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# **Evaluation of Predictive Models for the Viscosity of Biodiesel**

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Viscosity is an important biodiesel parameter, subject to specifications and with an impact on the fuel quality. A model that could predict the value of viscosity of a biodiesel based on the knowledge of its composition would be useful in the optimization of biodiesel production processes and the planning of blending of raw materials and refined products. This work aims at evaluating the predictive capability of several models previously proposed in the literature for the description of the viscosities of biodiesels and their blend with other fuels. The models evaluated here are Ceriani's, Krisnangkura's, and Yuan's models, along with a revised version of Yuan's model proposed here. The results for several biodiesel systems show that revised Yuan's model proposed provides the best description of the experimental data with an average deviation of 4.65%, as compared to 5.34% for Yuan's model, 8.07% for Ceriani's model, and 7.25% for Krisnangkura's model. The same conclusions were obtained when applying these models to predict the viscosity of blends of biodiesel with petrodiesel.

#### 1. Introduction

Biodiesel refers to a fuel derived from renewable sources that consists of a mixture of methyl or ethyl esters of longchain fatty acids, which is obtained by transesterification of vegetable oils or other feedstocks largely comprised of triacylglycerols with a simple alcohol, such as methanol or ethanol, in the presence of a catalyst. <sup>1,2</sup> It is nonflammable and non-explosive, with a flash point of 423 K compared to 337 K for petrodiesel.<sup>3</sup> As a fuel, it offers many benefits, such as ready availability, portability, renewability, domestic origin, lower sulfur and aromatic content, biodegradability, better ignition quality, inherent lubricity, higher cetane number, positive energy balance, higher density, greater safety, nontoxic character of the exhaust emissions, and cleaner burning.4-

It has expanded into the existing markets and infrastructures of gasoline and diesel and has undergone rapid development and acceptance as an alternative diesel fuel. Its worldwide production exceeded 2500 million tons in 2008.8

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It can be blended with diesel fuel to be used in conventional engines<sup>9</sup> and is able to reduce the carbon dioxide emissions by 78%. <sup>10</sup> Although most commercially available biodiesel is still between 5 and 20% biodiesel blended with petroleum diesel because of the higher prices of feedstocks for biodiesel production, the tendency of increasing production is expected to continue in the coming decades with the development and growth of nonfood feedstocks.11

One of the major problems associated with biodiesel is that its viscosity may be higher than that for diesel fuel. A fuel of high viscosity tends to form larger droplets upon injection, leading to poorer atomization during the spray and creating operation problems, such as increased carbon deposits, <sup>12</sup> and may enhance the polymerization reaction, especially for oils of a high degree of unsaturation. 13 It also leads to poor combustion and increased exhaust smoke and emissions, beyond the problems in cold weather because of the increase of viscosity with a decreasing temperature. On the other hand, a fuel with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. 14 Thus, the kinematic viscosity of biodiesel at 40 °C must be in the range of 3.5-5.0 mm<sup>2</sup>/s according to

352

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vegetable oil and biodiesel fuels. Energy Fuels 2009, 24, 664

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<sup>(7)</sup> Kerschbaum, S.; Rinke, G. Measurement of the temperature dependent viscosity of biodiesel fuels. Fuel 2004, 83, 287.

<sup>(8)</sup> Paton, J. M.; Schaschke, C. J. Viscosity measurement of biodiesel at high pressure with a falling sinker viscometer. Chem. Eng. Res. Des. 2009, 87, 1520.

<sup>(9)</sup> Benjumea, P.; Agudelo, J.; Agudelo, A. Basic properties of palm oil biodiesel-diesel blends. Fuel 2008, 87, 2069.

<sup>(10)</sup> Gerpen, J. V. Biodiesel processing and production. Fuel Process. Technol. 2005, 86, 1097.

<sup>(11)</sup> Wagner, E.; Koehle, M.; Moyle, T.; Lambert, P. Predicting temperature dependent viscosity for unaltered waste soybean oil blended with petroleum fuels. J. Am. Oil Chem. Soc. 2010, 87, 453.

<sup>(12)</sup> Shu, Q.; Yang, B.; Yang, J.; Qing, S. Predicting the viscosity of biodiesel fuels based on the mixture topological index method. Fuel 2007, 86, 1849.

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<sup>(14)</sup> Refaat, A. A. Correlation between the chemical structure of biodiesel and its physical properties. Int. J. Environ. Sci. Technol. 2009, 6,

EN-14214 specifications in Europe and 1.9-6.0 mm<sup>2</sup>/s in accordance with American Society of Testing and Materials (ASTM) D-6751 specifications in the U.S.A., 15 while the limit for diesel fuel is  $2.0-4.5 \text{ mm}^2/\text{s.}^{14}$ 

There is still a lack of viscosity data of biodiesel blends and biodiesel-diesel over the whole composition range at different operational conditions of pressure and temperature. In this regard, the use of theoretical approaches to estimate the viscosity of biodiesel systems is of great practical interest.

A number of works have presented predictive models and empirical equations with adjustable parameters for the viscosity of fatty acid esters, of which biodiesel is comprised. When the viscosity of fatty acid esters is known, it is possible to determine the viscosity of biodiesel using the mixture models suggested by Grunberg-Nissan or Hind. 12 Moreover, there is a possibility to realize the biodiesel maximum potential by simply changing the composition of fatty acid esters.

This paper aims at comparing the predictive capabilities of three models developed by Ceriani et al., 16 Krisnangkura et al., 13 and Yuan et al., 17 respectively, for the estimation of the viscosity of several biodiesels and their blends with diesel fuels. A revised version of Yuan's model is also proposed and evaluated.

## 2. Experimental Section

**2.1. Samples.** In this work, the viscosities of seven biodiesel samples were measured. Two of these samples were obtained from Portuguese biodiesel producers, namely, soy A and GP (mix of soy and rapeseed methyl esters at 50%, w/w). B1 is methyl oleate of technical grade, 70%, supplied by Sigma.

The other four biodiesel samples: sunflower, soy B, palm, and rapeseed were synthesized in our laboratory by a transesterification reaction of the respective vegetal oils. 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 distillated water until a neutral pH was achieved. Then, biodiesel was dried until the EN ISO 12937 limit for water was reached (less than 500 mg/kg of water). Some properties of produced biodiesel are presented in Table 1.

2.2. Experimental Measurements. Measurements of viscosity were performed in the temperature range of 278.15–363.15 K at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger viscometer. The temperature uncertainty is 0.02 K from 288.15 to 378.15 K. The relative uncertainty of the dynamic viscosity obtained is less than 0.5% for the standard fluid SHL120 (SH Calibration Service GMbH), in

Table 1. Properties of Biodiesel Synthesized on This Work

	sunflower	soy B	palm	rapeseed
density at 15 °C (kg/m <sup>3</sup> )	887.2	887.3	877.9	886
viscosity at 40 °C (mPa s)	3.636	3.548	3.961	3.942
ester content (%)	98.5	99.4	96.5	98.8

the range of the studied temperatures. This viscometer was previously tested for other compounds and presented a very good reproducibility. 18,19

### 3. Viscosity Models

The models described here are valid for the estimation of the viscosity of mixtures of fatty acid alkyl esters. The viscosities of biodiesel are calculated using the equation of Grunberg-Nissan, which is known to be the most suitable equation for computing the viscosity of liquid mixtures. 12,17 Given that biodiesel fuels are non-associated liquids (i.e., they have essentially a dispersive interaction between the individual components), their dynamic viscosity can be estimated using the following equation:

$$\ln \eta_{\rm m} = \sum_{i=1}^{n} x_i \ln \eta_i \tag{1}$$

where  $\eta_i$  is the dynamic viscosity of an individual compound,  $\eta_{\rm m}$  is the dynamic viscosity of the mixture, and  $x_i$  is the mole fraction.

The ester nomenclature adopted on this work is based on the fatty acid chain length. A  $C_{x,y}$  ester means the methyl ester of fatty acid with x carbons and y unsaturations.

**3.1. Ceriani's Model.** Ceriani et al. 16 proposed a model to predict the viscosity of fatty acid esters based on a group contribution method; i.e., a compound or a mixture of compounds is considered as a solution of groups, and its properties are the sum of the contributions of each group. 16 The model for the pure compounds is described in eqs 2-4

$$\ln(\eta_{i} \text{ (mPa s)}) = \sum_{k} N_{k} \left( A_{1k} + \frac{B_{1k}}{T/k} - C_{1k} \ln T/K - D_{1k}T/K \right) + \left[ M_{i} \sum_{k} N_{k} \left( A_{2k} + \frac{B_{2k}}{T/K} - C_{2k} \ln T/K - D_{2k}T/K \right) \right] + Q$$
(2)

with

$$Q = (f_0 + N_c f_1)q + (s_0 + N_{cs} s_1)$$
(3)

and

$$q = \alpha + \frac{\beta}{T/K} - \gamma \ln(T/K) - \delta T/K \tag{4}$$

where  $N_k$  is the number of groups k in the molecule i, M is the component molecular weight that multiplies the "perturbation term",  $A_{1k}$ ,  $B_{1k}$ ,  $C_{1k}$ ,  $D_{1k}$ ,  $A_{2k}$ ,  $B_{2k}$ ,  $C_{2k}$ , and  $D_{2k}$  are parameters obtained from the regression of the experimental data, k represents the groups of component i, Q is a correction term,  $f_0$ ,  $f_1$ ,  $s_0$ , and  $s_1$  are optimized constants,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are optimized parameters obtained by regression of the databank as a whole,  $N_c$  is the total number of carbon atoms in the molecule, and  $N_{cs}$  is the number of carbons of the alcohol side chain. The parameter values were found by Ceriani et al.16

**3.2. Krisnangkura's Model.** Krisnangkura et al. <sup>13</sup> fitted eq 5 to an experimental viscosity databank and provided a set of

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dependent viscosity of biodiesel fuels. Fuel 2009, 88, 1120.

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parameters for the description of the viscosity of pure fatty acid methyl esters (FAMEs).<sup>13</sup>

$$\ln(\mu) = \alpha + bz + \frac{c}{T} + \frac{zd}{T} \tag{5}$$

This equation was developed by considering the viscosity as the integral of the interaction forces of molecules. On the basis of this approach, the temperature dependency of the viscosity for short-chain methyl esters  $(C_6-C_{12})$  can be estimated by eq 6

$$\ln(\mu) = -2.915 - 0.158z + \frac{492.12}{T} + \frac{108.35z}{T}$$
 (6)

while for longer chain esters ( $C_{12:0}$ – $C_{18:0}$ ), the viscosity obeys eq 7.

$$\ln(\mu) = -2.177 - 0.202z + \frac{403.66}{T} + \frac{109.77z}{T} \tag{7}$$

The viscosity of unsaturated FAMEs is estimated by eqs 8–11.

$$\ln(\mu)_{18:1} = -5.03 + \frac{2051.5}{T} \tag{8}$$

$$\ln(\mu)_{18:2} = -4.51 + \frac{1822.5}{T} \tag{9}$$

$$\ln(\mu)_{18:3} = -4.18 + \frac{1685.5}{T} \tag{10}$$

$$\ln(\mu)_{22:1} = -5.42 + \frac{2326.2}{T} \tag{11}$$

In all of these equations,  $\mu$  is the kinematic viscosity expressed in mm<sup>2</sup>/s and T is the absolute temperature in kelvin.

Because Krisnangkura's model does not provide equations for several unsaturated FAMEs, such as  $C_{16:1}$ ,  $C_{20:0}$ ,  $C_{20:1}$ , and  $C_{22:1}$ , to predict the viscosity of biodiesel containing these compounds, it was necessary to resort to a pseudo-component approach, where the biodiesel composition was modified by adding  $C_{16:1}$  to  $C_{16:0}$ ,  $C_{20:0}$  and  $C_{20:1}$  to  $C_{18:3}$ , and  $C_{22:0}$  to  $C_{22:1}$ .

Beyond that, given that Krisnangkura's model provides only kinematic viscosities, their conversion into dynamic viscosities was performed by considering the density data for pure FAMEs reported by Pratas et al. 18,20

**3.3. Yuan's Model.** Yuan et al. <sup>17</sup> applied the Vogel Tammann–Fulcher (VTF) equation to describe the viscosity–temperature relationship of pure FAME commonly present in biodiesel fuels

$$\ln \eta \text{ (mPa s)} = A + \frac{B}{T/K - T_0}$$
 (12)

and then to estimate the viscosity of biodiesel fuels based on their FAME composition through the mixture model. In eq 12, A, B, and  $T_0$  are parameters with values determined by fitting experimental viscosity data available and are reported by Yuan et al.<sup>17</sup>

**3.4. Revised Yuan's Model.** In previous works, Pratas et al. <sup>18,20</sup> reported new and more accurate data for the viscosities of fatty acid methyl and ethyl esters. Revised

Table 2. VTF Parameters for Revised Yuan's Model

FAME	A	В	$T_0$
C <sub>8</sub>	-3.476	859.303	68.948
$C_{10}^{\circ}$	-3.316	814.674	93.317
$C_{12}$	-3.089	767.388	112.267
C <sub>14</sub>	-3.124	837.282	112.358
$C_{16}$	-2.808	746.528	132.676
$C_{16:1}$	-2.867	748.275	118.441
C <sub>18</sub>	-2.985	876.221	122.303
C <sub>18:1</sub>	-2.700	748.184	129.249
$C_{18:2}$	-2.618	733.236	119.641
$C_{18:3}$	-2.997	904.378	91.882
$C_{20}$	-3.074	967.596	115.000
$C_{20:1}^{20}$	-2.545	733.804	137.194
$C_{22}$	-2.528	768.640	145.057
$C_{22:1}^{22}$	-2.409	715.397	143.268
$C_{24}$	-2.870	951.526	127.000

Yuan's model consists of a version of Yuan's model where the parameters of the VTF model were refitted to the new data. The new parameters for FAME are presented in Table 2.

3.5. Database of Biodiesel Viscosities. Although values for the biodiesel viscosity are common in the literature, information concerning the biodiesel composition that is more detailed than the information about the oil used for the biodiesel synthesis is scarce. To apply the models studied here, detailed information about the biodiesel composition is required. The database used in this work was collected from the literature and supplemented with data for seven new biodiesels measured in our laboratory. The compositions in terms of FAMEs of all biodiesel used in this work are reported in Table 3. The biodiesels used in this study cover the most important oils used in biodiesel production, such as soy, palm, canola, rapeseed, and sunflower, but also other oils, such as cotton seed, coconut, and babassu, relevant because of their singular compositions. In terms of FAME distributions, it addresses both oils rich in short-chain and saturated fatty acids, such as coconut, rich in saturated fractions, such as palm, and rich in unsaturated compounds, such as soy and sunflower.

The database of blends analyzed in this work was collected from Knothe et al.<sup>1</sup> and Yuan et al.<sup>21</sup> The first author measured the low-temperature kinematic viscosity data of binary blends between methyl oleate, methyl linoleate, and commercial biodiesel and petrodiesel in different mixing ratios, while the last author reported the kinematic viscosities of blending of yellow grease methyl esters (YGMEs), soybean oil methyl esters (SMEA and SMEB), and genetically modified soy methyl esters (MGSMEs) with no. 2 diesel. The kinematic viscosities of the commercial petrodiesel and the no. 2 diesel are listed in Table 4.

#### 4. Results and Discussion

The viscosities of the seven biodiesel samples measured in this work as function of the temperature are reported in Table 5. The magnitude of the viscosities is in good agreement with other data previously reported in the literature for biodiesel produced from the same oils. <sup>13,17,21,22</sup>

<sup>(20)</sup> Pratas, M. J.; Freitas, S.; Oliveira, M. B.; Monteiro, S. C.; Lima, A. S.; Coutinho, J. A. P. Densities and viscosities of fatty acid methyl and ethyl esters of minority present in biodiesel. *J. Chem. Eng. Data* **2010**, in press.

<sup>(21)</sup> Yuan, W.; Hansen, A.; Zhang, Q.; Tan, Z. Temperature-dependent kinematic viscosity of selected biodiesel fuels and blends with diesel fuel. *J. Am. Oil Chem. Soc.* **2005**, *82*, 195.

<sup>(22)</sup> Duncan, A. M.; Ahosseini, A.; McHenry, R.; Depcik, C. D.; Stagg-Williams, S. M.; Scurto, A. M. High-pressure viscosity of biodiesel from soybean, canola, and coconut oils. *Energy Fuels* **2010**, *24*, 5708.

<sup>(23)</sup> Blangino, E.; Riveros, A. F.; Romano, S. D. Numerical expressions for viscosity, surface tension and density of biodiesel: Analysis and experimental validation. *Phys. Chem. Liq.* **2008**, *46*, 527.

Table 3. Composition of the Biodiesel Studied, in Mass Fraction

		Fatty	acids m	ethyl este	rs (FAM	E), 100.w										
References	Biodiesel	C8	C10	C12	C14	C16	C16:1	C18	C18:1	C18:2	C18:3	C20:0	C20:1	C22:0	C22:1	C24:0
Yuan et al. 17	Soy	0.02			0.08	10.61		4.27	24.2	51.36	7.48	0.36	0.28	0.4	0.07	0.14
	Palm					40.60		5.10	42.80	11.00	0.50					
	Canola					4.20		1.20	56.80	21.70	15.70					
	Coconut	9.20	6.40	48.70	17.00	7.70		2.20	5.40	2.20						
	$YGME^a$				1.70	19.47		14.38	54.67	7.96	0.69	0.25	0.52	0.21		
Yuan et al. 21	$SMEA^b$				0.08	10.49	0.12	4.27	24.2	51.36	7.48	0.36	0.28	0.40	0.07	0.14
	$SMEB^b$					10.81	0.11	4.54	24.96	50.66	7.27	0.37	0.32	0.42		0.12
	$GMSME^c$					3.97	0.13	2.99	82.54	4.98	3.7	0.30	0.50	0.36		0.12
	YGME*				1.27	13.44	2.03	12.38	54.67	7.96	0.69	0.25	0.52	0.21		
Blangino et al.23	Soy					9.27		3.77	22.83	57.46	6.67					
Krisnangkura et al. 13	$Palm^d$			0.40	1.06	40.05		5.83	42.21	10.46						
	Coconut <sup>d</sup>	4.80	6.20	52.70	17.50	7.40		2.40	7.60	1.40						
This work	Soy A					16.18		3.82	28.80	50.46						
	Soy B				0.07	10.78	0.07	3.95	23.02	53.66	7.03	0.38	0.23	0.80		
	$B1^e$				1.80	4.70	4.70	1.90	71.13	9.89		5.89				
	Sunflower			0.02	0.07	6.41	0.09	4.23	23.93	64.25	0.12		0.03	0.77	0.08	
	Rapeseed		0.01	0.04	0.07	5.26	0.20	1.63	62.49	20.94	6.99	0.60	1.23	1.35	0.19	
	Palm		0.03	0.25	0.57	42.52	0.13	4.03	41.99	9.81	0.09	0.36	0.15	0.09		
	$GP^f$			0.02	0.13	10.57	0.13	2.66	41.05	36.67	7.10	0.44	0.67	0.45	0.12	
Knothe et al. 1	Bg+Petroleum (B10 -					10.79		4.21	24.41	53.38	7.21					
	B90)															
Feitosa et al.24	Coconut	4.08	3.65	35.35	19.84	13.83		3.94	14.30	4.73						
Nogueira et al.25	Babassu		5.10	28.11	25.56	15.41		5.04	20.79							
-	Cotton Seed			_	0.62	24.09		2.56	15.74	56.99	_					

 $<sup>^</sup>a$ YGME = yellow grease methyl ester.  $^b$ SMEA and SMEB = soybean oil methyl esters.  $^c$ GMSME = genetically modified soy oil methyl ester.  $^d$ Mole fraction (100×).  $^c$ B1 = biodiesel composed by 71% methyl oleate.  $^f$ GP = blending of soy and rapeseed.  $^g$ B = biodiesel.

Table 4. Experimental Viscosity, in mm<sup>2</sup>/s, for Petrodiesel and No. 2

Diesei Useu ili Tilis Work							
T(K)	petrodiesel <sup>1</sup>	no. 2 diesel <sup>2</sup>					
273.15	8.58						
278.15	7.23						
283.15	6.21						
288.15	5.31						
293.15	4.55	3.94					
298.15	4.08						
303.15	3.64						
308.15	3.25						
313.15	2.90	2.56					
333.15		1.82					
353.15		1.35					
373.15		1.09					

To study the predictive ability of the various models studied in this work, the relative deviations (RDs) of the predicted viscosities for each biodiesel were estimated according to

$$RD (\%) = 100 \frac{\eta_{\text{calc}} - \eta_{\text{exp}}}{\eta_{\text{exp}}}$$
 (13)

where  $\eta$  is the dynamic viscosity in mPa s. The average relative deviation (ARD) was calculated as a somatory of the modulus of RD over N experimental data points. The overall average relative deviation (OARD) was calculated by

OARD (%) = 
$$\frac{\sum_{n} ARD}{N_{s}}$$
 (14)

where  $N_{\rm s}$  is the number of systems studied.

The ARDs for each biodiesel and biodiesel blend studied are reported in Table 6, while the RDs of the individual data points for the 22 biodiesel samples are shown in panels A-D

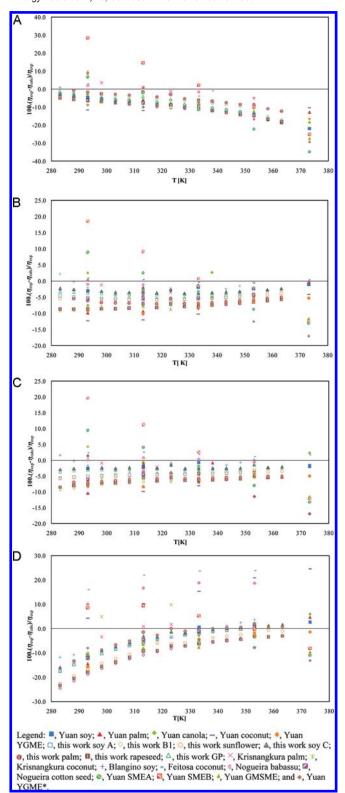
Table 5. Experimental Viscosities, in mPa s, for Biodiesels Measured in Our Laboratory

				biodiesel			
T(K)	soy A	soy B	B1	sunflower	rapeseed	palm	GP
278.15		8.812			10.33		9.315
283.15	8.016	7.555	9.359	7.940	8.763		7.958
288.15	6.916	6.535	7.998	6.844	7.518	7.814	6.856
293.15	6.021	5.711	6.894	5.965	6.517	6.748	5.971
298.15	5.286	5.033	6.000	5.243	5.701	5.883	5.244
303.15	4.679	4.478	5.271	4.658	5.034	5.152	4.655
308.15	4.170	3.995	4.663	4.143	4.467	4.550	4.137
313.15	3.740	3.548	4.154	3.636	3.942	3.961	3.630
318.15	3.372	3.249	3.722	3.356	3.594	3.632	3.349
323.15	3.057	2.922	3.354	2.988	3.217	3.214	2.981
328.15	2.784	2.697	3.037	2.776	2.955	2.968	2.769
333.15	2.546	2.473	2.767	2.542	2.699	2.702	2.534
338.15	2.338	2.276	2.529	2.337	2.475	2.471	2.329
343.15	2.154	2.102	2.321	2.156	2.278	2.269	2.148
348.15	1.992	1.948	2.138	1.996	2.104	2.091	1.988
353.15	1.848	1.794	1.976	1.831	1.933	1.911	1.823
358.15		1.686		1.726	1.811	1.794	1.718
363.15		1.575		1.612	1.688	1.669	1.604

of Figure 1. The results suggest that all of the models tend to underpredict the experimental viscosities. As one can see in panels A and D of Figure 1, the predictions of Ceriani's and Krisnangkura's models are systematically larger than the Yuan-type models (panels B and C of Figure 1) and temperature-dependent. Note, however, this dependency is opposite in the two cases: while Ceriani's deviations tend to increase with the temperature, the reverse effect is observed for Krisnangkura's model; i.e., the deviations are lower at the higher temperatures, where the viscosities have lower values. In both cases, the deviations at the temperature extremes tend to be very large (up to 25%). The temperature dependency of Ceriani's model

<sup>(24)</sup> Feitosa, F. X.; Rodrigues, M. d. L.; Veloso, C. B.; Cavalcante, C. L., Jr.; Albuquerque, M. C. G.; de Sant'Ana, H. B. Viscosities and densities of binary mixtures of coconut + colza and coconut + soybean biodiesel at various temperatures. *J. Chem. Eng. Data* **2010**, *55*, 3909.

<sup>(25)</sup> Nogueira, C. A.; Feitosa, F. X.; Fernandes, F. A. N.; Santiago, R. S.; de Sant'Ana, H. B. Densities and viscosities of binary mixtures of babassu biodiesel + cotton seed or soybean biodiesel at different temperatures. *J. Chem. Eng. Data* **2010**, *55*, 5305.



**Figure 1.** RD between experimental and predicted dynamic viscosities using (A) Ceriani's model, (B) Yuan's model, (C) revised Yuan's model, and (D) Krisnangkura's model for 22 types of pure biodiesel.

seems to be related to the poor description of the viscosity of unsaturated fatty acid esters as discussed in previous works. <sup>18,20</sup> A re-estimation of the parameters for these compounds should allow for a better description of the experimental viscosities. The temperature dependency of the fatty

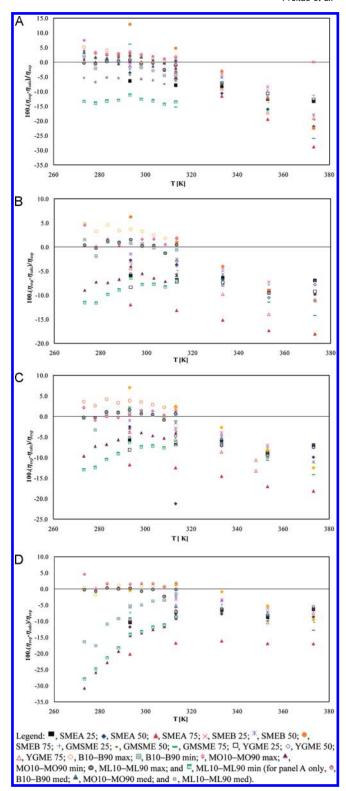


Figure 2. Deviation between experimental and predicted dynamic viscosities using (A) Ceriani's model, (B) Yuan's model, (C) revised Yuan's model, and (D) Krisnangkura's model for biodiesel blends with diesel fuel.

acid esters is better described in large temperature ranges by a VTF equation as suggested by Yuan et al.<sup>17</sup> than by the Arrhenius type adopted by Krisnangkura. The poor temperature dependency of this model is due to the equation used to describe the temperature dependency of the viscosity of the pure components of the mixture.

Table 6. Average Relative Deviations for Viscosity of Several Biodiesel Systems

References	Biodiesel	Average	relative deviation, %			
		Ceriani	Yuan	Revised Yuan	Krisnangkura	
Yuan et al. <sup>17</sup>	Soy	11.55	2.38	1.71	4.28	
	Palm	8.05	6.22	5.85	6.55	
	Canola	12.48	4.69	3.66	7.22	
	Coconut	10.93	9.10	7.14	13.61	
	YGME	8.45	7.92	6.77	7.44	
Yuan et al. <sup>21</sup>	SMEA	11.22	8.66	7.91	7.82	
	SMEB	14.59	9.12	11.18	8.12	
	GMSME	9.76	5.31	4.35	7.67	
	YGME*	8.72	8.56	6.93	7.72	
Blangino et al. <sup>23</sup>	Soy	9.01	3.25	2.39	5.73	
Krisnangkura et al. 13	Palm	1.93	2.38	1.39	2.49	
	Coconut	7.72	8.24	6.21	5.88	
This work	Soy A	8.12	5.25	4.57	7.00	
	Soy B	8.17	2.99	2.48	3.12	
	B1	5.41	7.75	6.55	10.84	
	Sunflower	9.64	5.48	5.64	7.60	
	Palm	4.77	6.21	5.59	2.61	
	Rapeseed	8.93	7.81	6.34	9.07	
	GP	6.39	3.58	2.77	3.61	
Knothe et al. <sup>1</sup>	Blending FAME (14 systems)	6.03	2.44	2.84	8.64	
Feitosa <i>et al.</i> <sup>24</sup>	Coconut	3.34	0.56	1.91	15.49	
Nogueira et al. <sup>25</sup>	Babassu	1.74	1.44	0.40	11.94	
	Cotton seed	9.06	5.35	4.42	3.53	
	Cotton seed+Babassu	7.69	3.48	2.49	6.06	
Overall average relative deviation (OARD), %		8.07	5.34	4.65	7.25	

Table 7. ARDs for Viscosities of Several Biodiesel Blends with Diesel Fuel

reference		ARD (%)						
	biodiesel + diesel	Ceriani	Yuan	revised Yuan	Krisnangkura			
	B + petroleum (B10-B90)	1.75	1.97	1.79	2.19			
Knothe et al. <sup>1</sup>	$MO^{a}$ + petroleum (MO10-MO90)	1.88	3.23	2.46	9.07			
	$ML^b$ + petroleum (ML10-ML90)	7.05	3.80	3.75	7.78			
	SMEA (25, 50, and 75%)	10.20	9.56	9.90	11.45			
21	SMEB (25, 50, and 75%)	7.18	5.46	5.29	4.02			
Yuan et al. <sup>21</sup>	GMSME (25, 50, and 75%)	9.40	6.47	5.49	8.26			
	YGME (25, 50, and 75%)	7.84	8.67	7.75	6.91			
OARD (%)	, , , , , ,	6.47	5.59	5.21	7.10			

 $<sup>^{</sup>a}$ MO = methyl oleate.  $^{b}$ ML = methyl linoleate.

Panels B and C of Figure 1 reveal that the RDs obtained with the two versions of Yuan's model are temperature-independent and the maximum deviations observed are in general lower than 10%. They are thus more robust and reliable, producing suitable ARDs in comparison to other models available in the literature. In numbers, both Ceriani's and Krisnangkura's models have global ARDs around 8%, Yuan's original model has ARDs of 5.3%, and the revised version of Yuan's model proposed here has ARDs of just 4.7% that must be close to the experimental uncertainty of many of the experimental data.

The prediction of the viscosities of mixtures of biodiesel with petroleum diesel was also studied here by using eq 1, where the biodiesel viscosity is estimated using the models studied here, and the petroleum diesel viscosity used was the experimental value (panels A—D of Figure 2). The RDs were estimated using eqs 13 and 14 and are reported in Table 7. It was found that the deviations observed for the individual mixtures and the global deviations are in good agreement with those observed for the pure biodiesel, showing that their predictive capabilities of the approach used here is not affected by the presence of hydrocarbons in the mixture. Ceriani's model shows an overall deviation of 6.47%, and Yuan's and Krisnangkura's models presented 5.59 and 7.10%, respectively,

while revised Yuan's model had the lowest global deviation of just 5.21%, suggesting that the Yuan-type models are also suitable to predict the viscosity data of biodiesel blends with petrodiesel.

### 5. Conclusions

Viscosity data for seven well-characterized biodiesel samples in terms of their FAME composition were measured and reported. Along with a database compiled from the literature, they were used to evaluate four models able to predict biodiesel viscosities based on information of their FAME compositions. It is shown that, although all of the models studied are able to predict the viscosities of both pure biodiesels and blends of biodiesel with petrodiesel with less than 10% deviation in general, the models of Krisnangkura et al. 13 and Ceriani et al. 16 present deviations that are temperature-dependent and that, at the extremes of the temperature range studied, can have deviations as high as 25%. The deviations presented by the Yuan-type models are more robust over temperature and also lower than those obtained with the two previous models. In particular, the revised version of Yuan's model proposed here on the basis of new and more accurate data for the FAMEs produces predictions with uncertainties that are close to the experimental uncertainties of the experimental data and can thus be an interesting tool to the design of biofuels or biofuel blends with viscosities that comply with legal specifications.

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