

# Biodiesel Density: Experimental Measurements and Prediction Models

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**ABSTRACT:** Density is an important biodiesel parameter, with impact on fuel quality. Predicting density is of high relevance for a correct formulation of an adequate blend of raw materials that optimize the cost of biodiesel fuel production while allowing the produced fuel to meet the required quality standards. The aim of this work is to present new density data for different biodiesels and use the reported data to evaluate the predictive capability of models previously proposed to predict biodiesel or fatty acid methyl ester densities. Densities were measured here for 10 biodiesel samples, for which detailed composition is reported, at atmospheric pressure and temperatures from 278.15 to 373.15 K. Density dependence with temperature correlations was proposed for the biodiesels, and isobaric expansivities are presented. The new experimental data presented here were used along with other literature data to evaluate predictive density models, such as those based on Kay's mixing rules and the GCVOL group contribution method. It is shown that Kay's mixing rules and a revised form of the GCVOL model are able to predict biodiesel densities with average deviations of only 0.3%. A comparison between biodiesel densities produced from similar vegetable oils, by different authors, highlights the importance of knowing the detailed composition of the samples. An extension of GCVOL for high pressures is also proposed here. It is shown that it can predict the densities of biodiesel fuels with average deviations less than 0.4%.

## 1. INTRODUCTION

Biodiesel is a promising alternative energy resource for diesel fuel, consisting of alkyl monoesters of fatty acids, obtained from vegetable oils or animal fats combined with a short-chain alcohol. It has properties similar to ordinary diesel fuel made from crude oil and can be used in conventional diesel engines without any motorization transformation. Transesterification by alkaline catalysis is the most common process for producing biodiesel at an industrial level. Biodiesel is more environmentally friendly, nontoxic, and biodegradable compared to diesel fuel.<sup>1–3</sup>

Biodiesel fuel has to fulfill a number of quality standards. In Europe, the biodiesel fuel standards are compiled in the Norm CEN EN 14214<sup>4</sup> and in U.S.A. in the ASTM D6751.<sup>5</sup> Norms specify minimum requirements and test methods for biodiesel fuel to be used in diesel engines and for heating purposes, to increase the biodiesel fuel quality and its acceptance among consumers. Density is an important fuel property, because injection systems, pumps, and injectors must deliver an amount of fuel precisely adjusted to provide proper combustion.<sup>6</sup> Boudy and Seers<sup>7</sup> and Baroutian et al.<sup>8</sup> show that fuel density is the main property that influences the amount of mass injected. Density data are also important in numerous unit operations in biodiesel production. Density data are required to be known to properly design reactors, distillation units and separation process, storage tanks, and process piping.<sup>9,10</sup> Density depends upon the raw materials used for biodiesel fuel production and the biodiesel methyl ester profile.<sup>11</sup> Following a previous work addressing biodiesel viscosity predictions,<sup>12</sup> this work aims at evaluating the best predictive models for biodiesel densities and subsequent revision of them.

Rapeseed, soybean, and palm oils are the most commonly used oils to produce biodiesel, although non-edible oils, such as *Jatropha*, are becoming more important.<sup>9</sup> The capacity to correctly predict biodiesel densities is of major relevance for a correct formulation of an adequate blend of raw materials aiming at producing biodiesel according to the required quality standards<sup>13,14</sup> with the lowest production costs.

Three main types of methods exist for estimating liquid densities of pure compounds. The first types are the methods based on the corresponding states theory, such as the Rackett equation and the Spencer and Danner method.<sup>8,9,11,15–19</sup> These methods have, however, some disadvantages, such as the requirement of critical properties, and because they often use experimental-data-adjusted parameters, they have a limited predictive ability. The second type of method is based on mixing rules, such as Kay's,<sup>20,21</sup> that allow for the estimation of a mixture density provided that the composition of the fuel and the densities of the pure compounds are known. They are only applicable to simple mixtures with a near ideal behavior. Finally, group contribution models are another approach that only require the chemical structure of the desired molecule to be known to estimate the thermophysical properties, such as liquid densities. The group contribution method GCVOL<sup>22</sup> is a predictive model that was shown in previous studies<sup>13,14</sup> to be able to provide pure fatty acid methyl ester (FAME) density descriptions within 1% deviation.

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Table 1. Biodiesels Used in This Study

reference	biodiesel	oil source	temperature range (K)	density range (kg m <sup>-3</sup> )
Baroutian et al. <sup>8</sup>	PalmS	palm	288.15–363.15	821.5–875.9
Benjumea et al. <sup>30</sup>	PalmA	palm	313.15–373.15	809.0–853.3
Hubber et al. <sup>28</sup>	SoyAB	soybean	278–333	849.41–893.23
	SoyBB	soybean	278–334	848.58–892.37
Tat and Van Gerpen <sup>18</sup>	SoyTG	soybean	273.15–373.15	831.40–897.60
Nogueira et al. <sup>29</sup>	SoyC	soybean	293.15–373.15	828.0–885.8
	Cotton	cottonseed	293.15–373.15	814.6–876.2
Veny et al. <sup>9</sup>	Jatrop	Jatropha	288.15–363.15	825.67–880.32

There are several publications in the literature presenting density data for biodiesels in wide ranges of temperatures, but usually no information about biodiesel compositions is provided; thus, these data cannot be used for model evaluation. The scarcity of biodiesel density data for which composition information is available limits the use of these models to predict this property for biodiesel fuels.

In the present work, we report new experimental density data for 10 biodiesel samples, for which a detailed composition is presented. They were produced from different vegetable oils or oil blends as reported below. The data cover the temperature range from 278.15 to 373.15 K at atmospheric pressure. Correlations for the temperature dependency of the experimental data are reported, and the isobaric expansivities are estimated.

These data, along with other data collected from the literature, are used to carry out a critical evaluation of biodiesel density predictive models.

## 2. EXPERIMENTAL SECTION

**2.1. Biodiesel Sample Synthesis.** A total of 10 biodiesel samples were studied in this work. A total of 2 of these samples were obtained from Portuguese biodiesel producers, namely, SoyA and GP (soybean + rapeseed). A total of 8 biodiesel samples were synthesized at our laboratory by a transesterification reaction of the vegetable oils, soybean (S), rapeseed (R), and palm (P), and their respective binary and ternary mixtures, soybean + rapeseed (SR), rapeseed + palm (RP), soybean + palm (SP), and soybean + rapeseed + palm (SRP), and sunflower (Sf). The molar ratio of oil/methanol used was 1:5, with 0.5% sodium hydroxide by weight of oil as the catalyst. The reaction was performed at 55 °C for 24 h under methanol reflux. The reaction time chosen was adopted for convenience and to guarantee a complete reaction conversion. Raw glycerol was removed in two steps: the first after 3 h of reaction and then after 24 h of reaction in a separating funnel. Biodiesel was purified by washing with hot distilled water until a neutral pH was achieved. The biodiesel was then dried until the EN ISO 12937 limit for water was reached (less than 500 ppm of water). The water content was checked by Karl-Fischer titration.

Biodiesel was characterized by gas chromatography–flame ionization detector (GC–FID) following the British Standard EN 14103 from EN 14214<sup>4</sup> to know the methyl ester composition of the samples.

**2.2. Experimental Measurements.** Density measurements were performed in the temperature range of 278.15–373.15 K and at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger viscometer. The apparatus was equipped with a vibrating U-tube densimeter. The absolute uncertainty of the density is 0.0005 kg m<sup>-3</sup>. The SVM 3000 uses Peltier elements for fast and efficient thermostability. The temperature uncertainty is ±0.02 K from 288.15 to 378.15 K. The SVM was previously tested for other compounds and presented very good reproducibility.<sup>13,23</sup> The instrument was rinsed

with ethanol 3 times and then pumped in a closed circuit at constant flow of the solvent for 20 min at 323 K. This cleaning cycle was repeated with acetone and then kept at 343 K for 30 min under a stream of air to ensure that the measurement cell was thoroughly cleaned and dried before the measurement of a new sample.

Capillary GC was used to determine the composition in methyl ester of biodiesel samples. A Varian CP-3800 with a FID in a split injection system with a select biodiesel for FAME column (30 m × 0.32 mm × 0.25 μm) was used to discriminate between all methyl esters in analysis, including the polyunsaturated ones. The column temperature was set at 120 °C and then programmed to increase up to 250 °C at 4 °C/min. The detector and injector were set at 250 °C. The carrier gas was helium with a flow rate of 2 mL/min.

## 3. DENSITY MODELS

**3.1. Linear Mixing Rules.** Kay's mixing rules<sup>20,21</sup> are the simplest form of mixing rules by which mixture properties are obtained by summing the products of the component properties by weighting factors, which are usually the concentrations of the components in a mixture. For example

$$\rho = \sum_i^m c_i \rho_i \quad (1)$$

where  $c_i$  is the concentration and  $\rho_i$  is the density of component  $i$ .

The major drawback in the application of linear mixing rules is that they require the knowledge of the experimental densities of the pure components present on the mixture and assume that the mixture excess volumes are negligible. This may not be feasible for many real fluids because they are either composed of a large number of compounds or have different natures, and consequently, the excess volumes are non-negligible. However, biodiesels are simple mixtures composed, in general, by less than 10 fatty acid esters all from the same family, and consequently, excess volumes are very small. In fact, they have been used before by several authors to predict biodiesel densities. Janarthanan and Clements<sup>24</sup> first used this approach with molar fractions as the weighting factor. Tat and Gerpen<sup>18</sup> proposed the use of mass fractions as the weighting factor. Nevertheless, the dimensionally correct way to use concentrations in Kay's mixing rules to predict densities would be as volumetric fractions. Recently, new accurate information about biodiesel fatty acid methyl ester composition was reported,<sup>13,14</sup> allowing for the application of Kay's mixing rules to predict biodiesel density data.

**3.2. GCVOL Group Contribution Method.** GCVOL is a group contribution method developed for the prediction of molar volumes of liquids. It is a completely predictive model exclusively based on the molecular structure of the compound. With this approach, liquid densities, even for strongly polar

Table 2. Experimental Density, in  $\text{kg m}^{-3}$ , for Methylic Biodiesel

T (K)	S	R	P	SR	RP	SP	SRP	Sf	GP	SoyA
278.15	894.6	893.3		893.2	889.5		890.4	894.8	891.8	
283.15	890.9	889.6		889.5	885.8	885.7	886.7	890.9	888.0	888.4
288.15	887.3	886.0	877.9	885.7	882.1	882.0	883.0	887.2	884.3	884.7
293.15	883.6	882.3	874.1	882.0	878.4	878.2	879.3	883.5	880.6	881.0
298.15	880.0	878.6	870.4	878.3	874.7	874.5	875.6	879.8	876.9	877.3
303.15	876.3	875.0	866.7	874.7	871.1	870.9	871.9	876.2	873.2	873.6
308.15	872.7	871.3	863.0	871.0	867.4	867.2	868.2	872.6	869.6	870.0
313.15	869.0	867.7	859.4	867.3	863.7	863.5	864.6	868.9	865.9	866.3
318.15	865.3	864.1	855.7	863.7	860.1	859.9	860.9	865.3	862.2	862.7
323.15	861.7	860.4	852.1	860.1	856.5	856.3	857.3	861.6	858.6	859.0
328.15	858.0	856.8	848.5	856.4	852.8	852.6	853.6	858.0	855.0	855.4
333.15	854.3	853.2	844.9	852.8	849.2	849.0	850.0	854.4	851.4	851.8
338.15	850.7	849.5	841.2	849.2	845.5	845.4	846.4	850.7	847.7	848.2
343.15	847.0	845.9	837.6	845.6	841.9	841.8	842.8	847.1	844.1	844.5
348.15	843.4	842.3	834.0	842.0	838.2	838.1	839.2	843.5	840.5	840.9
353.15	839.8	838.7	830.4	838.4	834.6	834.5	835.6	839.9	836.9	837.3
358.15	836.1	835.0	826.8	834.9	830.9	831.0	832.0	836.3	833.3	
363.15	832.5	831.4	823.2	831.3	827.3	827.4	828.4	832.8	829.8	

Table 3. Compositions of the Biodiesels Studied, in Mass Percentage

methyl esters	S	R	P	SR	PR	SP	SRP	Sf	GP	SoyA
C10		0.01	0.03		0.02	0.01	0.01			
C12		0.04	0.24	0.03	0.20	0.18	0.14	0.02	0.02	
C14	0.07	0.07	0.57	0.09	0.54	0.01	0.38	0.07	0.13	
C16	10.76	5.22	42.45	8.90	23.09	25.56	18.97	6.40	10.57	17.04
C16:1	0.07	0.20	0.13	0.15	0.17	0.11	0.14	0.09	0.13	
C18	3.94	1.62	4.02	2.76	3.02	4.04	3.28	4.22	2.66	3.73
C18:1	22.96	62.11	41.92	41.82	52.92	33.13	42.51	23.90	41.05	28.63
C18:2	53.53	21.07	9.80	37.51	15.47	31.72	27.93	64.16	36.67	50.45
C18:3	7.02	6.95	0.09	7.02	3.08	3.58	4.66	0.12	7.10	
C20	0.38	0.60	0.36	0.46	0.49	0.39	0.45	0.03	0.44	
C20:1	0.23	1.35	0.15	0.68	0.67	0.20	0.52	0.15	0.67	
C22	0.80	0.35	0.09	0.46	0.24	0.32	0.33	0.76	0.45	
C22:1	0.24	0.19	0.00	0.12	0.09	0.12	0.14	0.08	0.12	
C24		0.22	0.15			0.63	0.53			

solvents, can be predicted with an error of approximately 1% in the temperature range between the melting temperature and the normal boiling point.<sup>22</sup> In previous studies,<sup>13,14</sup> we have shown that good descriptions of fatty ester densities could be obtained with this model.

For the calculation of liquid densities, the relation between the molecular weight,  $MW_j$ , and molar volume,  $V_j$ , is used

$$\rho = \frac{\sum_j x_j MW_j}{\sum_j x_j V_j} \quad (2)$$

with  $x_j$  being the molar fraction of component  $j$ . The molar volume of a liquid  $j$  is calculated by the following equation:

$$V = \sum_i n_i \Delta v_i \quad (3)$$

where  $n_i$  is the number of group  $i$ , and the temperature dependency of the molar group,  $\Delta v_i$ , in  $\text{cm}^3 \text{mol}^{-1}$ , is given by the following simple polynomial function

$$\Delta v_i = A_i + B_i T + C_i T^2 \quad (4)$$

where  $T$  is the absolute temperature that can vary between the melting point and the normal boiling point when the model is used to predict densities of solvents. The  $A_i$ ,  $B_i$ , and  $C_i$  parameters were obtained from Elbro et al.<sup>22</sup> The original GCVOL model presented 36 different group parameters for a variety of chemical classes, such as alkanes, aromatic, alkenes, alcohols, ketones, aldehydes, esters, ethers, chlorides, and siloxanes.

**3.3. Extended GCVOL Group Contribution Method.** Since the publication of GCVOL in 1991, other new groups were defined and new parameters for different functional groups were published. In 2003, an extension and revised version of GCVOL,

**Table 4. Density Correlation Constants for Biodiesel Methyl Esters over the Temperature Range of 278.15–363.15 K and Corresponding 95% Confidence Limits<sup>a</sup>**

	$b$ (kg m <sup>-3</sup> K <sup>-1</sup> )	±	$s_b$	$a$ (kg m <sup>-3</sup> )	±	$s_a$
S	-0.731		0.001	1097.9		0.2
R	-0.728		0.001	1095.6		0.3
P	-0.728		0.002	1087.4		0.6
SR	-0.728		0.003	1095.4		0.9
RP	-0.731		0.001	1092.8		0.3
SP	-0.728		0.002	1091.7		0.7
SRP	-0.729		0.002	1093.0		0.7
Sf	-0.728		0.002	1097.0		0.7
GP	-0.729		0.002	1094.4		0.8
SoyA	-0.730		0.001	1094.8		0.4

<sup>a</sup>  $s$  = standard deviation.

**Table 5. Isobaric Expansivities,  $\alpha_p$ , for the Studied Biodiesel Methyl Esters and Corresponding 95% Confident Limits at 298 K<sup>a</sup>**

	$\alpha_p$ ( $\times 10^3$ K <sup>-1</sup> )	±	$s_{\alpha_p}$ ( $\times 10^3$ )
S	0.847		0.004
R	0.844		0.004
P	0.856		0.002
SR	0.844		0.002
RP	0.852		0.004
SP	0.851		0.002
SRP	0.849		0.002
Sf	0.843		0.002
GP	0.847		0.002
SoyA	0.846		0.002

<sup>a</sup>  $s$  = standard deviation.

with new parameters for all groups, was published.<sup>25</sup> This version of GCVOL was also tested in this work.

**3.4. Database for Biodiesel Densities.** Although some biodiesel density data can be found in the literature, information concerning the detailed biodiesel composition, other than just the oil used in the biodiesel synthesis, is scarce. Densities in a range of temperatures, instead of the standard value at 15 °C required by EN 14214,<sup>4</sup> are also rare.

Detailed biodiesel composition is required for the application of the models selected here. The database used in this study, reported in Table 1, was collected from the literature and supplemented with the new experimental data for 10 biodiesels measured in this work. The most important oils used in biodiesel production (soy, rapeseed, and palm) were covered by this study, and mixtures of them as well as other vegetable oils (sunflower and two biodiesel samples from a Portuguese biodiesel producer) were also used. Literature soybean biodiesel density data were compiled even without information about ester composition, to compare density data from distinct oil crops of the same kind.

## 4. RESULTS AND DISCUSSION

New experimental density data for eight biodiesels synthesized in this work and for two industrial biodiesels are reported in Table 2. For palm oil biodiesel, measurements were only carried

**Table 6. ARDs for the Models Tested<sup>a</sup>**

	GCVOL			Kay's mixing rules		
	original	extension	revised	$\nu$	$x$	$W$
S	0.750	4.01	0.039	0.306	0.302	0.292
R	0.789	2.09	0.173	0.520	0.520	0.520
P	0.349	3.95	0.068	0.314	0.340	0.356
SR	0.594	2.84	0.093	0.318	0.312	0.305
RP	0.430	1.22	0.046	0.476	0.485	0.464
SP	1.00	0.537	0.509	0.254	0.256	0.247
SRP	0.964	1.02	0.416	0.318	0.328	0.310
Sf	0.776	4.16	0.043	0.328	0.324	0.319
GP	0.473	2.49	0.239	0.174	0.170	0.161
SoyC	1.07	4.52	0.319	0.553	0.551	0.537
Cotton	0.187	1.32	0.693	0.393	0.372	0.406
SoyA	0.515	1.72	0.036	0.375	0.306	0.305
PalmS	0.144	3.95	0.285	0.124	0.142	0.130
PalmA	0.470	4.74	0.792	0.312	0.330	0.363
SoyAB	0.555	0.393	0.097	0.168	0.169	0.408
SoyBB	0.624	0.178	0.103	0.362	0.361	0.600
SoyTG	0.851	9.05	0.385	0.500	0.507	0.253
Jatrop	0.321	0.127	0.228	0.084	0.090	0.086
<b>OARD%</b>	<b>0.603</b>	<b>2.69</b>	<b>0.254</b>	<b>0.327</b>	<b>0.326</b>	<b>0.337</b>

<sup>a</sup> Bold numbers are the total group OARD.

out at temperatures above its cloud point. Table 3 reports the methyl ester compositions of the studied biodiesels.

The experimental data show that the biodiesel density decreases with an increasing temperature and with the level of unsaturation of the FAMEs, as expected from previous studies,<sup>13,14</sup> where the same behavior for pure compounds was observed.

The density data measured here were correlated using a linear temperature dependency using an optimization algorithm based on the least-squares method

$$\rho \text{ (kg m}^{-3}\text{)} = bT \text{ (K)} + a \quad (5)$$

and the parameter values along with their confidence limits are reported in Table 4. This approach was already adopted previously for several pure methyl and ethyl esters.<sup>13,14</sup>

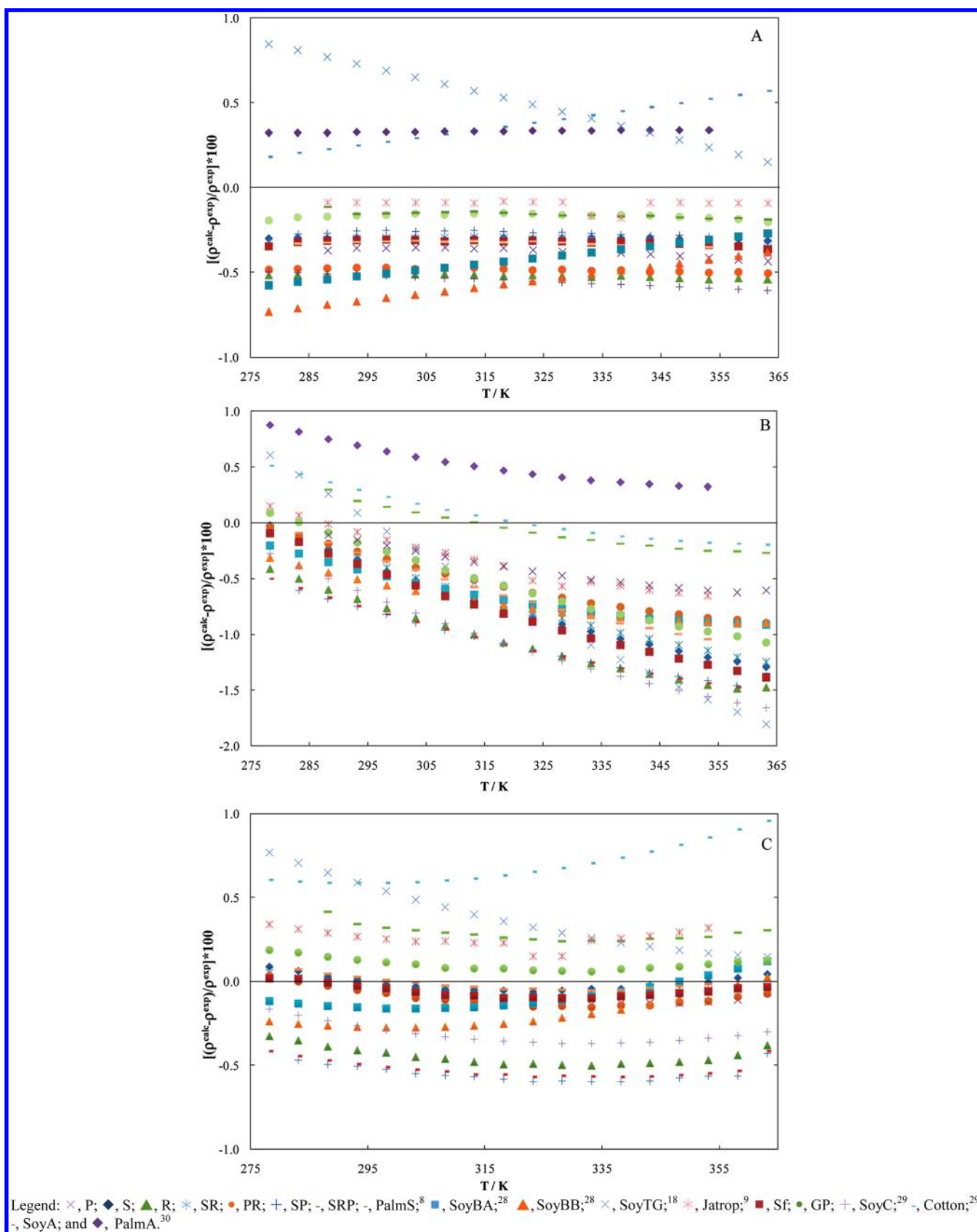
The isobaric expansivity coefficient at constant pressure ( $\alpha_p$ ) is defined as

$$\alpha_p = - \left( \frac{\partial \ln \rho}{\partial T} \right)_p \quad (6)$$

and was estimated from the measured data. In the temperature range investigated, the variation of  $\alpha_p$  with the temperature is below the precision of our data. The value of  $\alpha_p$  reported is estimated at 298 K and will be taken here as a constant for the biodiesel fuels studied. The isobaric expansivities estimated for the different biodiesels are reported in Table 5. These values are similar to those for other biodiesel fuels previously reported in the literature and the expansivities observed for pure fatty acid methyl esters.<sup>13,14</sup> Although the  $\alpha_p$  values obtained are statistically similar, a trend with the unsaturation content of biodiesels is observed.

To study the predictive ability of the various models investigated in this work, the relative deviations (RDs) for the predicted





**Figure 1.** RDs between experimental and predicted densities as a function of the temperature using (A) Kay's mixing rules with the molar fraction as a concentration factor, (B) original GCVOL model, and (C) revised GCVOL model for 18 biodiesel fuels. The zero line is experimental data.

Table 7. Parameters Used for the Models Tested: GCVOL, Extended GCVOL, and New Parameters Proposed in This Work

	GCVOL				extended GCVOL				revised GCVOL
	CH <sub>2</sub>	CH <sub>3</sub>	CH=	COO	CH <sub>2</sub>	CH <sub>3</sub>	CH=	COO	CH=
A	12.52	18.96	6.761	14.23	12.04	16.43	-1.651	61.15	11.43
B ( $\times 10^3$ )	12.94	45.58	23.97	11.93	14.1	55.62	93.42	-248.2	6.756
C ( $\times 10^5$ )	0	0	0	0	0	0	-14.39	36.81	0

Table 8. ARDs for Biodiesel and Methyl Ester Densities at High Pressures Calculated with the GCVOL Extension to High Pressures

compound	ARD (%)
MEC12	0.27
MEC14	0.28
MEC18:1	0.29
P	0.47
S	0.52
R	0.74
Sf	0.23
RP	0.30
SP	0.29
SR	0.40
SRP	0.32
OARD (%)	0.37

densities for each biodiesel were estimated according to eq 7

$$RD = \frac{\rho_{\text{calc}_i} - \rho_{\text{exp}_i}}{\rho_{\text{exp}_i}} \times 100 \quad (7)$$

where  $\rho$  is the density in  $\text{kg m}^{-3}$ . The average relative deviation (ARD) was calculated as a summation of the modulus of RD over  $N_p$  experimental data points. The overall average relative deviation (OARD) was calculated by eq 8

$$\text{OARD} = \frac{\sum \text{ARD}}{N_s} \quad (8)$$

where  $N_s$  is the number of systems studied.

The ARDs for each biodiesel studied are reported in Table 6, while the RDs of the individual data points for the 18 biodiesel samples are shown in panels A–C of Figure 1.

Three versions of Kay's mixing rules, with mass, molar, and volumetric fractions, were used to predict the biodiesel densities. Pure compound densities were obtained from our previous studies.<sup>13,14</sup> Detailed results are reported in Table 6 for all of the biodiesel studied. Very good predictions were obtained with all three approaches considered, with an ARD of about 0.33%. No significant differences between the results obtained with the different versions of Kay's mixing rules are observed, which may come as a surprise but can easily be justified by the similarity of the compounds in nature and size present in the biodiesels, resulting in similar concentration values regardless of the units adopted, resulting in a marginal impact on the prediction (Figure 1A).

The two versions of the GCVOL model were also used to predict biodiesel densities. Results for the RDs are reported for all of the biodiesels studied in Table 6. To define the ester group, parameters for both the  $-\text{COO}-$  and  $-\text{CH}_2\text{COO}-$  groups

were tested and large deviations were reported when using the  $-\text{CH}_2\text{COO}-$  group. Consequently, the  $-\text{COO}-$  group was adopted in this work to describe the ester group. The results reported suggest that the original version of GCVOL with overall average deviations of 0.60% is far superior to the extended GCVOL version with overall average deviations of 2.7%.

Results from previous studies of ours<sup>13,14</sup> and the ones shown in Figure 1B indicate that GCVOL has a poor performance for unsaturated methyl esters and biodiesels with a higher content of unsaturated esters, such as soybean biodiesel. The results suggest that the temperature dependency of the  $-\text{CH=}$  parameter is not correct and can be improved.

New values for  $A_i$ ,  $B_i$ , and  $C_i$  for the double-bond parameter ( $-\text{CH=}$ ) were estimated on the basis of the density data for fatty acid esters reported in previous studies of ours<sup>13,14</sup> and used to predict the densities of the biodiesels studied here. The new values for the  $-\text{CH=}$  parameter proposed here, reported in Table 7, reduce the overall relative deviations of the GCVOL predictions from 0.60 to 0.25%. Figure 1C presents the RDs obtained by the revised GCVOL model as a function of the temperature, and it is shown that the deviations are now essentially temperature-independent.

The revised GCVOL model was extended here to high pressures using an approach previously proposed by Gardas and Coutinho<sup>26</sup> for ionic liquids and described by eq 9

$$\rho(T, P) = \frac{M_w}{V(T)(1 + cP)} \quad (9)$$

where  $\rho$  is the density in  $\text{g/cm}^3$ ,  $M_w$  is the molecular weight in  $\text{g/mol}$ ,  $V(T)$  is the molar volume in  $\text{cm}^3 \text{mol}^{-1}$  predicted by GCVOL,  $P$  is the absolute pressure in MPa, and  $c$  is a fitting parameter. Experimental high-pressure densities of three methyl esters (laurate, myristate, and oleate) reported by us elsewhere<sup>27</sup> were used to estimate the  $c$  parameter with a value of  $-5.7 \times 10^{-4} \text{ MPa}^{-1}$ , describing high-pressure densities of the methyl esters with average deviations of 0.3%, as reported in Table 8. Equation 9, using this  $c$  value, was then used to predict high-pressure densities for seven biodiesel fuels.<sup>27</sup> The RDs between experimental and predicted densities as a function of the pressure at 293.15 K are presented in Figure 3. The ARDs for all compounds studied here are presented in Table 8. The overall average relative deviation (OARD) of only 0.37% confirms that the extension to high pressures of the GCVOL model proposed here can provide excellent predictions of densities of different biodiesel fuels at high pressure.

It may be argued that the requirement of knowing the biodiesel detailed composition to predict biodiesel densities requires too much effort when there are plenty of density data in the literature for biodiesels from a large number of vegetable oils. A comparison between the data reported by different authors for the densities of biodiesels produced from soybean

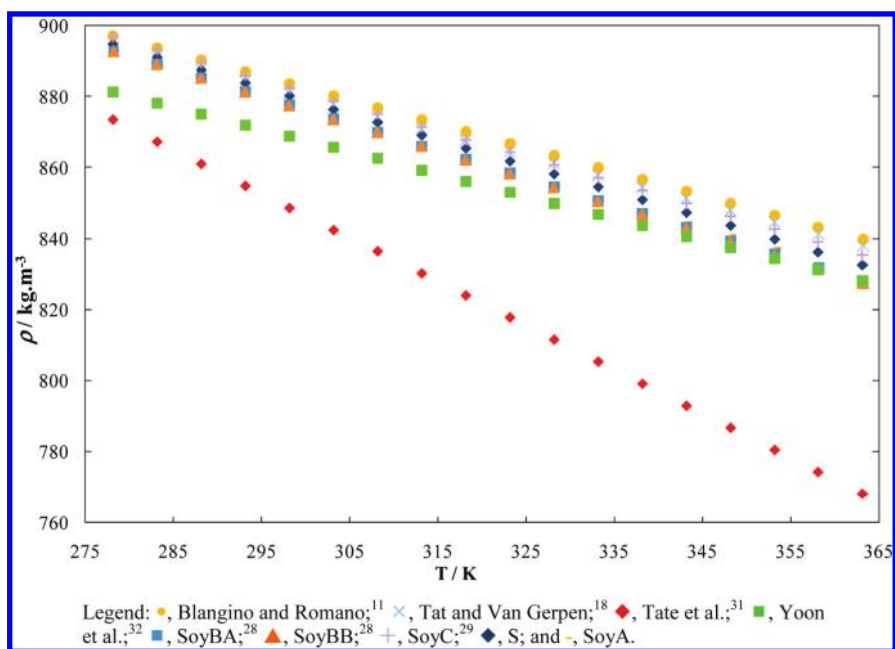


Figure 2. Density values as a function of the temperature for different soybean biodiesel samples.

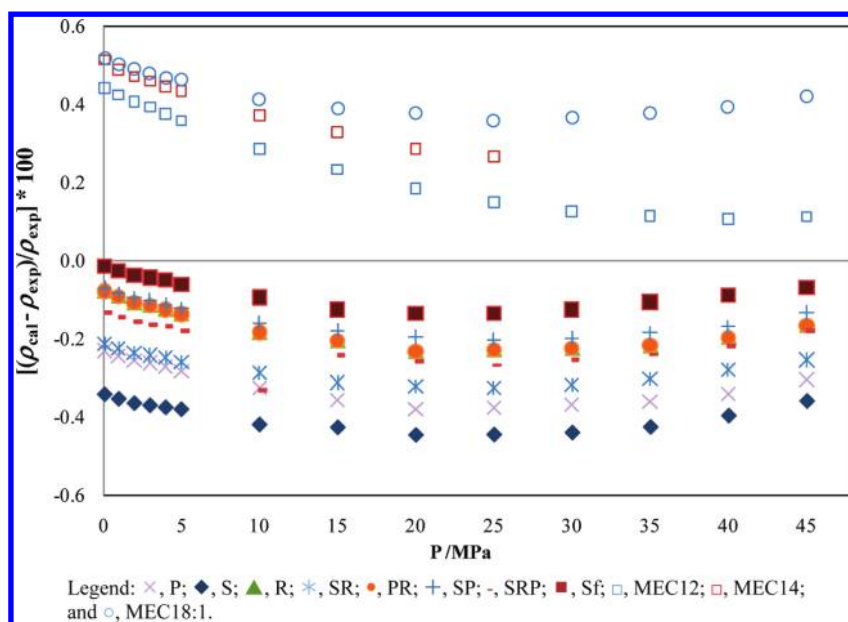


Figure 3. RDs between experimental and predicted densities as a function of the pressure at 293.15 K using an extension of the GCVOL model for three methyl esters and seven biodiesel fuels.<sup>27</sup>

oil, presented in Figure 2, shows large differences that cannot be assigned to experimental errors but to the differences in the oil compositions. These results clearly support the idea that a detailed characterization of the biodiesel composition is required even for estimating a simple property, such as density.

## 5. CONCLUSION

New experimental data for the density of 10 biodiesels in the temperature range of 273–363 K and at atmospheric pressure are reported.

The experimental data measured here were used to test predictive models for biodiesel densities. Three versions of Kay's mixing rules and two versions of the GCVOL model were investigated. With exception of the extended GCVOL model, all approaches seem to be able to describe the biodiesel densities with deviations smaller than 1%. The various approaches to Kay's mixing rules studied produce similar results, and the revised version of the GCVOL model proposed here predicts the biodiesel densities with deviations of only 0.25%.

An extension of the GCVOL model to high pressures is proposed here based on correlated data for three methyl esters.

It was tested in the seven biodiesel fuels studied, and it is shown that it can predict densities in a wide range of pressures and temperatures with an OARD of 0.37%, with these deviations not being sensible to the pressure.

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