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Speed of sound in pure fatty acid methyl esters and biodiesel fuels

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HIGHLIGHTS

- New data on sound speed is reported for fatty acid methyl esters.
- New data on speed of sound is reported for biodiesel fuels.
- Molar compressibility was calculated for fatty acid methyl esters and biodiesel.
- Predictive models for speed of sound and molar compressibility are proposed.

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ABSTRACT

The property changes associated with the differences in chemical composition of biodiesel may change the fuel injection timing which in turn cause different exhaust emissions and performance of engines. The property that has an important effect on the fuel injection timing is the speed of sound (related with isentropic bulk modulus). Despite the speed of sound of pure fatty acid (methyl and ethyl) esters being reasonably known in a wide range of temperature the experimental data for biodiesel are very scarce in the literature. In this work the speed of sound of six fatty acid methyl esters (FAME = laurate (MeC12:0), myristate (MeC14:0), palmitate (MeC16:0), stearate (MeC18:0), oleate (MeC18:1), linoleate (MeC18:2)) and six biodiesel fuel samples were measured using a non-intrusive ultrasonic methodology. The measurements for FAMEs were made at atmospheric pressure from a minimum of 288.15 K to a maximum of 353.15 K, and in the temperature range 298.15–353.15 K for biodiesel samples. The uncertainty of the measurements was estimated as less than ±1 m s^{-1}. The speed of sound data combined with available density data from literature was used to calculate the isentropic compressibility and the molecular compressibility for the FAMEs and for the biodiesel samples. The results for molecular compressibility evidenced that this property is almost independent of the temperature in the temperature range of calculations both for FAMES and biodiesel. Linear relationships were established between the molar compressibility and the molecular weight for FAMES and biodiesel. The before mentioned behavior of molar compressibility face to temperature and molecular weight make it possible to develop prediction methods for the calculation of the speed of sound.

1. Introduction

The conventional fossil fuels (petrofuels) are non-renewable, increasingly scarce, with growing emissions of combustion resulting pollutants, and with increasing costs of production. On the other hand, fuel reserves are concentrated in certain planet regions and most of them are reaching the production peak. All these circumstances make biomass sources more attractive in particular the biodiesel. Unlike petrodiesel, biodiesel is a renewable fuel offering important benefits including reduction of green-house emissions, biodegradability, and non-toxicity. Biodiesel shows total miscibility with petrodiesel and compatibility with modern engines [1,2]. Nowadays, biodiesel production has important economic and social impacts at the regional development level especially to developing countries [3]. Technically, biodiesel is a fuel formed by long chain of fatty acid esters produced from a large variety of feedstocks including vegetable oils and animal fats, with designation of B100, meeting the property and quality requirements of the American Society Testing (ASTM) D6751 standard. Biodiesel can be produced through transesterification chemical reaction along which the raw material reacts with alcohol (usually methanol or ethanol) in the presence of a catalyst that can be metal alkoxide [4], ionic liquids [5], or others [6]. The resulting products

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are the fatty acid (methyl or ethyl) esters (FAE or biodiesel) and glycerol.

Glycerol, which is a high value byproduct of the transesterification reaction forms one phase and (FAE) form another phase, which settles above the glycerol in the reactor. The biodiesel fuel must meet specifications contained in biodiesel standards, such as the (ASTM) D6751 and the EN14214 in Europe. Some of these specifications are related to the fuel quality such as completeness of transesterification reaction, storage conditions and other important properties as viscosity, density, oxidative stability, cetane number, and cold flow properties, depending all on the fatty acid composition of biodiesel. The injection process is of great importance for engine efficiency. In this process an appropriate quantity of fuel is feed to the engine cylinder forming a spray of tiny fuel droplets to optimize the combustion and reduce the fuel consumption and emissions. All injection process is strongly influenced by the thermophysical fuel properties. The properties of major influence in the injection time are the surface tension [7], the viscosity, and the isentropic bulk modulus [8], which is determined by the sound speed. Therefore, for the accurate design and maintenance of injection systems, the accurate knowledge of the sound speed of the fuel plays an important role. Biodiesel sound speed information is very scarce in the literature, although several authors have measured this property for pure methyl and ethyl FAEs. Some previous literature reports on speed of sound of pure FAMEs and biodiesel are summarized in Table 1, calculated for different temperature and pressure ranges, techniques and uncertainties of the measurements.

This work aims to evaluate the sound speed of pure liquid FAMEs most frequently found in biodiesel, and also of the biodiesel fuels. This property has been measured for MeC12:0, MeC14:0, MeC16:0, MeC18:0, MeC18:1, MeC18:2 considering wide ranges

Table 1
Previous sources of data for the speed of sound of the FAME compounds studied herein and biodiesel.

Authors	Year	N_p	T (K)	P (MPa)	(u) and (σ_u (m s^{-1})[a]	Method[b]	Purity (wt%)
Mehyl laurate (MeC12:0)							
Gouw and Vlugtert [9]	1964	2	293, 313	0.1	(1278, 1351) (0.08%)	Interf	>99.7
Tat and Gerpen [10][c]	2003	–	293–373	0.1–32.5	(1086–1502) (0.1–0.7%)	PE	[d]
Tat and Gerpen, NREL[11]	2003	30	293–373	0.1–34.5	(1080–1498) (0.1–0.7%)	PE	[d]
Freitas et. al. [12]	2013	12	288–343	0.1	(1171–1370) (0.01)	PE	97
Methyl myristate (MeC14:0)							
Gouw and Vlugtert [9]	1964	2	293, 313	0.1	(1299, 1372) (0.08%)	Interf	>99.7
Freitas et. al. [12]	2013	10	298–343	0.1	(1194–1353) (0.01)	PE	98
Daridon et. al. [13]	2013	8	303–373	0.1	(1098–1335) (<0.1%)	PE	99
Ndiaye et al. [14]	2013	53	303–393	0.1–80	(1036–1614) (0.2%)	PE	99
Methyl palmitate (MeC16:0)							
Gouw and Vlugtert [9]	1964	1	313	0.1	(1318) (0.08%)	Interf	>99.7
Tat and Gerpen [10][c]	2003	–	293–373	0.1–32.5	(1123–1537) (0.1–0.7%)	PE	>99
Tat and Gerpen, NREL[11]	2003	24	313–373	0.1–34.5	(1019–1463) (0.1–0.7%)	PE	[e]
Ott et al. [15]	2008	7	308–338	0.1	(1233–1338) (0.1%)	PE	>99.0
Daridon et. al. [13]	2013	7	313–373	0.1	(1171–1370) (<0.1%)	PE	99
Ndiaye et al. [14]	2013	35	303–393	0.1–50	(1057–1507) (0.2%)	PE	99
Freitas et al. [16]	2013	8	308–343	0.1	(1216–1337) (0.02)	DSA5000	99
Methyl Stearate (MeC18:0)							
Gouw and Vlugtert [9]	1964	1	313	0.1	(1333) (0.08%)	Interf	>99.7
Tat and Gerpen [10][c]	2003	–	293–373	0.1–32.5	(1141–1541) (0.1–0.7%)	PE	>99
Ott et al. [15]	2008	5	318–338	0.1	(1248–1317) (0.1%)	PE	>99.0
Freitas et al. [16]	2013	7	313–343	0.1	(1231–1333) (0.02)	DSA5000	99
Methyl oleate (MeC18:1)							
Gouw and Vlugtert [9]	1964	2	293, 313	0.1	(1338–1408) (0.08%)	Interf	>99.7
Ott et al. [15]	2008	7	278–338	0.1	(1250–1462) (0.1%)	PE	>99.0
Freitas et. al. [12]	2013	12	288–343	0.1	(1238–1427) (0.01)	PE	99
Daridon et. al. [13]	2013	10	283–373		(1139–1446) (<0.1%)	PE	99
Methyl linoleate (MeC18:2)							
Gouw and Vlugtert [9]	1964	2	293, 313	0.1	(1348–1419) (0.08%)	Interf	>99.7
Tat and Gerpen [10][c]	2003	–	293–373	0.1–32.5	(1156–1554) (0.1–0.7%)	PE	[f]
Tat and Gerpen, NREL[11]	2003	30	293–373	0.1–34.5	(1151–1550) (0.1–0.7%)	PE	[f]
Ott et al. [15]	2008	7	278–338	0.1	(1260–1472) (0.1%)	PE	>99.0
Daridon et. al. [13]	2013	10	283–373	0.1	(1149–1456) (<0.1%)	PE	99
Freitas et al. [16]	2013	11	288–343	0.1	(1246–1418) (0.02)	DSA5000	99
Biodiesel							
Tat and Gerpen [10,11]	2003	384	293–373	0.1–34.5	(1053–1551) (0.1–0.7%)	PE	–
Huber et al. [17]	2009	14	278–333	0.08	(1255–1467) (0.03–1.00)	PE	[g]
Payri et al. [18][c]	2011	–	298–343	15–180	(1213–1848) (≈0.3%)	TOF	[h]
Nicolic et al. [19][c]	2012	17	293	0.1–160	(1404–1893) (0.05)	PE	[i]
Freitas et al. [12]	2013	120	288–343	0.1	(1230–1432) (0.01)	DSA5000	[j]

[a] The uncertainty in speed of sound (σ_u) is given in m s^{-1} or percentage.

[b] Interf: interferometer; PE: pulse-echo; TOF: time of flight.

[c] Data is given in expression(s) form(s).

[d] Sample: MeC12:0 (99.2), MeC18:1 (0.6), and MeC18:2 (0.2).

[e] Sample: MeC12:0 (0.2), MeC14:0 (4.6), MeC16:0 (88.2); MeC17:0 (0.4), and MeC18:0 (6.3).

[f] Sample: MeC16:0 (1.4), MeC18:0 (0.7), MeC18:1 (5.2), MeC18:2 (86.5), and MeC18:3 (6.2).

[g] Two commercial samples from rapeseed oil were used.

[h] Rape methyl ester used in Spain.

[i] Rape methyl ester used in Serbia.

[j] Samples synthesized at laboratory: soybean (S), rapeseed (R), palm (P), soybean + rapeseed (SR), palm + rapeseed (PR), soybean + palm (SP), soybean + rapeseed + palm (SRP), sunflower (SF); from Portuguese biodiesel producers: soybean + rapeseed (GP) and SoyA.