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Measurement and prediction of speeds of sound of fatty acid ethyl esters and ethylic biodiesels

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HIGHLIGHTS

- Measurement of speed of sound for several fatty acid ethyl esters was carried.
- Speed of sound data for ethylic biodiesels is reported for the first time.
- Prediction of speed of sound was carried using the Wada's group contribution method.
- The Wada's model provides a good description of speed of sound.

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ABSTRACT

Speed of sound of fatty esters provides important information about biodiesel injection characteristics and enables the estimation of many other important properties of biodiesels. Nevertheless, the experimental speeds of sound of fatty esters are very scant. This work provides new data on speed of sound for nine fatty acid ethyl esters and four ethylic biodiesels, measured at atmospheric pressure and temperatures ranging from 293.15 to 343.15 K. These new data is used to evaluate the ability of the Wada's group contribution method to predict the biodiesel speed of sound. It is here shown that this model provides excellent description of the experimental data, with overall average relative deviations (OARDs) of 0.25% for the ethyl esters and between 0.45% and 0.59% for the biodiesels.

1. Introduction

Worldwide researchers, fuel industries and policy-makers have placed biofuels at the forefront of renewable energies, through various policies and incentives. Among the biofuels, in Europe the biodiesel has been playing a key-role in the promotion of energy sustainability, especially for the transport sector. This tendency is expected to keep increasing in the coming years when new feedstocks for biodiesel production are developed from agricultural residues and non-edible oils. Blends of biodiesel with diesel and ethanol with gasoline are expected to account for 54% of the growth in liquids fuel consumption between 2009 and 2035 [1]. This happens because biodiesel are obtained from vegetable oils, animal fats and greases, and its use as fuel is economically viable, technically compatible and environmentally friendly. Besides being produced from renewable sources, it contributes less to greenhouse gases emissions and can replace petrodiesel totally or partially in conventional diesel engines without modification [2–4].

The aforementioned advantages have fed the academic interest in biodiesel in the last few years. While some works focused on establishing novel approaches to improve the production and purification [5–7] others have oriented their line of research to the

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study of thermophysical properties of fatty esters and biodiesels [8–16] to enhance the quality of biodiesels, i.e., their properties in accordance with the Norm CEN EN 14214 [17] in Europe and the Norm ASTM D6751 in United States of America [18].

Speed of sound is one important acoustic property that affects directly the fuel injection characteristics, especially for injectors activated with pressure, and the amount of NOx emissions in the mechanically controlled in-line injection systems by simply changing the combustion temperature. High speeds of sound increase the combustion temperature and consequently the amount of NOx emissions [19]. This property also permits the estimation of other thermodynamic properties like isentropic and isothermal compressibilities, isobaric thermal expansion coefficient, thermal pressure coefficient and the reduced bulk modulus [20,21].

As biodiesels are composed of fatty esters, the knowledge of the properties of these pure compounds enables the prediction of the properties of those fuels as we have shown elsewhere for other biodiesel properties [10,14,15,22]. Unfortunately there are but a few data available in the literature for fatty acid methyl esters (FAMEs) [13,21,12,23–27] being the experimental speeds of sound of fatty acid ethyl esters (FAEEs) even more scant [28], although some studies were already done for the shorter methyl and ethyl esters [29]. There at, this work aims at providing new experimental data of speed of sound for nine saturated and unsaturated FAEE and four ethylic biodiesels, measured at atmospheric pressure and temperatures from 293.15 to 343.15 K, and then using them to evaluate the predictive ability of Wada's group contribution method [28].

2. Experimental section

2.1. Esters samples

The nine ethyl esters here studied were ethyl butyrate (98% quoted purity from Fluka), ethyl caprylate (>99% quoted purity from Aldrich), ethyl caprate (99% quoted purity from Fluka), ethyl laurate (99% quoted purity from Sigma), ethyl myristate (99% quoted purity from Aldrich), ethyl palmitate (>99% quoted purity from Sigma), ethyl stearate (>99.0% quoted purity from Fluka), ethyl oleate (>98% quoted purity from Aldrich), ethyl linoleate (>99% quoted purity from Sigma). These compounds were used as received without any further purification.

2.2. Biodiesel samples: synthesis and analysis

Three of the four biodiesel samples studied here were synthesized by a transesterification reaction of vegetable oils, such as soybean (S), sunflower (Sf) and palm (P), performed on a laboratory scale. The transesterification reaction was carried out with ethanol using sodium hydroxide (NaOH) as the catalyst. The amount of NaOH used was 1.0 wt.% of the oil. Oil and ethanol with a mole ratio of 1:6 reacted at 323.15 K for 180 min.

A fourth sample consisting of ethylic biodiesel derived from soybean oil and beef tallow (S+B) was also investigated. This sample was an industrial one kindly supplied by Fertibom (Catanduva, SP, Brazil), a Brazilian company that produces ethylic biodiesel in industrial scale.

The fatty acid ethyl esters (FAEEs) compositions for all biodiesel samples were determined in triplicate by gas chromatography. The chromatographic analyses were carried out using a GC capillary gas chromatograph system (Agilent, 6850 Series GC System, Santa Clara, CA, USA) under the following experimental conditions: Elite 225 capillary column (PERKIN ELMER, 50% Cyanopropylphenyl–Phenylmethylpolysiloxane, 0.25 μm × 29 m × 0.25 mm); helium as carrier gas at a flow rate of 2.17×10^{-8} m^3/s; injection temperature of 523 K; column temperature of 373 K for 120 s, 373–503 K (rate of 7 K/60 s), 503 K for 600 s; detection temperature of 523 K; and injection volume of 1.0 μL. The fatty acid ethyl esters were identified by comparison with external standards purchased from Nu Check Prep (Elysian, MN, USA). Quantification was done by internal normalization.

2.3. Measurement of density and speed of sound

Experimental measurements of density and speed of sound were made concurrently using an Anton Paar vibrating tube densimeter and ultrasound speed meter, model DSA 5000M, with an automatic temperature control within ±0.01 K. All measurements were made at ambient pressure. According to the procedure already described elsewhere [30], calibration of the speed of sound cell was made with degassed Millipore ultra-quality water. Measurement and comparison with literature values of speed of sound of toluene and cyclohexane at 25 °C leads us to assume an accuracy of 0.5 m s^{-1}, as claimed by the manufacturer. In the case of density, besides the usual method recommended by the manufacturer of using dry air and degassed ultra-pure water at 293.15 K as reference fluids, a new calibration procedure thoroughly described elsewhere [31] was performed. The calibrants used were ultra-pure water and dodecane with certified density values issued by H§D Fitzgerald, with expanded uncertainties of 0.01 kg m^{-3} (coverage factor $k = 2$, providing a 95% level of confidence). The use of this pair of calibrating fluids allowed a close bracketing of the densities measured, the importance of which has recently been emphasized by Fortin et al. [32] As the temperature range of certified density values for dodecane does not cover values higher than 323.15 K, an extrapolation of those values had to be made. However, a careful analysis of results based on comparison between direct density values (taken from direct readings of the densimeter) and final values obtained from the calibration procedure allowed a reassurance about the validity of that extrapolation.

Every day before starting the measurements, the usual routine procedure of performing a water and air check was invariably adopted. Before injection all samples were pre-heated, and degassed, at the maximum experimental temperature. Then, for the same single sample injection a complete series of measurements was made, decreasing the temperature from 343.15 K to 293.15 K in decrements of 5 K. At each temperature three to seven data readings were taken and some measurements were repeated with a new injection, allowing asserting an estimate for the repeatability and standard uncertainty for density values lower than 0.0006% and 0.005%, respectively, and for speed of sound of 0.01% and 0.02%, respectively. After each set of measurements the instrument was flushed several times with *n*-heptane at 333 K and with acetone at 313 K, sequentially, and then dried at 343 K during at least 1 h, with a stream of forced room air. To assess the effectiveness of these cleaning actions, new air and water checks were done and whenever deviations higher than 0.002% for density and 0.013% for sound speed were found, a new cycle of cleaning steps was executed.

3. Prediction of speed of sound

The prediction of speed of sound for ethyl esters and ethylic biodiesels here studied was done by using the Wada's Group Contribution Method previously proposed by us [28] to predict the speed of sound of alkyl esters. In a previous work, we showed that this model could provide a good prediction of the speed of sound of methyl esters and the corresponding methylic biodiesels [13]. This model simply relates speed of sound (u in m s^{-1}) with density (ρ in kg m^{-3}), molecular mass (M_w in g mol^{-1}) and molecular compressibility (κ_m) according to the following equation: