The repeatability in the density values determined from the vibration period measured by the DMA 4500 unit is 10⁻⁵ g·cm⁻³. The combinations of density determination repeatability and the accuracies in temperature and pressure measurement lead to an overall experimental density uncertainty value that is lower than 10⁻⁴ g·cm⁻³.

3. DENSITY MODELS

The modified Tait-Tammann equation,²⁷ the GCVOL group contribution method, the Halvorsen's model^{28,29} and the Zong's fragment-based approach model³⁰ were here used here to describe the temperature and pressure dependency of densities of vegetable oils. The first two approaches were previously applied elsewhere with success to the description of the experimental densities of fatty esters^{31,32} and biodiesels.²²

3.1. Modified Tait-Tammann Correlation. This correlation relates density (ρ /g·cm⁻³) with temperature (T /K) and pressure (P /MPa) in a polynomial form, involving several fitting parameters according to the eqs 1 to 3 that are adjusted to the experimental data.

$$\rho = \frac{\rho(T, P = 0.1 \text{ MPa})}{\left[1 - C \frac{(B+P)}{(B+0.1)}\right]} \quad (1)$$

where

$$\rho(T, P = 0.1 \text{ MPa}) = a_1 + a_2T + a_3T^2 \quad (2)$$

and

$$B = b_1 + b_2T + b_3T^2 \quad (3)$$

3.2. Halvorsen's Model. This model is detailed in Halvorsen et al.²⁸ Briefly it combines the fatty acid critical properties and

Table 2. Experimental Values of Density, ρ , at Temperature, T , and Pressure, P , for the Oils Studied^a

T/K	$\rho/\text{kg}\cdot\text{m}^{-3}$													
	P/MPa													
	0.10	1.00	2.00	3.00	4.00	5.00	10.00	15.00	20.00	25.00	30.00	35.000	40.00	45.00
C														
283.15	967.4	967.9	968.3	968.8	969.3	969.7	972.1	974.3	976.5	978.6	980.7	982.8	984.8	986.8
293.15	960.5	960.9	961.5	961.9	962.4	962.9	965.3	967.6	969.9	972.2	974.3	976.5	978.6	980.6
303.15	953.6	954.1	954.6	955.1	955.6	956.1	958.7	961.0	963.4	965.7	968.0	970.2	972.4	974.5
323.15	939.7	940.2	940.7	941.4	941.9	942.4	945.1	947.8	950.4	953.0	955.3	957.7	960.0	962.3
343.15	925.7	926.3	926.9	927.5	928.1	928.7	931.6	934.5	937.3	939.9	942.6	945.1	947.6	950.1
363.15	911.8	912.3	913.0	913.7	914.4	915.1	918.3	920.7	924.4	927.4	930.0	932.8	935.4	938.1
S														
283.15	927.9	928.3	928.9	929.3	929.9	930.4	932.9	935.3	937.7	940.1	942.2	944.5	946.6	948.8
293.15	920.7	921.2	921.8	922.3	922.9	923.4	925.9	928.4	930.9	933.4	935.7	938.0	940.3	942.4
303.15	913.8	914.4	914.9	915.4	916.0	916.6	919.3	921.8	924.5	927.0	929.4	931.7	934.0	936.3
323.15	900.1	900.7	901.2	901.9	902.5	903.1	906.0	908.8	911.6	914.3	916.9	919.4	921.9	924.4
343.15	886.5	887.2	887.8	888.5	889.1	889.8	893.0	896.1	899.1	901.9	904.7	907.4	910.0	912.6
363.15	873.3	873.9	874.6	875.3	876.0	876.8	880.2	883.5	886.7	889.8	892.8	895.6	898.3	901.1
R														
283.15	925.9	926.4	926.9	927.4	927.9	928.4	930.9	933.4	935.7	938.0	940.3	942.5	944.6	946.8
293.15	918.9	919.4	919.9	920.5	921.0	921.6	924.2	926.8	929.2	931.6	933.9	936.2	938.4	940.6
303.15	912.0	912.5	913.1	913.7	914.2	914.8	917.5	920.1	922.6	925.1	927.6	930.0	932.3	934.6
323.15	898.3	898.9	899.5	900.2	900.8	901.3	904.3	907.2	909.9	912.6	915.2	917.8	920.2	922.6
343.15	884.9	885.5	886.2	886.8	887.5	888.1	891.3	894.5	897.4	900.3	903.1	905.7	908.3	910.9
363.15	871.6	872.3	873.0	873.8	874.4	875.1	878.5	881.7	884.9	888.0	891.0	893.7	896.5	899.2
Sf														
283.15	928.2	928.6	929.2	929.6	930.2	930.7	933.2	935.7	938.1	940.4	942.6	944.9	947.0	949.1
293.15	921.3	921.8	922.3	922.9	923.4	923.9	926.6	929.0	931.5	934.0	936.3	938.6	940.8	943.0
303.15	914.5	915.0	915.6	916.1	916.7	917.3	920.0	922.5	925.1	927.5	930.0	932.4	934.8	937.0
323.15	900.8	901.3	902.0	902.6	903.2	903.8	906.7	909.6	912.4	915.1	917.6	920.2	922.7	925.0
343.15	887.3	887.9	888.6	889.2	889.9	890.6	893.8	896.9	899.8	902.6	905.5	908.1	910.8	913.4
363.15	874.0	874.6	875.3	876.0	876.8	877.5	880.9	884.2	887.4	890.5	893.5	896.4	899.2	902.0
P														
293.15	914.9	915.4	915.9	916.5	917.0	917.5	920.1	922.7	925.1	927.6	930.0			
303.15	907.9	908.4	909.0	909.5	910.1	910.6	913.3	915.9	918.5	921.0	923.5	925.9	928.2	930.5
313.15	900.3	900.8	901.4	902.0	902.6	903.2	906.0	908.8	911.5	914.1	916.6	919.0	921.4	923.9
323.15	893.4	893.9	894.6	895.2	895.8	896.4	899.4	902.2	905.0	907.7	910.3	912.9	915.4	917.8
343.15	879.7	880.4	881.0	881.7	882.3	883.0	886.2	889.3	892.3	895.2	898.0	900.7	903.3	906.0
363.15	866.4	866.9	867.7	868.4	869.2	869.9	873.4	876.6	879.9	883.0	886.1	889.0	891.8	894.6
Am														
283.15	927.5	928.0	928.5	929.0	929.5	930.0	932.6	935.0	937.5	939.8	942.0	944.3	946.4	948.5
293.15	920.4	920.9	921.5	922.0	922.5	923.1	925.7	928.3	930.7	933.2	935.5	937.8	940.1	942.3
303.15	913.4	913.9	914.5	915.0	915.6	916.2	918.8	921.5	924.0	926.5	929.0	931.4	933.8	936.0
323.15	899.6	900.1	900.7	901.4	901.9	902.5	905.5	908.3	911.1	913.9	916.5	919.0	921.5	924.0
343.15	886.0	886.6	887.3	887.9	888.6	889.2	892.5	895.5	898.6	901.4	904.3	907.0	909.6	912.2
363.15	872.5	873.1	873.8	874.6	875.3	876.0	879.4	882.7	886.0	889.1	892.2	895.2	898.0	900.7
Jc														
283.15	915.9	916.4	916.9	917.4	918.0	918.5	921.0	923.6	925.9	928.3	930.7	933.0	935.1	937.2
293.15	908.8	909.4	909.9	910.5	911.0	911.6	914.2	916.8	919.3	921.8	924.2	926.5	928.8	931.0
303.15	901.9	902.5	903.1	903.6	904.1	904.7	907.6	910.2	912.8	915.3	917.8	920.3	922.7	924.9
323.15	888.1	888.7	889.4	890.0	890.6	891.2	894.2	897.1	899.9	902.7	905.4	908.0	910.5	912.9
343.15	874.5	875.1	875.8	876.5	877.1	877.8	881.1	884.2	887.3	890.2	893.1	895.8	898.5	901.2
363.15	860.9	861.6	862.3	863.1	863.8	864.6	868.1	871.5	874.8	878.0	881.1	884.1	886.9	889.8

^aStandard uncertainties u are $u(T) = 0.05$ K, $u(P) = 2.10^{-3}$ MPa, and $u(\rho) = 0.1$ kg m⁻³.

the respective composition to predict the density of oils using eq 4

$$\rho_{\text{oil}} = \frac{(\sum_i x_i MW_i)}{R \left(\sum_i \frac{x_i T_c}{P_c} \right) (\sum_i x_i Z_{RA_i}) [1 + (1 - T_r)^{2/7}]} + F_c \quad (4)$$

where ρ_{oil} (g·cm⁻³) is the density of the vegetable oil, R (cm³·MPa·mol⁻¹·K⁻¹) is the universal gas constant, T_r is the reduced temperature, F_c is a correction factor characteristic of the oil, x_i is the mole fraction, MW_i (g·mol⁻¹) is the fatty acid molecular weight, P_c (MPa) is the critical pressure, Z_{RA_i} is the Rackett parameter and T_c (K) is the critical temperature.

T_r and F_c can be estimated using eqs 5 to 8.

$$T_r = \frac{T}{T_{c,mix}} \quad (5)$$

$$T_{c,mix} = \sum_i x_i T_{c_i} \quad (6)$$

$$F_c = 0.0236 + k|875 - MW_{oil}| \quad (7)$$

$$MW_{oil} = 3 \sum MW_{esters} + 38.0488 \quad (8)$$

In eq 7, the value of the constant k is equal to 0.000082 when the molecular weight of the oil is greater than 875 g·mol⁻¹ and 0.000098 when the molecular weight is less than 875 g·mol⁻¹. These restrictions are reported by Halvorsen et al.²⁸

3.3. Zong's Model. Zong et al.³⁰ developed a fragment-based approach to estimate the thermophysical properties of triglyceride mixtures. In case of density, this can be calculated using the eq 9, where ρ_{oil} is the oil density and ρ_i the density of triglyceride i (in g·cm⁻³) and w_i the mass fraction of triglyceride i .

$$\frac{1}{\rho_{oil}} = \sum_i w_i \frac{1}{\rho_i} \quad (9)$$

This approach requires the knowledge of representative triglyceride molecules. Then, the density of each triglyceride molecule is simply estimated from its molar volume using the eq 10, where V_A^l is the liquid molar volume contribution of fragment A (in cm⁻³·mol⁻¹) and $N_{frag,A}$ is the number of fragment A in the oil.

$$V^l = \sum_A N_{frag,A} V_A^l(T) \quad (10)$$

The temperature dependency of liquid molar volume, V_A^l , is given by eq 11, where $B_{1,A}$ and $B_{2,A}$ are the temperature dependency parameters of fragment A and T is the temperature (K). The values of parameters $B_{1,A}$ and $B_{2,A}$ are reported by Zong et al.³⁰

$$V_A^l = \frac{1 + B_{2,A}T}{B_{1,A}} \quad (11)$$

3.4. GCVOL Group Contribution Method. This method fractionates the molecule into various functional groups and then uses the molar volume of each group to estimate the density of the molecule according to the eq 12 where x is the molar fraction, M_w (g·mol⁻¹) is the molecular weight, and V (mol·cm⁻³) is the molar volume.

$$\rho = \frac{\sum_i x_i M_{w_i}}{\sum_i x_i V_i} \quad (12)$$

The oil molecular weight is calculated from the measured average composition of fatty acids using eq 8 while the molar volume is estimated using the eq 13.

$$V = \sum_i n_i \Delta v_i \quad (13)$$

In eq 13 n_i is the number of groups i , and the temperature dependency of the molar group, Δv_i (cm³ mol⁻¹), is given by the polynomial function described in eq 14 where T can vary between the melting point and the normal boiling point when the model is used to predict densities of solvents.

$$\Delta v_i = A_i + B_i T + C_i T^2 \quad (14)$$

According to the parameters A_i , B_i , and C_i used, the GCVOL method can be divided in different versions: The original version uses the parameters reported by Elbro et al.³³ This version presents 36 different group parameters for a variety of chemical classes, such as alkanes, aromatic, alkenes, alcohols, ketones, aldehydes, esters, ethers, chlorides, and siloxanes. The revised version here adopted uses the parameters proposed by Pratas et al.²²

3.5. Model Evaluation. To evaluate the predictive ability of the models aforementioned, the relative deviations (RDs) between predicted and experimental values of densities were calculated using eq 15 and the corresponding overall value (OARD) was calculated through eq 16, where N_s is the number of systems studied and the average relative deviation (ARD) is the summation of the modulus of RD over N_p experimental data points.

$$RD(\%) = \frac{\rho^v i_{calc} - \rho^v i_{exp}}{\rho^v i_{exp}} \times 100 \quad (15)$$

$$OARD(\%) = \frac{\sum_n ARD}{N_s} \quad (16)$$

4. RESULTS AND DISCUSSION

The experimental densities of seven vegetable oils measured at temperatures from (283.15 to 363.15) K and pressures from atmospheric to 45 MPa are reported in Table 2. The density differs between the oils according to the nature of fatty acids that compose the oil, following the same trends previously observed for biodiesels.²² The unsaturated oils have densities higher than those of saturated oils. However the effect of unsaturation level seems to outweigh the effect of carbon chain length, and thus, for the same level of unsaturation, the density of the short-chain oils is not necessarily higher than that of the longer ones. At similar conditions, the density of Sf, highly unsaturated, is higher than that of P, with low unsaturated content, even though it has a shorter chain length than that of the other. Due to the lack of data on high-pressure densities for vegetable oils, only the experimental data of Sf were compared to those studied by Guignon et al.³⁴ The data seemed to be in good agreement one another, even the deviations are slightly dependent on temperature and pressure as seen in Figure 1.

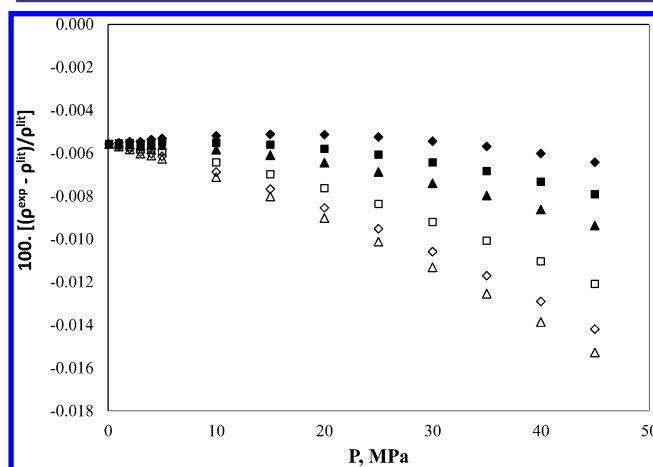


Figure 1. Experimental vs literature density for Sf: \blacklozenge , 283.15 K; \blacksquare , 293.15 K; \blacktriangle , 303.15 K; \square , 323.15 K; \diamond , 343.15 K; and \triangle , 363.15 K.

Table 3. Coefficients of the Tait-Tammann Correlation

oil	a_1 (kg·m ⁻³)	a_2 (kg·m ⁻³ ·K ⁻¹)	a_3 (10 ⁷ kg·m ⁻³ ·K ⁻²)	b_1	b_2 (MPa)	b_3 (10 ⁻⁴ MPa·K)	c
C	1158.3	-0.65699	-0.60509	559.07	-1.8349	17.0266	0.08654
S	1153.4	-0.88605	3.15489	515.56	-1.8490	19.2847	0.08227
R	1144.1	-0.84312	2.55582	544.20	-2.0660	23.0248	0.08104
Sf	1134.1	-0.76542	1.35090	453.02	-1.4354	12.7604	0.08382
Am	1149.3	-0.85776	2.62644	484.07	-1.5960	14.9382	0.08568
Jc	1127.3	-0.79324	1.64399	464.03	-1.5057	13.6891	0.08576
P	1181.1	-1.08028	5.88217	476.10	-1.5472	14.1997	0.08627

Table 4. ARDs from the Modified Tait-Tammann Correlation, the Revised GCVOL Method, Halvorsen's Model, and Zong's Model

oil	ARD, %			
	modified Tait-Tammann	revised GCVOL	Halvorsen	Zong
C	0.0042	0.74	0.55	
S	0.0039	1.6	0.088	1.3
R	0.0027	1.5	0.19	1
Sf	0.0030	0.36	0.090	0.23
Am	0.0040	1.1	0.29	1.6
Jc	0.0031	0.51	0.99	2.1
P	0.011	1.8	0.16	0.46
OARD, %	0.0045	1.1	0.34	1.1

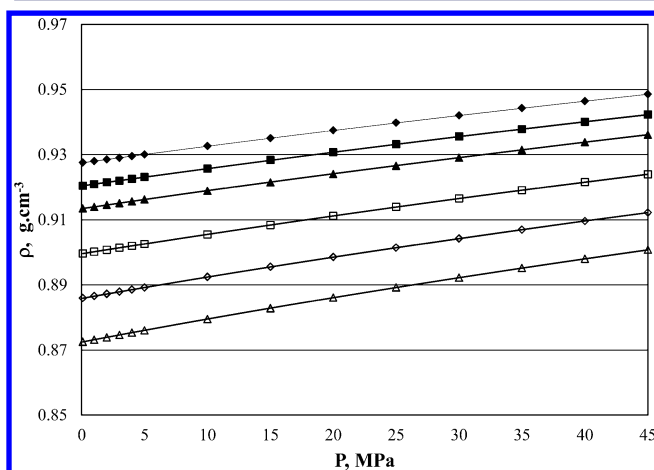


Figure 2. Density isotherm for Am. Experimental data (◆, 283.15 K; ■, 293.15 K; ▲, 303.15 K; □, 323.15 K; ◇, 343.15 K; and △, 363.15 K) and modified Tait-Tammann results (solid lines).

The correlation of the densities with the modified Tait-Tammann equation was carried by fitting the equation parameters to the experimental data. The values of the parameters are reported in Table 3. A description of the data with an OARD of only 0.0045 % (Table 4) was obtained. The adequacy of this correlation to describe the data is illustrated in Figure 1 for Am oil and by the RDs between the experimental and the correlated densities shown in Figures 2 and 3. The correlated results are very coherent with the experimental data and the deviations are shown to be pressure and temperature-independent with a maximum deviation of ± 0.020 %.

Halvorsen's model requires the prior knowledge of the critical properties of fatty acids to estimate the densities of vegetable oils. So these properties were obtained directly from Halvorsen et al.²⁸ for the majority of fatty acids except for the ricinoleic acid whose critical properties were calculated apart using the Joback's method. Using these properties, along with the fatty acid

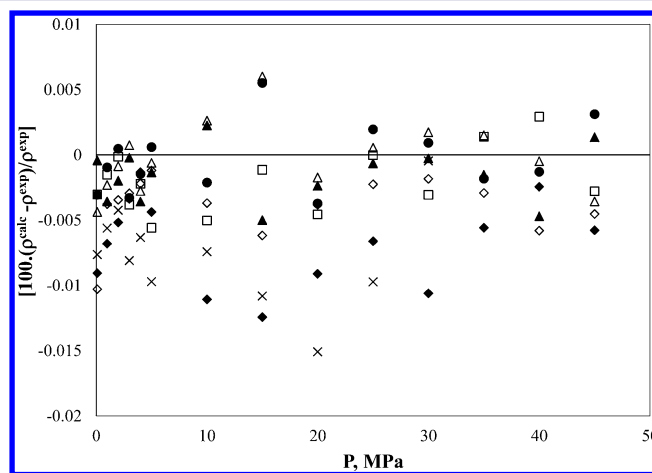


Figure 3. RDs between experimental and predicted densities as a function of the pressure at 293.15 K using a modified Tait-Tammann correlation for seven vegetable oils. □, C; ◆, S; △, R; ●, Am; ◇, Jc; ▲, Sf; and ×, P.

composition, the description of densities for seven vegetable oils was excellent with an OARD of only 0.34 % (Table 4). Nevertheless, the relative deviations are slightly temperature-dependent with a maximum of 1.4 %, especially for C, as shown in Figure 4.

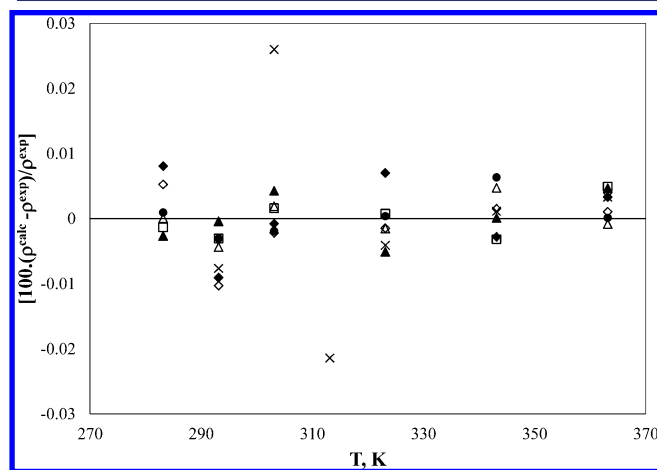
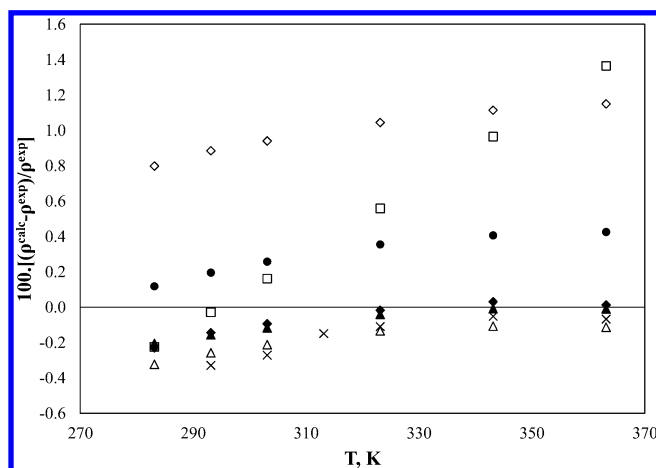
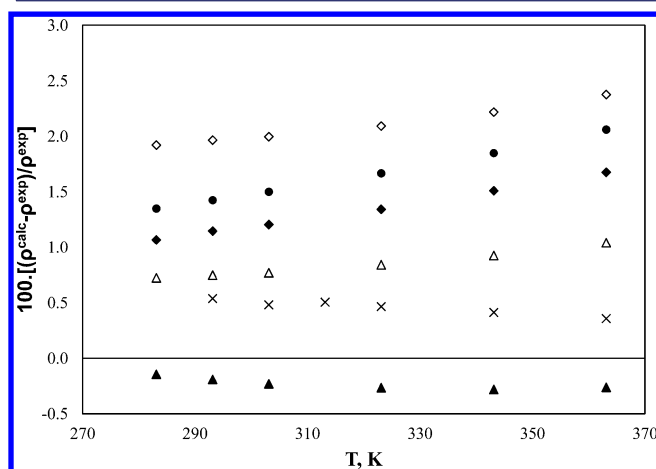


Figure 4. RDs between experimental and predicted densities as a function of the temperature at atmospheric pressure using a modified Tait-Tammann correlation for seven vegetable oils. □, C; ◆, S; △, R; ●, Am; ◇, Jc; ▲, Sf; and ×, P.

Zong's model estimates the density of vegetable oils from that of the triglyceride molecules. Thus, the first step of prediction was the building up of the triglyceride molecules to represent the fatty acid fragments present in oils. For example, Zong et al.³⁰

Table 5. ARDs from the Revised GCVOL Method, Halvorsen's Model, and Zong's Model at High Pressures

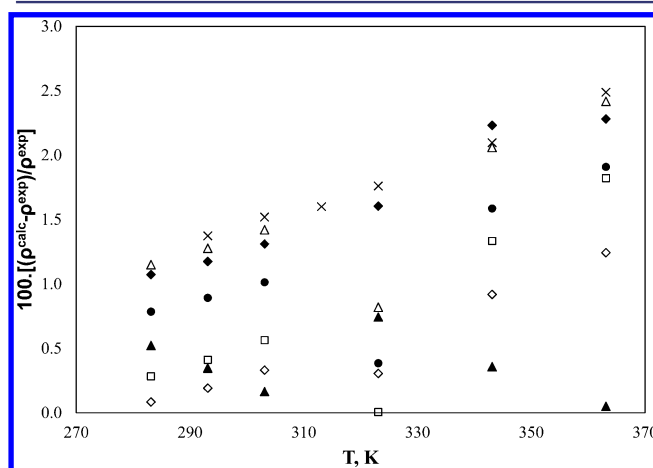
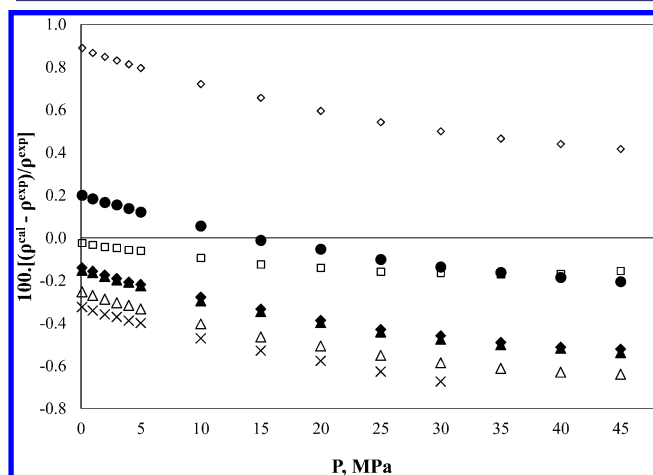
oil	ARD, %		
	revised GCVOL	Halvorsen	Zong
C	0.14	0.41	
S	0.11	0.37	0.81
R	0.12	1.8	0.49
Sf	0.11	0.49	0.68
Am	0.12	0.22	1.1
Jc	1.2	0.7	1.5
P	1.0	1.3	1.7
OARD, %	0.41	0.75	1.0

**Figure 5.** RDs between experimental and predicted densities as a function of the temperature at atmospheric pressure using Halvorsen's model for seven vegetable oils. □, C; ♦, S; △, R; ●, Am; ◇, Jc; ▲, Sf; and ×, P.**Figure 6.** RDs between experimental and predicted densities as a function of the temperature at atmospheric pressure using Zong's model for six vegetable oils. ♦, S; △, R; ●, Am; ◇, Jc; ▲, Sf; and ×, P.

used 8 of 33 representative triglyceride molecules to describe successfully the experimental densities of three Brazilian oils (buriti oil, brazil nut oil, and grape seed oil) with an average relative deviation of less than 0.80 %. Since on this work the composition of the oil in triglycerides was unknown and only the fatty acid profile was available, to use this method we defined pseudocompounds to describe the oil composition. The pseudocomponents were triglycerides, formed by three identical

fatty acids, with compositions defined to match the fatty acid profile of the oils as reported in Table 5. The temperature-dependency parameters of the fragments, $B_{1,A}$ and $B_{2,A}$, were reported by Zong et al.³⁰ Based on these parameters, Zong's model provided a good description of the density of the six vegetable oils here studied, with an OARD of 1.2 % (Table 3). The density of castor oil was not predicted with this method because there were no values of parameters $B_{1,A}$ and $B_{2,A}$ for the ricinoleic acid. This model produced deviations that are almost stable over the range of temperatures studied, with a maximum of 2.5 % as shown in Figure 5.

The density prediction with the GCVOL group contribution method began with the division of the molecule of vegetable oil into several functional groups: CH_3 and CH_2 to describe the contribution of the linear and saturated alkyl chain, $\text{CH}=\text{CH}$ to consider the unsaturation of the alkyl chain, and finally CHCOO and CH_2COO to take into account the ester contributions and CHOH to consider the alcohol contribution. This method was then applied in three different versions according to the values of parameters A_i , B_i , and C_i for the groups described above. As stated above, the revised version uses most of the parameters reported

**Figure 7.** RDs between experimental and predicted densities as a function of the temperature at atmospheric pressure using revised version of GCVOL group contribution method for seven vegetable oils. □, C; ♦, S; △, R; ●, Am; ◇, Jc; ▲, Sf; and ×, P.**Figure 8.** RDs between experimental and predicted densities as a function of the pressure at 293.15 K using an extension of the Halvorsen's model for seven vegetable oils. □, C; ♦, S; △, R; ●, Am; ◇, Jc; ▲, Sf; and ×, P.

by Elbro et al.³³ plus the new parameters proposed by Pratas et al.²² to describe the unsaturation group.

The revised GCVOL provides a good description of the temperature dependency of density for oils with an OARD of only 1.1%. The performance of this method is presented in Figure 6.

An extension of the three models here studied to high pressure is also proposed to describe the pressure-dependency of density for vegetable oils according to the eq 17, where ρ is the density in $\text{g}\cdot\text{cm}^{-3}$, M_w is the molecular weight in $\text{g}\cdot\text{mol}^{-1}$, $V(T)$ is the molar volume at atmospheric pressure in $\text{cm}^3\cdot\text{mol}^{-1}$, P is the absolute pressure in MPa, and c is a fitting parameter.

$$\rho(T, P) = \frac{M_w}{V(T)(1 + cP)} \quad (17)$$

To estimate the c parameter, the experimental data of three vegetable oils (P, S, and Jc) were used for the fitting purpose. The c values obtained were $-4.29 \times 10^{-4} \text{ MPa}^{-1}$ for the Halvorsen method, $-2.80 \times 10^{-4} \text{ MPa}^{-1}$ for Zong's model, and $-5.99 \times 10^{-4} \text{ MPa}^{-1}$ for the revised GCVOL method.

The description of the experimental high-pressure densities for all vegetable oils was very good for the three methods studied,

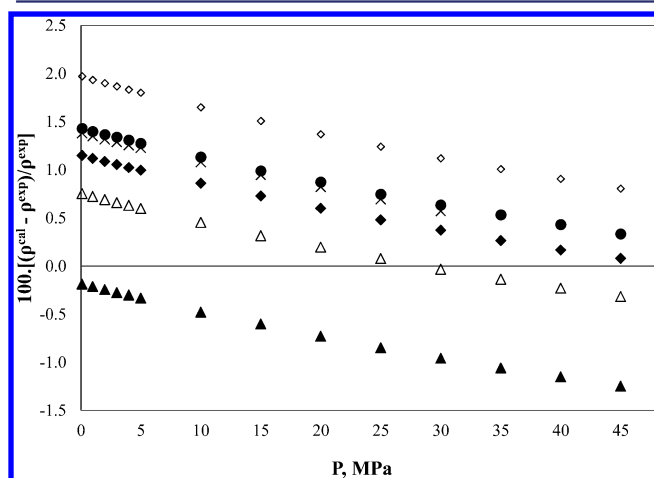


Figure 9. RDs between experimental and predicted densities as a function of the pressure at 293.15 K using an extension of the Zong's model for six vegetable oils. ◆, S; Δ, R; ●, Am; ▽, Jc; ▲, Sf; and ×, P.

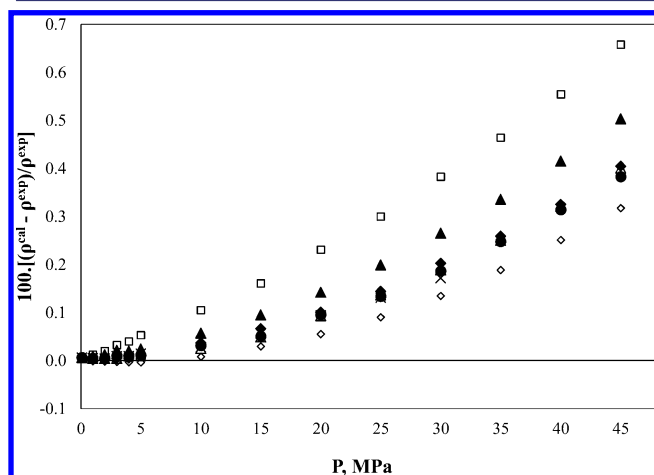


Figure 10. RDs between experimental and predicted densities as a function of the pressure at 293.15 K using an extension of the revised GCVOL model for seven vegetable oils. ◻, C; ◆, S; Δ, R; ●, Am; ▽, Jc; ▲, Sf; and ×, P.

presenting OARDs of (0.75, 1.04, and 0.41) % for the models of Halvorsen, Zong, and revised GCVOL, respectively, as shown in Table 5. Moreover, the RDs for all methods are slightly pressure-dependent with maximum deviations of less than 2.0% as seen in Figures 7, 8, 9, and 10. These models are thus adequate to describe the temperature and pressure dependency of the density for vegetable oils, provided that the fatty acid profile is known.

5. CONCLUSIONS

The experimental densities of S, R, C, P, Sf, Am, and Jc oils were here reported at temperatures from (283.15 to 363.15) K and pressures up to 45 MPa. These data were well correlated with the Tait-Tammann equation with an overall average relative deviations (OARDs) of 0.0045% and used to assess the adequacy of GCVOL group contribution method, Halvorsen's model, and Zong's model for prediction of vegetable oils densities based on the fatty acid profile of the vegetable oils. The temperature dependency of oil density was well described by Halvorsen's model, Zong's model, and the revised version of the GCVOL method with OARDs of (0.34, 1.1, and 1.2) %, respectively. The models here studied were also extended to elevated pressures and shown to be able to predict the densities of vegetable oils with OARDs of (0.75, 1.04, and 0.41) % for the models of Halvorsen, Zong, and revised GCVOL, respectively. Moreover the predictive deviations were just slightly pressure-dependent with a maximum value of less than 2.0%. Thus, these models are recommended for predicting the density of any type of oils provided that the fatty acid profiles are known.

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Notes

The authors declare no competing financial interest.

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