

# Densities and Viscosities of Fatty Acid Methyl and Ethyl Esters

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To develop reliable models for the densities and viscosities of biodiesel fuel, reliable data for the pure fatty acid esters are required. Densities and viscosities were measured for seven ethyl esters and eight methyl esters, at atmospheric pressure and temperatures from (273.15 to 363.15) K. A critical assessment of the measured data against the data previously available in the literature was carried out. It is shown that the data here reported presents deviations of less than 0.15 % for densities and less than 5 % for viscosities. Correlations for the densities and viscosities with temperature are proposed. The densities and viscosities of the pure ethyl and methyl esters here reported were used to evaluate three predictive models. The GCVOL group contribution method is shown to be able to predict densities for these compounds within 1 %. The methods of Ceriani and Meirelles (CM) and of Marreiro and Gani (MG) were applied to the viscosity data. It is shown that only the first of these methods is able to provide a fair description of the viscosities of fatty acid esters.

## Introduction

In consequence of environmental, economical, and also political turmoil, caused by the excessive use and dependency of conventional petroleum-based fuels, the attention of several countries has been addressed toward the development of alternative fuels from renewable resources.<sup>1,2</sup>

Among those alternatives, biodiesel fuel, along with bioethanol fuel, is in the forefront of the substitutes to petroleum-based fuels in the transportation sector, being considered as an important short-time option, as its prices can be similar to petroleum-based fuels and no motor changes are required.<sup>3</sup>

Biodiesel is a fuel comprised of monoalkyl esters of long chain fatty acids derived from vegetable oils, animal fats, or mixtures of them. It is produced by the transesterification of triglycerides with a short chain alcohol, usually methanol or ethanol, in the presence of a catalyst, leading to the formation of mixtures of fatty acid methyl esters (FAMES) or fatty acid ethyl esters (FAEEs), respectively.<sup>3,4</sup> The main components of biodiesel fuel are palmitate, stearate, oleate, and linoleate esters.<sup>5</sup> However, depending on the raw materials used, a larger range of esters can be present.<sup>6</sup>

The 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>7</sup> and in United States of America in the Norm ASTM D6751.<sup>8</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. Viscosities and densities are two of the main properties evaluated which will depend on the raw

materials used on the biodiesel fuel production and in consequence on the profile of methyl or ethyl esters of the biodiesel fuel.<sup>6</sup>

Density data are relevant because injection systems, pumps, and injectors must deliver the amount of fuel precisely adjusted to provide proper combustion.<sup>9</sup> Boudy and Seers show that fuel density is the main property that influences the amount of mass injected.<sup>10,11</sup> The viscosity is required not only for the design of pipes, fittings, and equipment to be used in industry of oil and fuel,<sup>12</sup> but also for monitoring the quality of fuel itself to be used in diesel engines. A viscous fuel, causing a poorer atomization, which is the first step of combustion, is responsible for premature injector cooking and poor fuel combustion.<sup>10,13</sup>

Many studies have been devoted to the measurement and prediction of the density and viscosity of biodiesel fuel as a function of temperature. Being able to predict those properties is of high relevance for the correct formulation of an adequate blend of raw materials that optimize the cost of biodiesel fuel production while allowing the fuel to meet the required quality standards. In fact, in process operation and optimization the use of correlative and predictive models for biodiesel fuel properties could be a most useful tool.

Several models have been proposed in the literature to calculate biodiesel fuel density. The most important among them rely on the accurate knowledge of the properties of the pure compounds. Tat and Van Gerpen<sup>14</sup> and Clements<sup>15</sup> used a linear mixing rule of pure densities based on the empirical equation proposed by Janarthanan.<sup>15</sup> Huber<sup>16</sup> et al. also use density mixing rule to develop preliminary thermodynamic model for biodiesel fuel. Similarly, for the viscosities the approaches proposed by Krisnangkura et al.<sup>17</sup> and Yuan et al.<sup>18</sup> allow the estimation of the viscosity of biodiesel fuel using the Grunberg–Nissan equation that requires accurate values of the viscosities of pure FAMES or FAEEs.<sup>19</sup>

For the higher FAEEs and FAMES, the density and viscosity data for a wide range of temperatures available in the literature

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Table 1. Methyl and Ethyl Esters Studied in This Work

compound	common name	purity m/m%	source	CAS
octanoic acid, ethyl ester	ethyl caprylate	99	Aldrich	106-32-1
decanoic acid, ethyl ester	ethyl caprate	99	Fluka	110-38-3
dodecanoic acid, ethyl ester	ethyl laurate	99	Sigma	106-33-2
tetradecanoic acid, ethyl ester	ethyl myristate	99	Aldrich	124-06-1
hexadecanoic acid, ethyl ester	ethyl palmitate	99	Sigma	628-97-7
octadecanoic acid, ethyl ester	ethyl stearate	99	Fluka	111-61-5
(Z)-9-octadecenoic acid, ethyl ester	ethyl oleate	98	Aldrich	111-62-6
octanoic acid, methyl ester	methyl caprylate	99	Fluka	111-11-5
decanoic acid, methyl ester	methyl caprate	99	Acros Org.	110-42-9
dodecanoic acid, methyl ester	methyl laurate	98	Sigma	111-82-0
tetradecanoic acid, methyl ester	methyl myristate	98	SAFC	124-10-7
hexadecanoic acid, methyl ester	methyl palmitate	99	SAFC	112-39-0
octadecanoic acid, methyl ester	methyl stearate	99	Fluka	112-61-8
(Z)-9-octadecenoic acid, methyl ester	methyl oleate	99	Aldrich	112-62-9
(Z,Z)-9,12-octadecadienoic acid, methyl ester	methyl linoleate	99	Sigma	112-63-0

Table 2. Experimental Density, in  $\text{kg}\cdot\text{m}^{-3}$ , for Ethyl Esters

T/K	ethyl						
	caprylate	caprate	laurate	myristate	palmitate	stearate	oleate
278.15	880.2						881.5
283.15	875.9	872.5	870.3	868.7			877.9
288.15	871.6	868.4	866.4	864.8			874.1
293.15	867.3	864.3	862.4	861.0			870.5
298.15	863.0	860.2	858.5	857.2			866.9
303.15	858.7	856.2	854.6	853.4	852.6		863.2
308.15	854.4	852.1	850.7	849.6	848.9		859.5
313.15	850.0	848.0	846.8	845.8	845.2	844.8	855.8
318.15	845.7	843.9	842.9	842.0	841.5	841.1	852.2
323.15	841.4	839.8	839.0	838.2	837.9	837.5	848.5
328.15	837.1	835.7	835.1	834.5	834.2	833.9	844.9
333.15	832.8	831.6	831.1	830.7	830.5	830.3	841.2
338.15	828.4	827.5	827.2	826.9	826.9	826.7	837.6
343.15	824.1	823.4	823.3	823.1	823.2	823.1	834.0
348.15	819.7	819.2	819.4	819.4	819.5	819.5	830.3
353.15	815.3	815.1	815.4	815.6	815.9	815.9	826.7
358.15	810.8				812.2	812.3	823.1
363.15	806.4				808.6	808.7	819.5

are sometimes scarce or contradictory, limiting the use of these models to predict those properties for biodiesels.

To address this limitation, in this work densities and viscosities of seven ethyl esters and eight methyl esters, from C8 to C18, were measured at atmospheric pressure and temperatures from (273.15 to 363.15) K. A comparison with the experimental data available and its critical evaluation is performed. Correlations of these experimental data using the equations on which the multicomponent models are based, a linear correlation of the densities with temperature, and the Vogel–Tamman–Fulcher (VTF) equation for the viscosities were carried and reported.

Table 3. Experimental Density, in  $\text{kg}\cdot\text{m}^{-3}$ , for Methyl Esters

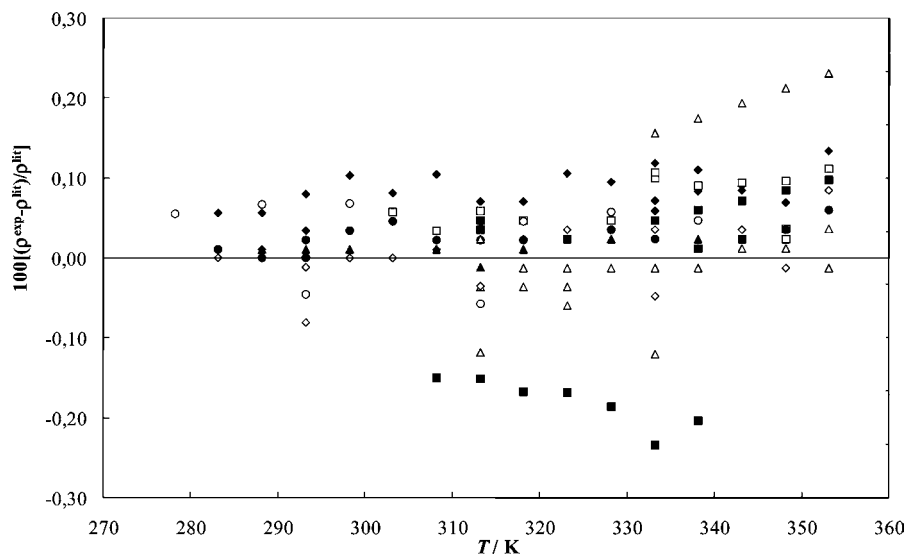
T/K	methyl								
	caprylate	caprate	laurate	myristate	palmitate	stearate	oleate	linoleate	
278.15		884.7							897.2
283.15	885.9	880.6	877.7				881.4		893.5
288.15	881.5	876.4	873.7				877.7		889.9
293.15	877.1	872.3	869.8				874.1		886.2
298.15	872.8	868.2	865.8	863.7			870.4		882.5
303.15	868.4	864.1	861.8	859.9			866.8		878.8
308.15	864.0	860.0	857.9	856.0	854.5		863.1		875.2
313.15	859.6	856.0	853.9	852.2	850.8	849.8	859.5		871.5
318.15	855.2	851.9	850.0	848.4	847.0	846.1	855.9		867.9
323.15	850.8	847.8	846.1	844.6	843.3	842.5	852.3		864.3
328.15	846.4	843.6	842.1	840.8	839.6	838.9	848.7		860.7
333.15	841.9	839.5	838.1	837.0	835.8	835.3	845.1		857.0
338.15	837.5	835.3	834.2	833.1	832.1	831.7	841.5		853.4
343.15	833.0	831.2	830.2	829.3	828.4	828.1	837.9		849.8
348.15	828.5	827.0	826.2	825.5	824.7	824.5	834.3		846.1
353.15	824.0	822.9	822.3	821.8	821.0	820.9	830.7		842.5
358.15		818.7			817.3	817.3			838.7
363.15		814.5			813.6	813.7			835.1

The densities and viscosities of the pure ethyl and methyl esters here measured were also used to evaluate the performance of three predictive models. The group contribution method GCVOL<sup>20</sup> was evaluated for the prediction of densities, while the models of Ceriani et al.<sup>12</sup> (CM) and Marrero and Gani<sup>21,22</sup> (MG) were evaluated for the viscosity.

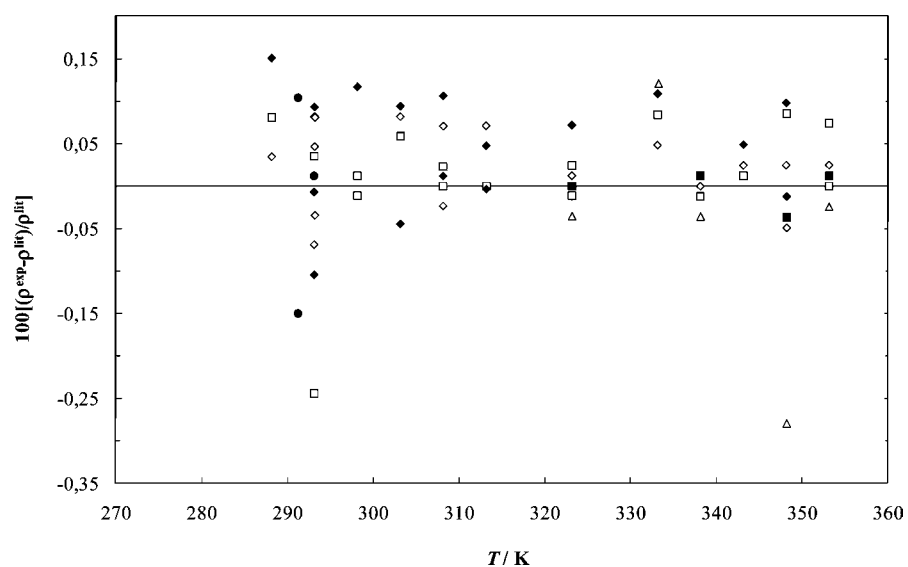
## Experimental Section

**Materials and Procedure.** Seven ethyl ester and eight methyl esters were used in this study. Table 1 reports the name, purity, supplier, and CAS number of each compound used in this study. Compound purity was confirmed by gas chromatography/flame ionization detection (GC-FID).

**Experimental Measurements.** Measurements of viscosity and density were performed in the temperature range of (273.15 to 363.15) K at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The viscometer is based on a tube filled with the sample in which floats a hollow measuring rotor. Because of its low density, the rotor is centered in the heavier liquid by buoyancy forces. Consequently, a measuring gap is formed between the rotor and the tube. The rotor is forced to rotate by shear stresses in the liquid and is guided axially by a built-in permanent magnet, which interacts with a soft iron ring. The rotating magnetic field delivers the speed signal and induces eddy currents in the surrounding copper casing. These eddy currents are proportional to the speed of the rotor and exert a retarding torque on the rotor. Two different torques influence the speed of the measuring rotor; at the equilibrium, the two torques are



**Figure 1.** Relative deviations for methyl ester density data available in the literature<sup>28–32,34–39</sup> as a function of temperature: ●, methyl caprylate; ◇, methyl caprate; ◆, methyl laurate; □, methyl myristate; ■, methyl palmitate; △, methyl stearate; ▲, methyl oleate; and ○, methyl linoleate. Zero line is this work's experimental data.



**Figure 2.** Relative deviations for ethyl ester density data available in the literature<sup>32,35,40–47</sup> as a function of temperature: ●, ethyl caprylate; ◇, ethyl caprate; ◆, ethyl laurate; □, ethyl myristate; ■, ethyl palmitate; and △, ethyl stearate. Zero line is this work's experimental data.

equal, and the viscosity can be traced back to a single speed measurement. 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 absolute uncertainty of the density is  $0.0005 \text{ g}\cdot\text{cm}^{-3}$ , and the relative uncertainty of the dynamic viscosity obtained is less than 1.5 % for the standard fluid SHL120 (SH Calibration Service GmbH), in the range of the studied temperatures. The repeatability of the equipment was measured with temperature and presents a maximum standard deviation relative value of 0.15 % in the studied viscosity range for the same temperature range. Also the reproducibility of the equipment was evaluated with time and presents a maximum of 0.25 %.<sup>23</sup> Further details about the equipment and method can be found elsewhere.<sup>24</sup> This viscometer was previously tested for other compounds and presented a very good reproducibility.<sup>25</sup>

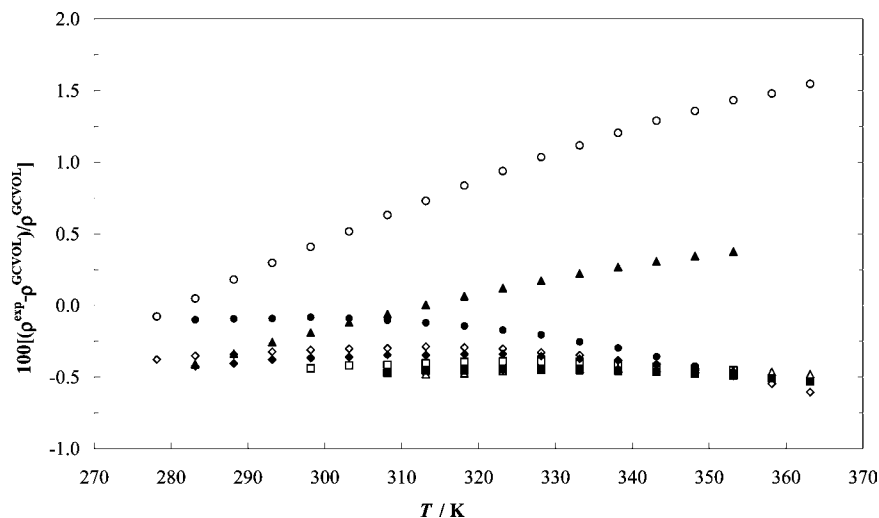
## Results and Discussion

**Density.** The experimental data obtained are reported in Tables 2 and 3. For methyl myristate, palmitate, and stearate

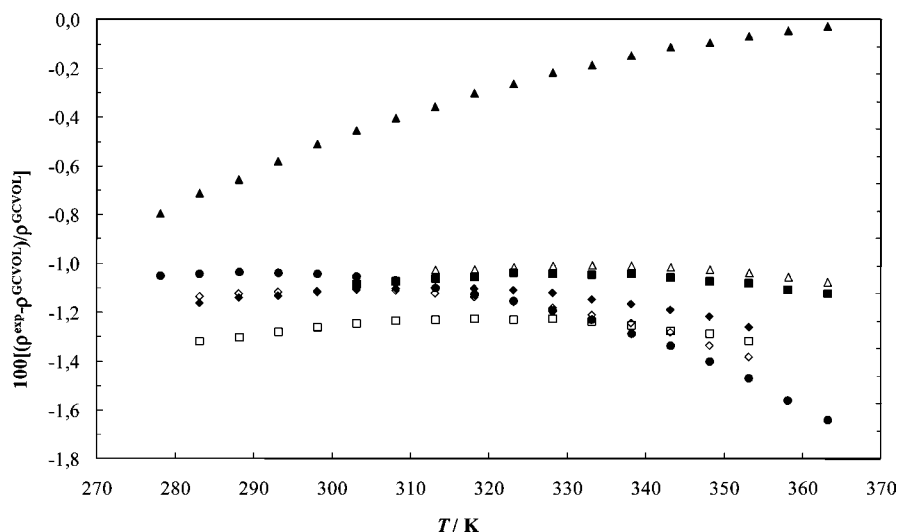
**Table 4.** Density Correlation Constants for Pure Methyl and Ethyl Esters over the Temperature Range (278.15 to 363.15) K and Corresponding 95 % Confidence Limits<sup>a</sup>

	<i>b</i>			<i>a</i>		
	$\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$	±	<i>t</i> · <i>s</i> <sub>b</sub>	$\text{kg}\cdot\text{m}^{-3}$	±	<i>t</i> · <i>s</i> <sub>A</sub>
ethyl caprylate	-0.8668	±	0.0021	1121.4	±	0.7
ethyl caprate	-0.8194	±	0.0013	1104.5	±	0.4
ethyl laurate	-0.7832	±	0.0009	1092.0	±	0.3
ethyl myristate	-0.7576	±	0.0014	1083.1	±	0.4
ethyl palmitate	-0.7334	±	0.0011	1077.9	±	0.3
ethyl stearate	-0.7209	±	0.0012	1070.5	±	0.4
ethyl oleate	-0.7209	±	0.0013	1084.5	±	0.4
methyl caprylate	-0.8832	±	0.0027	1136.1	±	0.8
methyl caprate	-0.8244	±	0.0018	1114.0	±	0.6
methyl laurate	-0.7912	±	0.0009	1101.7	±	0.3
methyl myristate	-0.7629	±	0.0017	1091.1	±	0.5
methyl palmitate	-0.7438	±	0.0015	1083.7	±	0.5
methyl stearate	-0.7209	±	0.0012	1075.5	±	0.4
methyl oleate	-0.7236	±	0.0015	1086.2	±	0.5
methyl linoleate	-0.7294	±	0.0012	1100.0	±	0.4

<sup>a</sup> *s*: standard deviation.



**Figure 3.** Relative deviations between the density of methyl esters predicted by GCVOL and this work's experimental data as a function of temperature: ●, methyl caprylate; ◇, methyl caprate; ◆, methyl laurate; ◊, methyl myristate; □, methyl palmitate; ■, methyl palmitate; △, methyl stearate; ▲, methyl oleate; and ○, methyl linoleate.



**Figure 4.** Relative deviations between the density of ethyl esters predicted by GCVOL and this work's experimental data as a function of temperature: ●, ethyl caprylate; ◇, ethyl caprate; ◆, ethyl laurate; ◊, ethyl myristate; □, ethyl palmitate; ■, ethyl palmitate; △, ethyl stearate; ▲, ethyl oleate.

and ethyl palmitate and stearate the measurements were only carried at temperatures above the melting point of these compounds.

Data shows that the density of FAMES decreases with increasing alkyl chain length and increases with the level of unsaturation, the same happening with FAEEs. Surprisingly the FAMES present a much higher value for density than the corresponding FAEEs with the same number of carbon atoms in acid side chain. This difference is higher than what would be expected from the addition of a methylene ( $\text{CH}_2$ ) group to the molecule. This results from a change in the ordering of the molecules in the liquid state akin to what can be observed in the crystal structures of methyl stearate and ethyl stearate.<sup>26</sup> It was also previously observed for other light esters that the addition of  $\text{CH}_2$  group into the alcohol moiety induces a lower molecular packing efficiency, decreasing density.<sup>27</sup>

Figures 1 and 2 present the relative deviations between this work's experimental data and density data available in the literature as a function of temperature for FAEEs and FAMES, respectively. This comparison shows a good agreement with a relative average deviation of lower than 0.10 % for FAEEs and lower than 0.15 % for FAMES, with the exception of methyl

stearate measured by Gaikward and Subrahmanyam,<sup>28</sup> that presents a deviation below 0.25 % and methyl palmitate measured by Ott et al.<sup>29</sup> that present a relative deviation of  $-0.25$  %. The density values for methyl palmitate reported in this work were repeated using samples from various suppliers with a good agreement among them and with the data previously reported in the literature by other authors for this compound.<sup>28,30–32</sup>

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

$$\rho/\text{g}\cdot\text{cm}^{-3} = b\cdot T/\text{K} + a \quad (1)$$

and the parameter values along with their confidence limits are reported in Table 4. These correlations can be used for the estimation of the densities of biodiesels using the Janarthanan et al.<sup>15</sup> approach.

The GCVOL model<sup>20</sup> was used to predict the densities of the compounds studied in this work. The results reported in Figure 3 show that the densities of FAMES can be predicted

**Table 5. Isobaric Expansivities,  $\alpha_p$ , for the Studied Fatty Acid Esters and Corresponding 95 % Confidence Limits<sup>a</sup>**

	$\alpha_p \cdot 10^3 / \text{K}^{-1}$	$\pm$	$t \cdot s_{\alpha_p} \cdot 10^3$
ethyl caprylate	1.028	$\pm$	0.009
ethyl caprate	0.971	$\pm$	0.007
ethyl laurate	0.929	$\pm$	0.005
ethyl myristate	0.900	$\pm$	0.003
ethyl palmitate	0.883	$\pm$	0.003
ethyl stearate	0.872	$\pm$	0.003
ethyl oleate	0.859	$\pm$	0.003
methyl caprylate	1.033	$\pm$	0.009
methyl caprate	0.971	$\pm$	0.008
methyl laurate	0.931	$\pm$	0.005
methyl myristate	0.905	$\pm$	0.004
methyl palmitate	0.892	$\pm$	0.003
methyl stearate	0.867	$\pm$	0.003
methyl oleate	0.845	$\pm$	0.003
methyl linoleate	0.842	$\pm$	0.004

<sup>a</sup> s: standard deviation.**Table 6. Experimental Viscosities, in mPa·s, for FAEEs**

T/K	ethyl					
	caprate	laurate	myristate	palmitate	stearate	oleate
278.15						10.9040
283.15	2.8960	4.3353	6.2601			9.2553
288.15	2.5882	3.8135	5.4303			7.9421
293.15	2.3263	3.3797	4.7492			6.8906
298.15	2.1029	3.0152	4.1880			6.0236
303.15	1.9111	2.7073	3.7207	5.0107		5.3094
308.15	1.7453	2.4455	3.3278	4.4399		4.7156
313.15	1.6000	2.2198	2.9928	3.9558	5.0823	4.2137
318.15	1.4729	2.0240	2.7056	3.5472	4.5285	3.7876
323.15	1.3599	1.8531	2.4579	3.1973	4.0574	3.4247
328.15	1.2594	1.7037	2.2423	2.8969	3.6535	3.1102
333.15	1.1695	1.5703	2.0549	2.6373	3.3073	2.8367
338.15	1.0892	1.4529	1.8891	2.4121	3.0072	2.5988
343.15	1.0171	1.3486	1.7432	2.2140	2.7439	2.3901
348.15	0.9516	1.2543	1.6139	2.0391	2.5153	2.2065
353.15	0.8929	1.1708	1.4986	1.8842	2.3132	2.0434
358.15				1.7464	2.1355	1.8978
363.15				1.6233	1.9777	1.7683

within an uncertainty of  $\pm 0.5$  % with exception of methyl linoleate due to a poor model description of the unsaturation effect on the densities. In Figure 4 the deviations for the FAEEs are reported. Because of the different effect of the introduction of a methylene group in the acid or alcohol moieties discussed above, a group contribution model cannot produce an adequate description of the densities, and an overestimation of between

(1 and 1.5) % of the experimental densities is obtained. Again, a problem associated to the unsaturation is observed, although in this case it contributes to minimize the model deviations.

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

$$\alpha_p = - \left( \frac{\partial \ln \rho}{\partial T} \right)_p \quad (2)$$

In the studied temperature range the logarithm of density exhibits a linear behavior with temperature. The value of  $\alpha_p$  will thus be a constant for the studied compounds within the temperature range investigated. The isobaric expansivities estimated from the experimental data are reported in Table 5. It is observed that  $\alpha_p$  decreases with the increment of carbons in alkyl acid side chain and also decreases with the unsaturation level for both ethyl and methyl esters. The isobaric expansivities are identical for the FAMES and FAEEs within the experimental uncertainty of the data here reported.

**Viscosity.** The experimental data of viscosity of the ethyl and methyl esters here studied are reported in Tables 6 and 7, respectively. As expected, the viscosity of all esters increases with the ester chain length and decreases with its level of unsaturation. The ethyl esters also present a higher viscosity than the corresponding methyl ester of the equivalent fatty acid.

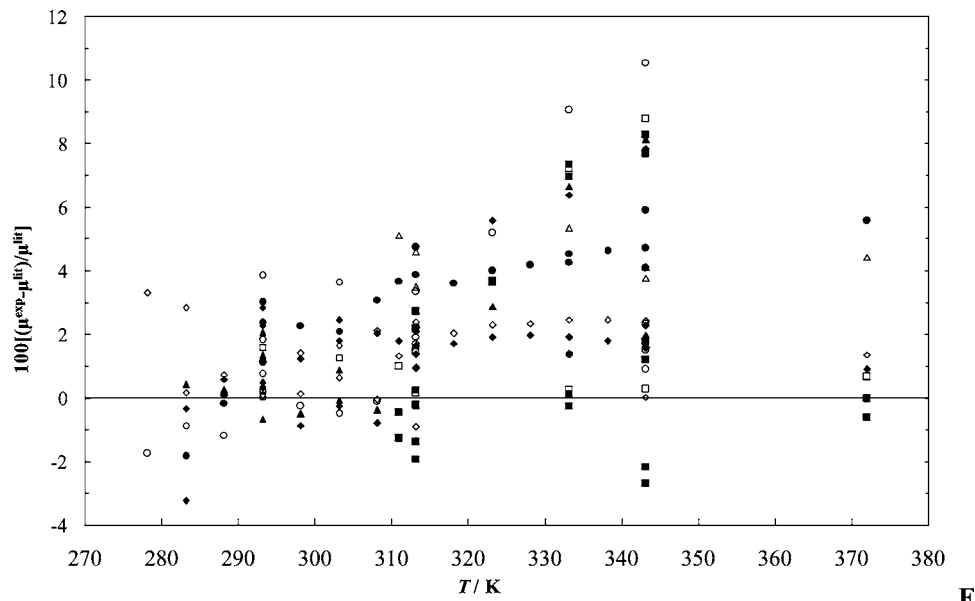
The experimental data here measured were compared with viscosity data previously reported in the literature for the same systems. The relative deviations for the FAMES and FAEEs are presented in Figures 5 and 6. For the FAMES the deviations are within  $\pm 4$  % of the literature data with the exception of the data by Meirelles et al.<sup>33</sup> at high temperatures that show large deviations when compared with both our data and data from other authors. For the FAEEs the data available are far more scarce, but in spite of being more than 50 years old it is in good agreement with the viscosities here reported with relative deviations of less than 1 %.

The experimental viscosities here measured were correlated using the VTF equation:

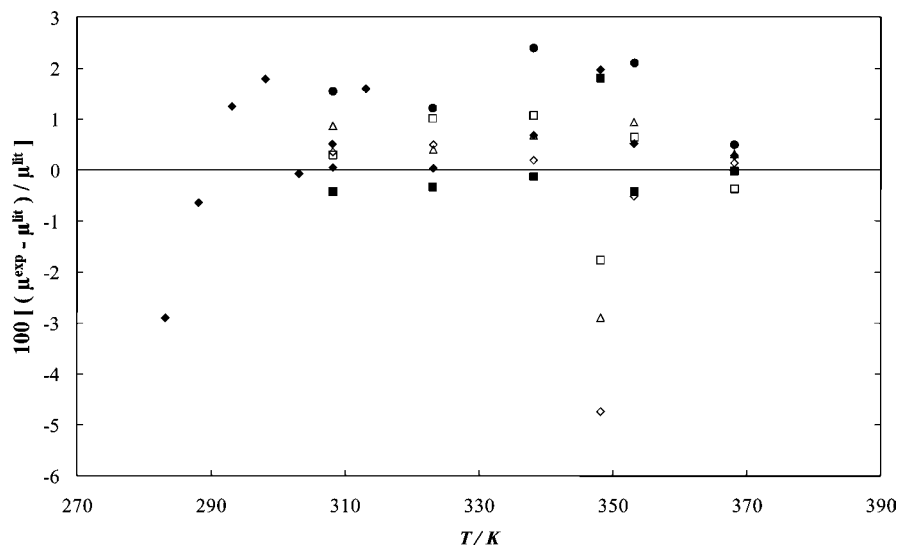
$$\mu / \text{mPa} \cdot \text{s} = \exp \left( A + \frac{B}{(T/\text{K} - T_0)} \right) \quad (3)$$

**Table 7. Experimental Viscosities, in mPa·s, for FAMES**

T/K	methyl							
	caprylate	caprate	laurate	myristate	palmitate	stearate	oleate	linoleate
278.15		2.9888						7.4664
283.15	1.7103	2.6543	4.0678				8.6987	6.4658
288.15	1.5593	2.3733	3.5771				7.4518	5.6550
293.15	1.4275	2.1360	3.1668				6.4499	4.9822
298.15	1.3127	1.9335	2.8237	3.9821			5.6336	4.4275
303.15	1.2120	1.7601	2.5356	3.5430			4.9612	3.9615
308.15	1.1233	1.6091	2.2893	3.1651	4.2122		4.4012	3.5666
313.15	1.0444	1.4773	2.0776	2.8447	3.7551	4.9862	3.9303	3.2270
318.15	0.97334	1.3613	1.8944	2.5709	3.3682	4.4348	3.5306	2.9358
323.15	0.90926	1.2589	1.7347	2.3343	3.0378	3.9645	3.1892	2.6822
328.15	0.85178	1.1675	1.5948	2.1295	2.7540	3.5684	2.8944	2.4605
333.15	0.79980	1.0864	1.4714	1.9498	2.5083	3.2252	2.6377	2.2660
338.15	0.75279	1.0133	1.3621	1.7932	2.2947	2.9293	2.4160	2.0934
343.15	0.71014	0.94770	1.2651	1.6549	2.1073	2.6724	2.2216	1.9403
348.15	0.67130	0.88860	1.1781	1.5321	1.9421	2.4477	2.0499	1.8038
353.15	0.63589	0.83420	1.1002	1.4233	1.7960	2.2504	1.8974	1.6816
358.15		0.78595			1.6659	2.0762		
363.15		0.74207			1.5499	1.9217		



**Figure 5.** Relative deviation of methyl ester dynamic viscosity vs temperature: ●, methyl caprylate; ◇, methyl caprate; ◆, methyl laurate; □, methyl myristate; ■, methyl palmitate; △, methyl stearate; ▲, methyl oleate; and ○, methyl linoleate.<sup>30,31,36,41,48</sup> Zero line is this work's experimental data.



**Figure 6.** Relative deviation of ethyl ester viscosity vs temperature: ●, ethyl caprylate; ◇, ethyl caprate; ◆, ethyl laurate; □, ethyl myristate; ■, ethyl palmitate; and △, ethyl stearate.<sup>32,41,48</sup> Zero line is this work's experimental data.

where  $A$ ,  $B$ , and  $T_0$  are fitting parameters whose values were estimated using an optimization algorithm based on the least-squares method. The parameter values along with their uncertainty and the average absolute deviations (AAD %) of the correlation are reported in Table 8. As can be seen, the VTF equation provides a very good description of the experimental data.

The measured data were also used to test two predictive viscosity models. The CM<sup>33</sup> and the MG<sup>21,22</sup> group contribution models were used to estimate the dynamic viscosity of the fatty acid esters as a function of temperature. The average deviations of viscosity between the measured data and those estimated by CM and MG are shown in Table 9. The CM method predicts the experimental data here measured with a global deviation of 4.53 % for FAMEs with maximum deviations of 9.50 %, while for FAEEs the average deviations are of 7.92 % with maximum deviations of 14.8 %. The MG method is far less accurate with average deviations of 12.0 % and 23.5 % for FAMEs and FAEEs, respectively, and maximum deviations of 25.5 % and 54.6 %. While the CM method provides a good description of

**Table 8.** Viscosity Correlation Constants for Pure Ethyl and Methyl Esters over the Temperature Range (278.15 to 363.15) K and Corresponding 95 % Confidence Limits<sup>a</sup>

	$A$	$t \cdot s_A$	$B/K$	$t \cdot s_B$	$T_0/K^{-1}$	$t \cdot s_{T_0}$	AAD (%)
ethyl caprylate	-3.58	0.055	926.963	28.2	63.493	3.8	0.078
ethyl caprate	-3.42	0.086	883.295	39.8	85.943	5.2	0.10
ethyl laurate	-3.15	0.073	818.076	30.5	105.827	3.9	0.096
ethyl myristate	-2.97	0.058	793.873	22.7	117.701	2.8	0.084
ethyl palmitate	-3.00	0.053	854.539	22.0	117.650	2.6	0.046
ethyl stearate	-3.04	0.025	920.174	10.8	115.962	1.3	0.010
ethyl oleate	-2.65	0.040	759.323	15.5	127.32	1.9	0.11
methyl caprylate	-3.48	0.054	859.303	26.1	68.948	3.7	0.046
methyl caprate	-3.32	0.070	814.674	30.7	93.317	4.2	0.13
methyl laurate	-3.09	0.054	767.388	21.4	112.267	2.8	0.075
methyl myristate	-3.12	0.036	837.282	15.2	112.358	1.9	0.019
methyl palmitate	-2.81	0.056	746.528	22.5	132.676	2.9	0.049
methyl stearate	-2.98	0.034	876.221	14.7	122.303	1.8	0.015
methyl oleate	-2.70	0.043	748.184	16.0	129.249	2.0	0.070
methyl linoleate	-2.62	0.068	733.236	26.3	119.641	3.4	0.12

<sup>a</sup>  $s$ : standard deviation. AAD =  $(1/N_p) \sum_{i=1}^N \text{ABS}[(\text{exp}_i - \text{lit}_i)/\text{lit}_i] \cdot 100$ .

the viscosities, the deviations for the FAEEs are clearly superior than for FAMEs, meaning that the inclusion of a methyl group

**Table 9. Average Deviation between the Measured Viscosity of Pure Ethyl and Methyl Esters over the Temperature Range (278.15 to 363.15) K and Those Estimated by CM and MG Models**

	CM (%)	MG (%)
ethyl caprylate	14.8	16.4
ethyl caprate	13.0	18.6
ethyl laurate	3.35	18.9
ethyl myristate	6.47	20.8
ethyl palmitate	7.32	19.8
ethyl stearate	12.4	54.6
ethyl oleate	8.68	24.8
methyl caprylate	4.67	6.27
methyl caprate	4.24	7.40
methyl laurate	3.66	7.85
methyl myristate	2.03	8.64
methyl palmitate	2.72	10.1
methyl stearate	4.88	10.3
methyl oleate	3.61	20.4
methyl linoleate	9.50	25.5

affects the viscosities differently depending on its location as also observed for the densities. Moreover, this model also provides poor estimates for the viscosities of unsaturated esters at high temperatures. This may be related with the use of Ceriani et al.<sup>33</sup> data on the estimation of the model parameters that, as discussed above, present large deviations from the data of other authors.

## Conclusions

New experimental data for the density and viscosity of pure saturated and unsaturated methyl and ethyl esters in the temperature range (273 to 363) K and at atmospheric pressure are presented. An extensive critical review of the data available for these systems was carried out to identify spurious or poor quality data among the often conflicting data previously available in the literature.

The experimental data here reported were used to test predictive models for these properties. The liquid densities were compared with GCVOL model predictions to show that it is able to describe the FAMES with deviations smaller than 1 %. However, larger deviations were found for the correlation of FAEs densities and GCVOL model predicted values, presenting a maximum deviation from the experimental data of 1.5 %.

The CM method is shown to be superior to the MG method with viscosity predictions with an average deviation of 4.53 % for FAMES and 7.92 % for FAEs.

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