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Novel data and a group contribution method for the prediction of the speed of sound and isentropic compressibility of pure fatty acids methyl and ethyl esters

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HIGHLIGHTS

- ▶ Speed of sound measurements in FAME and FAAE are reported.
- ▶ Data are new.
- ▶ A group contribution was proposed to predict speed of sound and compressibility of pure fatty acid methyl and ethyl esters.
- ▶ The accuracy of the prediction method in very good (in the range of the experimental uncertainty).
- ▶ The group contribution can be used to determine the acoustic properties of all FAME and FAAE present in biodiesels.

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ABSTRACT

Speed of sound of fatty acid esters are relevant for the formulation of biodiesel fuels but data on this property are scarce on literature. In this work speeds of sound of three saturated fatty acid methyl esters (caprate, myristate, palmitate) two unsaturated (oleate, linoleate) as well as two fatty acid ethyl esters (caprate, myristate) were measured using a pulse echo technique operating at 3 MHz. The measurements were carried out at atmospheric pressure in the temperature range 283.15–373.15 K. Additional density measurements were performed in order to estimate the isentropic compressibility and the molecular compressibility. From these data, a group contribution method was developed to predict the molecular compressibility and speed of sound of both methyl and ethyl esters with an uncertainty of circa 0.1%.

1. Introduction

Biodiesels appear as promising products as substitutes for fossil fuels in the short run as they are renewable, biodegradable and they come from agricultural resources available in most countries [1]. Moreover, blending biodiesels with petroleum diesel may improve engine performance and significantly reduce most exhaust emissions when diesels engines are specially designed and optimized for working with such alternative fuels [2]. In compression–ignition engine, one of the major parameters that influence engine efficiency is the injection process. Its purpose is to introduce the appropriate quantity of fuel into the engine cylinder and to form a spray with small droplet size in order to optimize the combustion and consequently reduce the fuel consumption and minimize emissions. This process is strongly affected by the

physical properties of fuel. This is particularly true for the injection timing [3] that is related to the bulk modulus and compressibility and thus to the speed of sound. Therefore, the adaptation of injection systems to biodiesels requires an accurate knowledge of the sound speed of these fluids.

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Biodiesels are produced from various vegetable oils (palm, rape-seed, soybean, etc) or animal fats by a transesterification process with a short chain alcohol such as methanol or ethanol. Thus, they consist in mixtures of methyl or ethyl esters of the fatty acids present on the parent oil. Fats and oils of natural origin usually consist in glycerol esters of straight chain aliphatic carboxylic acids with an even number of carbon atoms ranging between 10 and 24 [4]. The chain may differ in length as well as in its degree of unsaturation. Consequently, biodiesels coming from varied sources contain esters with various compositions. This difference affects the physical properties of biodiesels [5] and therefore the engine efficiency. Optimization of biodiesel formulation and fuel injection system requires the knowledge of biodiesel properties with accuracy [6].

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These properties can be evaluated from ester composition by using mixing rules when properties of pure esters components are known. Although many measurements were performed and predictive methodologies were proposed to determine properties such as density [7–9], viscosity [8–10], surface tension [11] of fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs), no correlation were proposed to calculate the speed of sound and the compressibility of FAME and FAEE.

With the aim in mind to develop a reliable correlation for speed of sound and compressibility of both FAME and FAEE, speed of sound were measured as a function of temperature for a number of selected fatty acid esters. The speed of sound data, combined with complementary density measurements were used to estimate the isentropic compressibility and the molecular compressibility also known as Wada's constant [12]. The esters were selected in order to divide them in three groups. The first contains saturated methyl esters. The second is composed of methyl esters of C18 acids with various degrees of saturation. The last is made up of saturated ethyl esters. Thanks to this selection and previous measurements performed on linear alkanes a group contribution has been proposed to predict the properties FAME FAEE whatever the chain length and the degree of unsaturation.

2. Experimental

Speed of sound was measured using a variable path pulse echo technique operating at 3 MHz. The apparatus, which has been described previously in detail [13], is essentially made up of a stainless steel hollow cylindrical cell closed at the bottom by a piezoelectric transducer and filled with the liquid to study. A piston, acting as a reflector of the acoustic waves, can move into the cylinder thanks to a worm drive. The displacement of the piston is measured by a mechanical comparator with an absolute uncertainty of 5 µm. The cell is positioned vertically into a thermoregulated bath with a stability of 0.01 K. The temperature of the liquid is measured by using PT 100 probe inserted directly into the sample through an orifice machined into the cell and fitted with a seal. This probe is coupled to a standard thermometer (AOIP brand). The sensor unit can determine temperature to within an uncertainty estimated at 0.1 K. Measurements were performed by direct chronometry of the time delay associated with the variation in acoustic trajectory following displacement of the reflecting piston over a distance of the order of 20 mm selected so that total variation in the propagation distance is 40 mm. With these operational conditions the speed of sound is measured with an error less than 0.1%. This uncertainty was confirmed by tests performed with

The complementary density measurements were carried out by means of an Anton Parr densimeter (DMA) The principle of this apparatus is to measure the period of oscillation of a U-shaped tube and to deduce the density which is related to the square of the period by a linear law whose the parameters are calibrated by the method proposed by Comuñas et al. [15] using vacuum and a liquid of known densities (Water [16] and decane [17]). The temperature of the densimeter is regulated by an external circulating fluid and is measured with a Pt100 with an uncertainty of 0.1 K in the temperature range investigated. Taking into account the uncertainty in the measurements and the calibration, the overall experimental uncertainty in the reported density values is estimated to be 0.05%.

Seven fatty acid methyl or ethyl esters, presented in Table 1, were investigated. They were selected and divided into three sets. The first set contains three saturated fatty acid methyl esters, i.e. MeC10:0, MeC14:0 and MeC16:0 whose decomposition in groups involves only the ester group CH₃COO— and the alkyl group s

—CH₃ and —CH₂—. The second set is composed of MeC18:1 and MeC18:2. It is used to take into account the unsaturation thanks to a new group —CH=CH—. Finally the last set is made of two ethyl esters EeC10:0, EeC14:0. They were added to the database to evaluate the contribution of the group —CH₂COO—. All the components were supplied by by Sigma−Aldrich with a mass fraction purity higher than 0.99 and were used without further purification.

3. Results and discussion

Measurements of both speed of sound, c, and density, ρ , were performed from 283.15 to 373.15 K with 10 K steps. For the heaviest saturated FAMEs, MeC14:0 and MeC16:0, the minimum temperature was 303.15 and 313.15 K respectively due to their melting temperatures being above 283.15 K. The results are presented in Table 2 and plotted in Fig. 1. It can be observed that speeds of sound have a linear decreasing trend with a slope independent of the chain length.

Few previous works present measurements of speed of sound in FAME. Gouw et al. [18] reported data for saturated FAME ranging from MeC6:0 to MeC18:0 as well as for various unsaturated FAME but only at two temperatures, 293.15 and 313.15 K. Ott et al. [19] reported speed of sound data between 278.15 and 338.15 K for five pure fatty acid methyl esters. Recently Freitas et al. [20] studied the influence of temperature on the speed of sound of three FAME. On the other hand, no sound speed data are available concerning FAEE. Our data at 293.15 and 313.15 K are highly consistent with the measurements of Gouw et al. [18] for which the absolute average deviations is 0.05%. This is lower than the experimental uncertainty. Furthermore, comparison of our measurement fitted with a cubic polynomial in temperature with those of Freitas et al. [20] and Ott et al. [19] shows respective deviations of 0.14% and 0.15% in absolute average.

From the combination of the measurements of both density and speed of sound, the isentropic compressibility κ_s was evaluated with an uncertainty of 0.3% according to the following relationship:

$$\kappa_{S} = \frac{1}{\rho c^2},\tag{1}$$

These data are presented in Table 2 for the fluids here studied. Finally, the molecular compressibility κ_m was determined with an uncertainty of 0.1% and is also given in Table 2. This property also called Wada's constant was defined by Wada [12] by the following relationship:

$$\kappa_m = \frac{M_w}{\rho} \, \kappa_s^{-1/7} \tag{2}$$

where M_w is the molecular weight. This property, assumed independent of temperature in liquids, comes from integration of the differential law [21]:

$$\frac{1}{\kappa_s} \left(\frac{\partial \kappa_s}{\partial T} \right)_P = -7 \, \alpha_P \tag{3}$$

in which α_p corresponds to the isobaric expansion. The values of this property are reported in Table 2 at each temperature for the fluids here investigated. Analysis of all the data sets reveals that Wada's constant is indeed not really independent of temperature. A small (less than 1% for a 100 K variation) but monotonically decreasing tendency is observed for all compounds here studied as shown in Fig. 2. Here it can be seen that the values of κ_m are far more affected by the nature of the component than by temperature. In a previous work [13] concerning paraffins, it was observed a linear increase of the molecular compressibility with respect to molecular weight. This linear behavior is also observed for the fatty

Table 1Components studied and group decomposition.

Name	Formula	Purity	−CH ₃	—СH ₂ —	—CH=CH—	CH₃COO—	-CH ₂ COO-
Group 1							
Methyl caprate	MeC 10:0	99	1	8	0	1	0
Methyl myristate	MeC 14:0	99	1	12	0	1	0
Methyl palmitate	MeC 16:0	99	1	14	0	1	0
Group 2							
Methyl oleate	MeC 18:1	99	1	14	1	1	0
Methyl linoleate	MeC 18:2	99	1	12	2	1	0
Group 3							
Ethyl caprate	EeC 10:0	99.5	2	8	0	0	1
Ethyl myristate	EeC 14:0	99	2	12	0	0	1

Table 2Experimental sound speed, density, and related properties for FAME and FAEE.

T (K)	c (ms ⁻¹)	$ ho$ (kg m $^{-3}$)	κ_S (GPa $^{-1}$)	$\kappa_m \times 10^3$	$c ({\rm m s^{-1}})$	$ ho$ (kg m $^{-3}$)	κ_S (GPa $^{-1}$)	$\kappa_m \times 10^{\circ}$
MeC 10:0								
283.15	1363.8	880.0	0.611	4.3854				
293.15	1324.6	871.9	0.654	4.3834				
303.15	1286.7	863.9	0.699	4.3818				
313.15	1249.2	855.7	0.749	4.3805				
323.15	1212.9	847.5	0.802	4.3796				
333.15	1176.6	839.2	0.861	4.3786				
343.15	1142.1	830.9	0.923	4.3786				
MeC 14:0					MeC 16:0			
303.15	1335.4	859.8	0.652	5.7856				
313.15	1299.5	852.2	0.695	5.7846	1317.8	850.7	0.677	6.4897
323.15	1265.7	844.6	0.739	5.7856	1281.2	843.3	0.722	6.4863
333.15	1230.1	837.0	0.790	5.7834	1246.3	835.9	0.770	6.4845
343.15	1196.3	829.3	0.843	5.7831	1214.2	828.5	0.819	6.4855
353.15	1163.2	821.7	0.899	5.7825	1181.2	821.0	0.873	6.4849
363.15	1131.1	814.1	0.960	5.7823	1147.5	813.6	0.933	6.4817
373.15	1097.9	806.4	1.029	5.7798	1114.4	806.1	0.999	6.4786
MeC 18:1					MeC 18:2			
283.15	1445.5	880.8	0.543	7.090	1456.7	892.1	0.528	6.9811
293.15	1408.8	873.7	0.577	7.087	1419.3	885.1	0.561	6.9769
303.15	1371.4	866.6	0.614	7.0832	1382.7	878.0	0.596	6.9730
313.15	1337.7	859.4	0.650	7.083	1348.1	870.8	0.632	6.9713
323.15	1302.5	852.2	0.692	7.0804	1312.3	863.6	0.672	6.9676
333.15	1269.1	845.0	0.735	7.0792	1278.4	856.4	0.715	6.9657
343.15	1233.6	837.8	0.784	7.0741	1244.9	849.1	0.760	6.9637
353.15	1201.7	830.5	0.834	7.0741	1212.3	841.7	0.808	6.9630
363.15	1170.2	823.2	0.887	7.0742	1179.8	834.4	0.861	6.9614
373.15	1139.1	815.8	0.945	7.0741	1149.0	826.9	0.916	6.9627
EeC 10:0					EeC 14:0			
283.15	1352.7	871.4	0.627	4.744				
293.15	1313.7	863.7	0.671	4.7406	1360.5	861.0	0.627	6.1459
303.15	1277.6	855.8	0.716	4.7402	1323.9	853.3	0.669	6.1451
313.15	1240.6	847.8	0.766	4.7386	1288.7	845.8	0.712	6.1445
323.15	1205.3	839.6	0.820	4.7392	1252.7	838.2	0.760	6.1422
333.15	1169.7	831.3	0.879	4.7387	1218.4	830.8	0.811	6.1405
343.15	1134.4	822.9	0.944	4.7384	1183.3	823.2	0.868	6.1374
353.15	1101.4	814.5	1.012	4.7402	1151.6	815.6	0.924	6.1384
363.15	1066.4	806.1	1.091	4.7388	1118.2	808.0	0.990	6.1360
373.15	1034.9	797.6	1.171	4.7409	1086.5	800.3	1.059	6.1363

acid esters here studied as shown in Fig. 3. However, the line for the fatty acid esters appears parallel to that of paraffins. This result shows that the molecular compressibility is actually not function of the molecular weight but on the chemical structure of molecules. The parallelism observed between the alkanes and esters lines reveals that the ester group has a constant contribution to the κ_m independent of the fatty acid ester considered. Therefore the group contribution concept can be straightforwardly applied to this property. The molecular compressibility and of pure component can thus be expressed as a summation of group contributions plus a contribution due to temperature influence.

$$K_m(T) = \sum_{j=1}^{n_G} N_j K_{m,j} (1 - \chi (T - T_0))$$
 (4)

where $\kappa_{m,j}$ is the contribution of the group type-j to κ_m which occurs N_j times in the given molecule, T_0 is a temperature of reference and χ is a constant parameter used to take into account the influence of temperature. Five functional groups are needed to describe the fatty acid methyl or ethyl esters present in biodiesels. Two are needed for the linear and saturated alkyl chain (—CH₃ and —CH₂—). Another group must be added to take into account the unsaturation

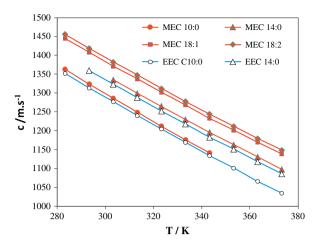


Fig. 1. Speed of sound in FAME and FAEE as a function of temperature.

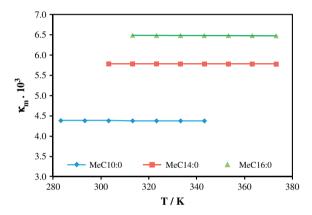
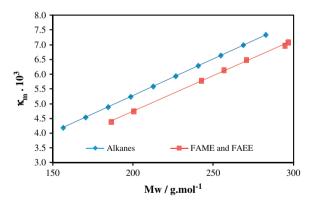


Fig. 2. Molecular compressibility of saturated FAME as a function of temperature.



 $\textbf{Fig. 3.} \ \ Molecular compressibility as a function of molecular weight for all temperatures investigated.$

of the alkyl chain —CH=CH—. Finally two groups were considered to take into account the ester contributions; one for methyl esters (CH₃COO—), and other for longer esters (—CH₂COO—).

Values of parameters for the groups — CH_3 and — CH_2 — were first regressed from the alkane database [13]. Then, ester contributions (CH_3COO — and — CH_2COO —) were evaluated separately from data of sets 1 and 3. Finally, unsaturation contribution (—CH=CH—) was evaluated by considering data of set 2. The results are listed in Table 3.

Deviations (in average and absolute average) between experimental and calculated molecular compressibility are given in

Table 3Group contribution values for molecular compressibility estimation.

	-СH ₃	-СH ₂ -	СН=-СН	CH ₃ COO—	-CH ₂ COO-
$\kappa_m \times 10^3$ $T_0 (K)$ $\chi \times 10^3$	0.50969	0.35196	0.59074 298.15 0.034852	1.05856	0.90610

Table 4Error analysis of molecular compressibility and speed of sound predictions by group contribution method for the compounds used in the development of the method.

	κ_m		С	
	AD%	AAD%	AD%	AAD%
Alkanes (C ₁₁ -C ₂₀) [13]	0.004	0.02	0.01	0.08
FAME (group 1)	-0.01	0.03	0.01	0.11
FAME (group 2)	0.03	0.03	0.02	0.11
FAEE (group 3)	0.04	0.06	0.02	0.21

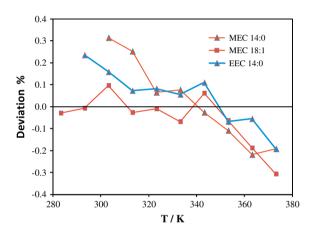


Fig. 4. Deviation between experimental and calculated speed of sound from group contribution method.

Table 4. As can be observed, the group contribution leads to a very good representation with an average deviation of less than 0.1%. It can be noted from the calculation of molecular compressibility that it becomes possible to evaluate the speed of sound from density measurements by using the following relationship:

$$c = \rho^3 \left(\frac{\kappa_m}{M_w}\right)^{7/2} \tag{5}$$

A comparison between these calculations and speed of sound data are also given in Table 3 and plotted as a function of temperature in Fig. 4 for three different components. The method leads to somewhat larger deviations for speeds of sound than for Wada's constant. However, it is still quite satisfactory, the results are in the range of experimental uncertainty (0.1% in AAD%). The AD% information also indicates that the model does not introduce systematic errors. The main interest of a group contribution method is to be able to determine properties of compounds for which no experimental information is available, that is, in case of purely prediction. Therefore, the predictive character of the proposed method has been tested with data available in the literature and not used in the regression process. For this test four saturated FAME were considered i.e. MeC6:0 [18], MeC8:0 [18], MeC12:0 [18,20], MeC18:0 [18,19] and two unsaturated FAME (MeC18:3 [18,19], MeC22:10 [18]). Densities required for the calculation of speed of sound using Eq. (5) were taken from works of Pratas et al. [8,9]. Results of these comparisons are presented in Table 5 for both molecular com-

Table 5Error analysis of molecular compressibility and speed of sound predictions by group contribution method for the compounds not used in the development of the method.

	κ_m		С		
	AD%	AAD%	AD%	AAD%	
MeC6:0 [18]	0.03	0.03	-0.05	0.11	
MeC8:0 [18]	0.05	0.05	0.17	0.17	
MeC12:0 [18]	0.08	0.08	0.29	0.29	
MeC12:0 [20]	0.03	0.03	0.11	0.11	
MeC18:0 [18]	-0.01	0.01	0.002	0.002	
MeC18:3 [18]	0.06	0.06	0.20	0.20	
MeC18:3 [19]	0.04	0.04	0.03	0.15	
MeC22:1 [18]	0.03	0.03	0.08	0.11	

pressibility and speed of sound. The proposed method yields property predictions with the same error as data used in the regression process. All these comparisons show clearly the reliability of the method when applied in extrapolation and confirm its purely predictive character.

4. Conclusion

Measurements of speed of sound were carried in five pure fatty acid methyl esters and two fatty acid ethyl esters at temperatures ranging from 283.15 to 373.15 K and at atmospheric pressure. Together with the densities here measured for the same compounds, these data were used to estimate the isentropic compressibility as well as the molecular compressibility, the so called Wada's constant. Based on these data, along with data from previous measurements for alkanes, a group contribution method was proposed for estimating both molecular compressibility and speed of sound of fatty acid esters. This procedure yields very accurate correlations of these properties in a wide range of temperatures (from 283 K to 373 K). The mean deviation obtained for a wide variety of hydrocarbons used in the development of the method is less than 0.1%. The predictive character of the method has been demonstrated for fatty acid methyl esters for which predictions were compared to literature data. Due to its predictive and accurate features, the method presented in this work can be considered as a useful correlation to predict acoustic properties of components present in biodiesels and hopefully also of biodiesel fuels at atmospheric pressure. This work constitutes a part of a program of measurements of speed of sound in biodiesels systems. It will be carried on with measurements under high pressure as biodiesel injection must be performed under high pressure in future engine [22,23] in order to improve combustion performance and reduce harmful emissions.

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