

Application of Wada's Group Contribution Method to the Prediction of the Speed of Sound of Biodiesel

Samuel V. D. Freitas,[†] Deivisson L. Cunha,[‡] Rodrigo A. Reis,[‡] Álvaro S. Lima,[§] Jean-Luc Daridon,^{||} João A. P. Coutinho,[†] and Márcio L. L. Paredes^{*:‡}

[†]Center for Research in Ceramics and Composite Materials (CICECO), Department of Chemistry, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

[‡]Programa de Pós, Graduação em Engenharia Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier, 524, Maracanã 20550-013, Rio de Janeiro, Rio de Janeiro (RJ), Brazil

[§]Universidade Tiradentes, Avenida Murilo Dantas, 300, Farolândia 49032-490, Aracaju, Sergipe (SE), Brazil

^{||}Laboratoire des Fluides Complexes et leurs Réservoirs, Faculté des Sciences et Techniques, UMR 5150, Université de Pau, BP 1155, 64013 Pau Cedex, France

ABSTRACT: Biofuels are an important alternative to environmental sustainability, and biodiesel has a detached contribution to this scenario. The increasing use of biodiesel requires the knowledge of several thermophysical properties of this biofuel. This work addresses the measurements of the speed of sound and density at atmospheric pressure of five fatty acid methyl esters (methyl caprylate, methyl caprate, methyl palmitate, methyl stearate, and methyl linoleate). These data are used to test Wada's group contribution method recently proposed by us and its ability to predict the speed of sound of biodiesel fuels and to expand the application of this model to the prediction of the speed of sound of biodiesel fuels. The overall average relative deviations (OARD) obtained were 0.12% for the methyl esters and 0.29% for biodiesels. An extension of this model to high pressures is also proposed and tested with success, presenting an OARD of 1.0% for six biodiesel fuels.

■ INTRODUCTION

Since the 1970s, with the first oil crisis, biofuels began to excel in science and technology, first with the ethanol produced from sugarcane and then with other biofuels using different sources of biomass. Biofuels are defined as fuels produced from biological (biomass) and renewable sources, such as sugarcane and corn, to produce ethanol and other alcohols, such as castor, palm, corn, rapeseed, soybean, and other oils, as raw material for biodiesel, and also agro-industrial residues that are being used to produce bio-oil. Biofuels have emerged as an alternative to fossil fuels, and their use contributes to the reduction of global warming, minimizing the generation of greenhouse gases, and to the energetic independence of the producing countries.^{1,2}

Among the most prominent biofuels is biodiesel, which a mixture of monoalkyl esters of vegetable oils or animal fats, obtained by transesterification of an oil or fat with an alcohol.³ Using methanol, fatty acid methyl esters (FAMEs) are obtained, while fatty acid ethyl esters (FAEEs) are readily obtained with ethanol. Biodiesel seems very interesting for several reasons: it is highly biodegradable and has minimal toxicity; it can replace diesel fuel in many different applications, such as boilers and internal combustion engines without modifications; a small decrease in performance is reported, with almost zero emissions of sulfates, aromatic compounds, and other chemical substances that are destructive to the environment; and it produces no net carbon dioxide.⁴ However, it should not be used alone as fuel (100% FAME, often designated as B100) because of its high viscosity (usually in the range of 28–40 mm² s⁻¹) that leads to operational

problems in a diesel engine, including the formation of deposits and injector coking because of poorer atomization upon injection into the combustion chamber.³ Therefore, the blending of conventional fuel with others from nonconventional sources will lead to a continuous change in the chemical nature of the fuels. For these reasons, this work is concerned with the continuous change of physical and chemical properties of diesel fuel that should persist increasingly during the next few decades.

The physical and chemical fuel properties of biodiesel basically depend upon the type of feedstock and their fatty acid composition.⁴ The major components of biodiesel fuels are straight-chain fatty acids, with the most common ones containing 16 and 18 carbon atoms. Knothe et al.³ and latter Atabani et al.⁴ reported some results showing how the composition of a fuel influences its properties and the consequences in diesel engine performance.

The fluid properties of the speed of sound and isentropic bulk modulus have important impacts on the injection process. The isentropic bulk modulus is a measure of the compressibility of a fluid under pressure; it affects the amount of pressure rise that will occur from the fuel pump pulse. The speed of sound in the fuel affects the time required for the pressure rise to proceed through the fuel line and reach the injector. In comparison to petroleum fuel, biodiesel is less compressible and has a higher speed of sound. Injection timing advance can

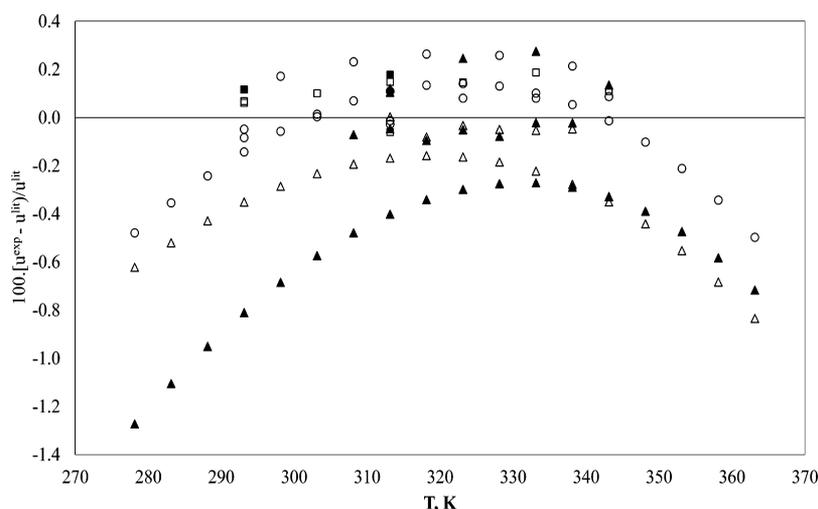
Received: November 6, 2012

Revised: January 30, 2013

Published: February 4, 2013

Table 1. Experimental Densities and Speed of Sounds for Esters Measured at Atmospheric Pressure and Temperatures from 288.15 to 293.15 K

T (K)	methyl caprylate		methyl caprate		methyl palmitate		methyl stearate		methyl linoleate	
	ρ (kg/m ³)	u (m/s)								
288.15	881.258	1312.31	876.476	1344.23						
293.15	876.925	1293.2	872.382	1325.5					887.589	1418.11
298.15	872.575	1274.01	868.279	1306.68					883.942	1400.39
303.15	868.219	1254.99	864.175	1287.99					880.294	1382.74
308.15	863.852	1236.03	860.065	1269.46	854.327	1337.04			876.65	1365.15
313.15	859.479	1217.25	855.95	1251.04	850.621	1319.38	849.804	1333.43	873.005	1347.72
318.15	855.093	1198.54	851.831	1232.81	846.92	1301.76	846.176	1315.93	869.363	1330.49
323.15	850.696	1179.99	847.706	1214.66	843.224	1284.34	842.551	1298.56	865.723	1313.35
328.15	846.285	1161.53	843.573	1196.69	839.526	1267	838.934	1281.36	862.082	1296.33
333.15	841.862	1143.22	839.43	1178.8	835.829	1249.72	835.319	1264.32	858.438	1279.42
338.15	837.426	1124.98	835.284	1161.06	832.132	1232.72	831.704	1247.41	854.794	1262.69
343.15	832.97	1106.88	831.116	1143.35	828.444	1215.83	828.094	1230.65	851.137	1245.98

**Figure 1.** RDs between experimental and literature data of the speed of sound for esters: (■) methyl caprylate,⁷ (□) methyl caprate,^{7,13} (▲) methyl palmitate,^{7,9,10,13} (△) methyl stearate,^{7,9,10,13} and (○) methyl linoleate.^{7,9,10,13}

lead to earlier start of combustion, which raises peak in-cylinder temperature, thereby increasing thermal NO_x formation.⁵ The bulk modulus and speed of sound values are thus indispensable parameters for system modeling and experimental injection rate determination.⁶

Despite the importance aforementioned, the literature on the speed of sound data for FAMES and biodiesels is still very scant. Most data are available only at atmospheric pressure and in a narrow range of temperatures, and few studies have focused on the modeling of this property. The oldest experimental data of the speed of sound include those reported by Gouw et al.⁷ at 20 and 40 °C for methyl esters and by Tat et al.⁸ for biodiesel fuels at pressures from atmospheric to 35 MPa. Later, these authors also proposed correlations to estimate the speeds of sound of alkyl monoesters at higher temperatures and pressures.⁹ Ott et al.¹⁰ provided the speeds of sound for five methyl esters as a function of the temperature at 83 kPa. Recently, some experimental data were reported by Huber et al.¹¹ for two commercial biodiesels and by Kumar et al.¹² for *Jatropha curcas* biodiesel at atmospheric pressure. Daridon et al.¹³ provided experimental data for several pure fatty acid esters at atmospheric pressure and temperatures from 283.15 to 373.15 K and published¹⁴ high-pressure speeds of sound for methyl caprate and ethyl caprate. In a previous work,¹⁵ we also

reported the experimental data for 3 methyl esters and 10 biodiesel fuels and evaluated some predictive models for their description.

This work aims at completing this study of the speed of sound for FAMES with novel data for C8:0, C10:0, C16:0, C18:0, and C18:2 esters that also assess the group contribution model for Wada's constant previously proposed.¹³ An extension of this model to the prediction of the speed of sound of biodiesel fuels and to high pressure is proposed here.

■ EXPERIMENTAL SECTION

Five methyl esters present in biodiesel fuels were studied here: methyl caprylate, MeC8:0 (with 99% purity from Sigma-Aldrich); methyl caprate, MeC10:0 (with 99% purity from Fluka); methyl palmitate, MeC16:0 (with 99% purity from Sigma-Aldrich); methyl stearate, MeC18:0 (with 99% purity from Fluka); and methyl linoleate, MeC18:2 (with 99% purity from Sigma-Aldrich).

The density and speed of sound were obtained using an automatic digital densimeter (Anton Paar DSA 5000). DSA 5000 simultaneously determines two physically independent properties within one sample. The instrument is equipped with a density cell and a sound velocity cell combining the known oscillating U-tube method with a highly accurate measurement of the speed of sound.¹⁶ The density and speed of sound meter was calibrated against ultrapure water and air at atmospheric pressure. The calibration was accepted if the measurements were estimated to be within $\pm 2 \times 10^{-3}$ kg m⁻³ and ± 0.02 m s⁻¹

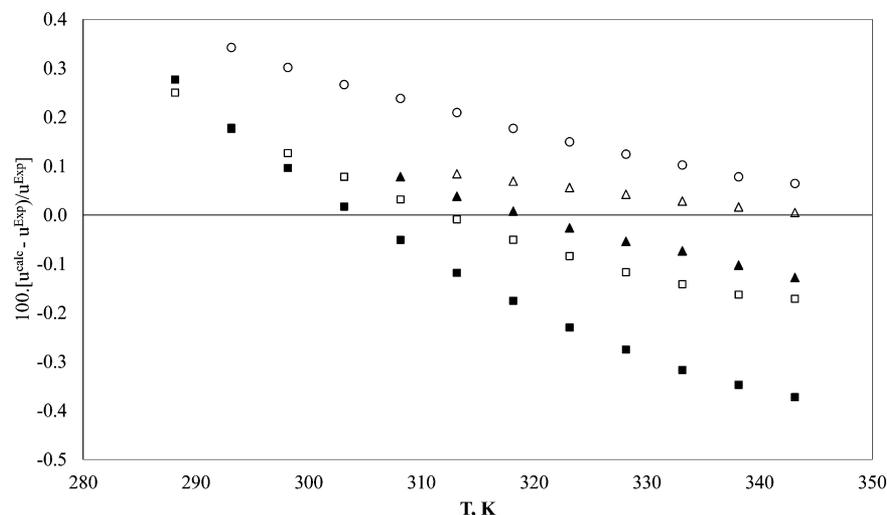


Figure 2. RDs between experimental and predicted data of the speed of sound for methyl esters using Wada's model: (■) methyl caprylate, (□) methyl caprate, (▲) methyl palmitate, (△) methyl stearate, and (○) methyl linoleate.

of the reference values, respectively. The measurements were obtained in duplicates, and the experimental uncertainty was obtained as described elsewhere.¹⁶ The estimated standard uncertainties in density and speed of sound measurements are $2 \times 10^{-2} \text{ kg m}^{-3}$ and 0.1 m s^{-1} , respectively. The standard uncertainty in the temperature is 0.01 K.

RESULTS AND DISCUSSION

In this work, a series of measurements of density and speed of sound at atmospheric pressure and temperatures from 288.15 to 343.15 K was carried out with 5 K steps for four saturated FAMEs (methyl caprylate, methyl caprate, methyl palmitate, and methyl stearate) and one unsaturated FAME (methyl linoleate), as presented in Table 1. The densities for these esters are in good agreement with those previously reported by Pratas et al.¹⁷ The experimental speeds of sound were also compared here to those previously reported in the literature.^{7,9,10,13} The results show a good agreement between the experimental and literature data, presenting only a maximum deviation of 0.5%, as seen in Figure 1, except for methyl palmitate reported by Tat and van Gerpen with a sample of questionable purity.⁹ Unlike the densities, the speed of sound increases with the carbon chain length and then with the level of unsaturation because the density shows that the two properties are uncorrelated. At the same conditions, the speed of sound for methyl linoleate is thus higher than that of methyl palmitate and methyl stearate, as seen in Table 1. These results in biodiesels with a high level of saturated short-chain compounds, such as those based on palm¹⁵ or coconut oil, present lower speeds of sound than those containing high levels of unsaturated compounds, such as biodiesel based on sunflower oil.¹⁵

The experimental speeds of sound for the esters measured on this work were used to assess Wada's group contribution model previously proposed by us¹³ to predict the speed of sound of methyl and ethyl esters. This model based on the limited data available for alkanes and fatty acid esters predicts the speed of sound of pure compounds based on Wada's constant (also called molecular compressibility, K_m) described by eqs 1 and 2

$$\text{Wada} = K_m = \frac{k_s^{-1/7}}{\rho} M_w \quad (1)$$

$$k_s = \frac{1}{u^2 \rho} \quad (2)$$

where ρ (kg m^{-3}) is the density, M_w (g mol^{-1}) is the molar mass, u (m s^{-1}) is the speed of sound, and k_s (GPa^{-1}) is the isentropic compressibility.

Wada's constant or molecular compressibility, K_m , is estimated by an additive group contribution method according to eq 3

$$K_m(T) = \sum_{j=1}^{n_G} N_j K_{m,j} (1 - \chi(T - T_0)) \quad (3)$$

where $K_{m,j}$ is the contribution of the group type j to K_m , which occurs N_j times in the given molecule, χ is a constant parameter used to take into account the influence of the temperature, and T (K) is the absolute temperature. The parameter values were previously reported by Daridon et al.¹³ The speed of sound is estimated according to eq 4.

$$u = \rho^3 \left(\frac{K_m}{M_w} \right)^{7/2} \quad (4)$$

To evaluate the predictive ability of the model, the relative deviations (RDs) between predicted and experimental values of the speed of sound and the corresponding overall value (OARD) were calculated using eqs 5 and 6, 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.

$$\text{RD} (\%) = \frac{u_{\text{calc}}^i - u_{\text{exp}}^i}{u_{\text{exp}}^i} \times 100 \quad (5)$$

$$\text{OARD} (\%) = \frac{\sum_n \text{ARD}}{N_s} \quad (6)$$

The adequacy of Wada's model for predicting the speeds of sound of the fatty acid esters studied on this work is reported in Figure 2. The results show that the speed of sound of the methyl esters is well-described by this model, with temperature-dependent deviations that change only slightly, within $\pm 0.3\%$,

in the range of temperatures studied. Individual deviations for each ester are reported in Table 2, with maximum values for methyl caprylate and methyl linoleate that are lower than 0.2% and an OARD of just 0.12%.

Table 2. ARDs of the Speed of Sound for Esters Using Wada's Model

esters	ARD (%)
methyl caprylate	0.20
methyl caprate	0.10
methyl palmitate	0.064
methyl stearate	0.043
methyl linoleate	0.19
OARD (%)	0.12

In a previous work,¹⁵ we have shown that the molar additivity rule constituted the best approach for the description of experimental speeds of sound for biodiesel fuels, providing that the composition of the biodiesel and the data for the pure components were available. This same approach is used here to predict the speed of sound of the biodiesel fuels using Wada's group contribution model. The deviations between the predicted and experimental data are shown in Figure 3, where it is shown that the model provides a good description of the experimental data. The ARDs for the individual fuels are presented in Table 3, where it is shown that the model can describe 19 fuels at atmospheric pressure with an OARD of 0.29%. Unlike the pure esters, for the biodiesels studied here, the deviations seem to be stable within the range of temperatures studied and present deviations within $\pm 0.5\%$. The largest deviations, with a maximum of 1.5%, are only observed for an oxidized soy biodiesel, as shown in Figure 3. In comparison to the models described in our previous work,¹⁵ the accuracy of Wada's model seems to be better than that of Auerbach's relation and closer to the ideal mixture mixing rules.

An extension of Wada's model was also developed to predict the speed of sound of biodiesel fuels at high pressures. For this purpose, a linear pressure dependency, described by eq 7, was

Table 3. ARDs of Wada's Group Contribution Model for the Speed of Sound for Biodiesel Fuels

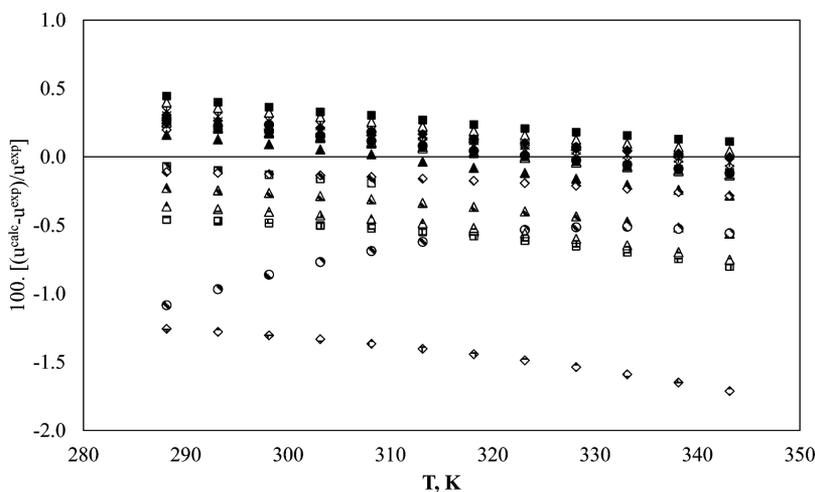
biodiesel ^a	ARD (%)	
	atmospheric pressure	high pressure
BD-A ¹¹	0.11	
BD-B ¹¹	0.10	
BD-JC ¹²	0.13	
methyl soy ester ⁹	0.11	0.58
methyl canola ⁹	0.18	0.74
methyl tallow ⁹	0.37	1.1
methyl lard ⁹	0.68	0.99
methyl oxidized soy ⁹	0.59	1.7
methyl hydrogenated soy ⁹	1.4	1.0
S (soybean) ¹⁸	0.52	
soy A (soybean) ¹⁸	0.26	
R (rapeseed) ¹⁸	0.15	
P (palm) ¹⁸	0.11	
Sf (sunflower) ¹⁸	0.13	
SP (soybean + sunflower) ¹⁸	0.21	
SR (soybean + rapeseed) ¹⁸	0.13	
PR (palm + rapeseed) ¹⁸	0.15	
SRP (soybean + rapeseed + palm) ¹⁸	0.11	
GP (soybean + rapeseed) ¹⁸	0.11	
OARD (%)	0.29	1.0

^aBD-A and BD-B are two types of commercial B100 studied by Huber et al.¹¹ BD-JC is the *Jatropha curcas* biodiesel reported by Kumar et al.¹² Methyl soy ester, canola, tallow, lard, oxidized soy, and hydrogenated soy are reported by Tat et al.⁹ Biodiesel S, soy A, etc. are reported in our previous work.¹⁸

fitted to the high-pressure speed of sound of methyl caprate recently reported by Ndiaye et al.¹⁴

$$u_{BD}(P) = u_{BD}(P_0) + aP \quad (7)$$

In this equation, $u_{BD}(P_0)$ (m/s) is the speed of sound of biodiesel at atmospheric pressure, estimated by Wada's group contribution model, a is the fitting parameter, and P (MPa) is the pressure. The best fitting was obtained for a value of a of



(□) Soy A,¹⁸ (■) S,¹⁸ (◆) Sf,¹⁸ (◇) R,¹⁸ (▲) P,¹⁸ (△) GP,¹⁸ (×) SR,¹⁸ (✱) SP,¹⁸ (−) RP,¹⁸ (●) SRP,¹⁸ (○) BD-A,¹¹ (+) BD-B,¹¹ (◻) BD-JC,¹² (◊) methyl soy ester,⁹ (▲) methyl canola,⁹ (⊙) tallow,⁹ (◼) lard,⁹ (◊) oxidized soy,⁹ and (△) hydrogenated soy.⁹

Figure 3. RDs between experimental and predicted data of the speed of sound for biodiesel fuels using Wada's model.

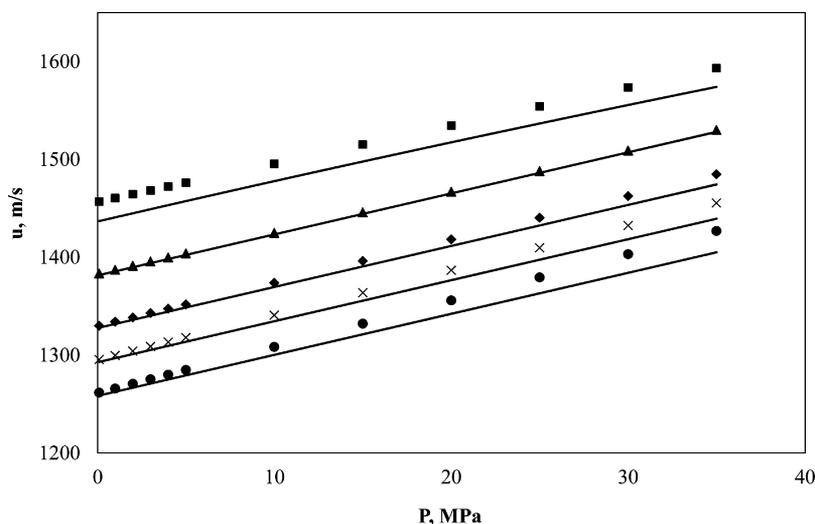


Figure 4. Comparison of experimental data to predicted data of the speed of sound for methyl soy ester⁹ at high pressures and different temperatures: (■) 283.15 K, (▲) 303.15 K, (◆) 318.15 K, (×) 328.15 K, and (●) 338.15 K. The full line is the predicted data.

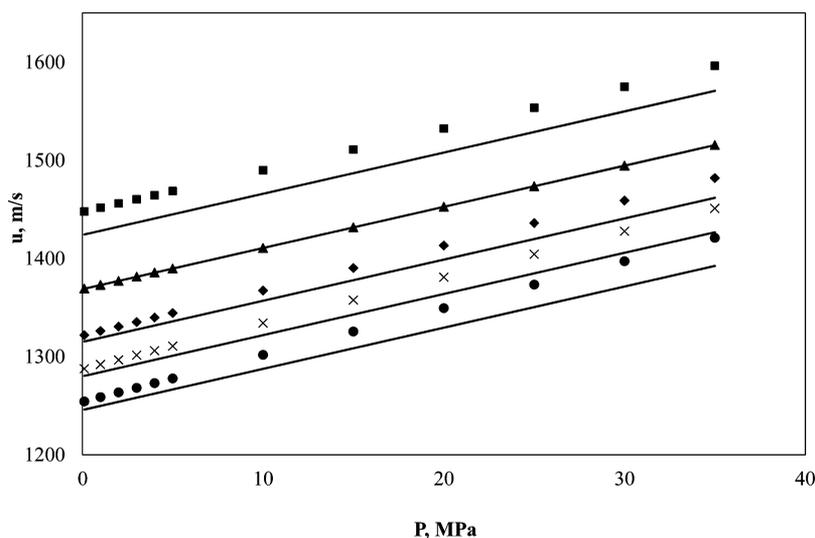


Figure 5. Comparison of experimental data to predicted data of the speed of sound for methyl hydrogenated soy ester⁹ at high pressures and different temperatures: (■) 283.15 K, (▲) 303.15 K, (◆) 318.15 K, (×) 328.15 K, and (●) 338.15 K. The full line is the predicted data.

$4.19 \text{ m s}^{-1} \text{ MPa}^{-1}$. The model proposed here was tested against the speed of sound for six biodiesel fuels reported by Tat and van Gerpen⁸ for pressures up to 35 MPa with an OARD of 1.0%. These results are comparable to those reported in our previous work.¹⁵ Deviations for the individual fuels are presented at Table 3, while the predictive profile is presented in Figures 4 and 5 for methyl soy ester and methyl hydrogenated soy, respectively. As shown in the figures, the pressure dependency of the speed of sound is correctly described and is approximately linear in the pressure range considered. The data by Ndiaye et al.¹⁴ suggest that the pressure dependency of the speed of sound for higher pressures may no longer be linear, and thus, eq 7 should not be used to extrapolate the speed of sound to higher pressures. Unfortunately, no data for biodiesel fuels are currently available for higher pressures, preventing the development of a more comprehensive approach. Further studies of the speed of sound of biodiesel for a broader pressure range will be the object of a future work.

CONCLUSION

To complete the study on the speed of sound of FAMES, experimental data of density and speed of sound for esters were measured here at atmospheric pressure and temperatures from 288.15 to 343.15 K. Wada's group contribution model previously proposed by us was evaluated against the new data reported here, showing an OARD of 0.12%. The model was further extended to predict the speed of sound of biodiesel fuels with an OARD of 0.29%. An extension of Wada's group contribution model was applied to describe the high-pressure dependency of the speed of sound for biodiesel fuels, presenting a global deviation of only 1.0%. On the basis of these results, Wada's group contribution model seems to be a powerful and accurate model to predict the acoustic properties of biodiesel fuels whenever its composition in FAMES is known.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +55-23340563. Fax: +55-23340159. E-mail: paredes@uerj.br.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Samuel V. D. Freitas acknowledges funding from Fundação para a Ciência e a Tecnologia through his Ph.D. Grant SFRH/BD/51476/2011, Fundação Oriente, and the University of Aveiro. CICECO is being funded by Fundação para a Ciência e a Tecnologia through Pest-C/CTM/LA0011/2011.

REFERENCES

- (1) Naik, S. N.; Goud, V. V.; Rout, P. K.; Dalai, A. K. *Renewable Sustainable Energy Rev.* **2010**, *14*, 578–597.
- (2) Mohan, D.; Pittman, C. U.; Steele, P. H. *Energy Fuels* **2006**, *20*, 848–889.
- (3) Knothe, G. *Prog. Energy Combust. Sci.* **2010**, *36*, 364–373.
- (4) Atabani, A. E.; Silitonga, A. S.; Badruddin, I. A.; Mahlia, T. M. I.; Masjuki, H. H.; Mekhilef, S. *Renewable Sustainable Energy Rev.* **2012**, *16*, 2070–2093.
- (5) Hoekman, S. K.; Robbins, C. *Fuel Process. Technol.* **2012**, *96*, 237–249.
- (6) Payri, R.; Salvador, F. J.; Gimeno, J.; Bracho, G. *Fuel* **2011**, *90*, 1172–1180.
- (7) Gouw, T.; Vlugter, J. *J. Am. Oil Chem. Soc.* **1964**, *41*, 524–526.
- (8) Tat, M.; Van Gerpen, J.; Soylu, S.; Canakci, M.; Monyem, A.; Wormley, S. *J. Am. Oil Chem. Soc.* **2000**, *77*, 285–289.
- (9) Tat, M.; Van Gerpen, J. *J. Am. Oil Chem. Soc.* **2003**, *80*, 1249–1256.
- (10) Ott, L. S.; Huber, M. L.; Bruno, T. J. *J. Chem. Eng. Data* **2008**, *53*, 2412–2416.
- (11) Huber, M. L.; Lemmon, E. W.; Kazakov, A.; Ott, L. S.; Bruno, T. *J. Energy Fuels* **2009**, *23*, 3790–3797.
- (12) Kumar, S.; Yadav, J. S.; Sharma, V. K.; Lim, W.; Cho, J. H.; Kim, J.; Moon, I. *J. Chem. Eng. Data* **2011**, *56*, 497–501.
- (13) Daridon, J. L.; Coutinho, J. A. P.; Ndiaye, E. H. I.; Paredes, M. L. *Fuel* **2013**, *105*, 466–470.
- (14) Ndiaye, E. H. I.; Nasri, D.; Daridon, J. L. *J. Chem. Eng. Data* **2012**, *57*, 2667–2676.
- (15) Freitas, S. V. D.; Paredes, M. L. L.; Daridon, J. L.; Lima, A. S.; Coutinho, J. A. P. *Fuel* **2013**, *103*, 1018–1022.
- (16) Paredes, M. L. L.; Reis, R. A.; Silva, A. A.; Santos, R. N. G.; Santos, G. J.; Ribeiro, M. H. A.; Ximango, P. B. *J. Chem. Thermodyn.* **2012**, *45*, 35–42.
- (17) Pratas, M. J.; Freitas, S.; Oliveira, M. B.; Monteiro, S. C.; Lima, A. S.; Coutinho, J. A. P. *J. Chem. Eng. Data* **2010**, *55*, 3983–3990.
- (18) Pratas, M. J.; Freitas, S. V. D.; Oliveira, M. B.; Monteiro, S. C.; Lima, A. S.; Coutinho, J. A. P. *Energy Fuels* **2011**, *25*, 2333–2340.