Density and Speed of Sound Measurements on Five Fatty Acid Methyl Esters at 83 kPa and Temperatures from (278.15 to 338.15) K†

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The densities and speeds of sound of five fatty acid methyl esters (FAMEs) were measured at approximately 83 kPa (atmospheric pressure in Boulder, CO) at temperatures from (278.15 to 338.15) K. The FAMEs measured were the five primary components of biodiesel fuel, namely, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. The densities and speeds of sound were measured concurrently with a commercial instrument equipped with a vibrating U-tube densimeter and pulse-echo speed of sound measurement cell. The densities of the FAMEs agreed with and expanded upon limited available literature values. The speed of sound measurements provide much needed experimental data for equation of state development.

Introduction

Biodiesel fuel is composed primarily of fatty acid methyl esters (FAMEs) produced by a catalyzed transesterification reaction between a triglyceride oil and a light primary alcohol. The main components of biodiesel fuel are considered to be the following five FAMEs: methyl palmitate (hexadecanoic acid, methyl ester; CAS 112-39-0; InChI 1/C17H34O2/c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17(18)19-2/h3-16H2,1-2H3), methyl stearate (octadecanoic acid, methyl ester; CAS 112-61-8; InChI 1/C19H38O2/c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/h3-18H2,1-2H3), methyl oleate (octadecenoic acid, methyl ester; CAS 112-62-9; InChI1/C19H36O2/c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/h10-11H,3-9,12-18H2,1-2H3/b11-10-), methyl linoleate (octadecadienoic acid, methyl ester; CAS 112-63-0; InChI 1/C19H34O2/c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/h7-8,10-11H,3-6,9,12-18H2,1-2H3/b8-7-,11-10-), and methyl linolenate (octadecatrienoic acid, methyl ester; CAS 301-00-8; InChI 1/C19H32O2/c1-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19(20)21-2/h4-5,7-8,10-11H,3,6,9,12-18H2,1-2H3/b5-4-,8-7-,11-10-). As biodiesel fuel continues to grow in popularity and use, the demand for physical property measurements of its constituent fluids also grows. Some density and speed of sound measurements have been reported in the literature,[1−12] but further measurements are still needed to develop reliable equations of state for these fluids. Speed of sound measurements of the pure constituent fluids, which are needed for the calculation of the adiabatic compressibility of the constituent fluids and are also important for fuel injection timing in diesel engines,[13] appear to be present in only one manuscript and only for two temperatures.[14] Tat and Van Gerpen measured speeds of sound of the five FAMEs,[13] but the purities of the FAMEs ranged from (52.6 to 88.2) %, and the data are not suitable for development of pure fluid correlations. Therefore, speeds of sound have been measured on pure FAMEs and are reported herein. The densities of the five FAMEs were also measured since densities are also useful in calculations of fuel atomization efficiency. Some prior reports with limited density and speed of sound measurements are available for comparison,[1−10,14] and these previous literature reports are summarized in Tables 1 and 2.

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Experimental

The five FAMEs were purchased from a commercial supplier with stated purities greater than or equal to 99 %. These purities were examined by gas chromatography with flame ionization detection (GC-FID). Each FAME was diluted in *n*-hexane and examined separately on a 30 m capillary column with a 0.1 mm coating of 50 % cyanopropyl−50 % dimethylpolysiloxane as the stationary phase. This phase provides separations based upon polarity[15] and is intended specifically for the analysis of the fatty acid methyl esters (FAMEs) that compose biodiesel fuel. Samples were injected via syringe into a split/splitless injector set with a 10 to 1 split ratio. The injector was operated at a temperature of 325 °C and a constant head pressure of 10 psig (69 kPa), with an approximate column flow rate of 3 $mL \cdot min^{-1}$. The sample residence time in the injector was very short; thus the effect of sample exposure to this high temperature is expected to be minimal. Initially, the temperature was maintained isothermally at 80 °C for 2 min, followed by a an 8 $°C \cdot min^{-1}$ ramp to 285 °C, and finally maintained at 285 °C for 5 min. In each case, the purity met or exceeded the stated purity from the supplier: methyl palmitate, 99.6 %; methyl stearate, 99.7 %; methyl oleate, 99.3 %; methyl linoleate, 99.3 %; methyl linolenate, 99.0 %.

The FAMEs were stored in a dark box in a refrigerator maintained at 7 °C. The methyl oleate, methyl linoleate, and methyl linolenate were shipped in sealed ampoules and opened immediately before initiating the density and speed of sound measurements.

The densities and speeds of sound were measured concurrently with a commercial instrument equipped with a vibrating U-tube densimeter and pulse-echo speed of sound measurement cell. The instrumental uncertainty in both density and speed of sound measurements is stated as 0.01 % to 0.1 %, with repeatabilities of 0.001 $kg \cdot m^{-3}$ in the density and 0.1 $m \cdot s^{-1}$

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Table 1. Previous Literature Reports for the Density of Each of the Five FAMEs Studied Herein

	author(s)	year	T/K	no. of points	purity (%)	stated uncertainty (%)	method
methyl palmitate	Eykman[8]	1919	353.829	1	not stated	0.24	not stated
	Drake and Spies[9]	1935	293.145	1	not stated	0.10	not stated
	Gros and Feuge[4]	1952	348.081	1	99	0.07	specific gravity bottles
	Gouw and Vlugter[2]	1964	313.14	1	> 99.7	0.09	modified Sprengel pycnometer
	Rusling et al.[10]	1969	298.144	1	> 99	0.59	not stated
	Bonhorst et al.[5]	1948	310.941 to 372.025	3	not stated	0.62	modified Sprengel tubes
	Gaikwad and Subrahmanyam[7]	1988	333.084 to 353.079	5	not stated	0.62	
methyl stearate	Bonhorst et al.[5]	1948	310.941 to 372.025	3	not stated	0.62	modified Sprengel tubes
	Boelhouwer et al.[6]	1950	323.087 to 513.061	5	not stated	0.14	pycnometer
	Gaikwad and Subrahmanyam[7]	1988	333.084 to 353.079	5	not stated	0.62	
	Hosman et al.[3]	1949	313.09	1	98.5	0.64	not stated
	Gros and Feuge[4]	1952	348.081	1	99	0.07	specific gravity bottles
	Gouw and Vlugter[2]	1964	313.14	1	>99.7	0.09	modified Sprengel pycnometer
	Liew and Seng[11]	1992	313.15 to 353.15	9	> 99	not stated	pycnometer
methyl oleate	Bridgman[1]	1932	299.14	1		0.06	
	Keffler and McLean[17]	1935	293.15 to 303.15	4	> 99.5	0.09	U-tube pycnometer
	Wheeler and Riemenschneider[18]	1939	293.15 to 298.15	2	> 99	not stated	not stated
	Hammond and Lundberg[12]	1954	293.15	1	not stated	0.04	not stated
	Gouw and Vlugter[2]	1964	293.145 to 313.14	2	> 99.7	0.09	modified Sprengel pycnometer
	Rusling et al.[10]	1969	298.15	1	> 99	not stated	not stated
	Mitrofanova et al.[19]	1966	293.15	1	not stated	not stated	not stated
methyl linoleate	Gouw and Vlugter[2]	1964	293.145 to 313.14	2	> 99.7	0.10	modified Sprengel pycnometer
	Mitrofanova et al.[19]	1966	293.15	1	not stated	not stated	not stated
methyl linolenate	Gouw and Vlugter[2]	1964	293.145 to 313.14	2	> 99.7	0.12	modified Sprengel pycnometer

Table 2. Previous Literature Reports for the Speed of Sound of Each of the Five FAMEs Studied Herein

	author(s)	year	T/K	no. of points	purity (%)	stated uncertainty (%)	method
methyl palmitate	Gouw and Vlugter[14]	1964	313.15	1	> 99.7	0.08	interferometer
methyl stearate	Gouw and Vlugter[14]	1964	313.15	1	> 99.7	0.08	interferometer
methyl oleate	Gouw and Vlugter[14]	1964	293.15 and 313.15	2	> 99.7	0.08	interferometer
methyl linoleate	Gouw and Vlugter[14]	1964	293.15 and 313.16	2	> 99.7	0.08	interferometer
methyl linolenate	Gouw and Vlugter[14]	1964	293.15 and 313.17	2	> 99.7	0.08	interferometer

Table 3. Density, in kg·m^{-3}, of the Five FAME Compounds Measured at 83 kPa[a]

T/K	methyl palmitate	methyl stearate	methyl oleate	methyl linoleate	methyl linolenate
278.15	---[b]	---[b]	884.8(9)	896.7(9)	910.7(9)
288.15	---[b]	---[b]	877.6(9)	889.3(9)	903.3(9)
298.15	---[b]	---[b]	870.3(9)	881.9(9)	895.8(9)
308.15	856.1(9)	---[b]	863.0(9)	875(1)	888.4(9)
313.15	852.4(9)	---[b]	---	---	---
318.15	848.7(8)	846.2(8)	855.8(9)	867.5(9)	881.0(9)
323.15	845.0(8)	842.6(8)	---	---	---
328.15	841.4(8)	839.0(8)	848.5(8)	860.2(9)	873.5(9)
333.15	837.9(8)	835.4(8)	---	---	---
338.15	834.0(8)	831.8(8)	841.3(8)	853.0(9)	866.1(9)

[a] The uncertainty of each measurement, discussed in the text, is the number in parentheses. [b] The measurement was not performed since the FAME is a solid at this temperature.

Table 4. Speed of Sound, in m·s^{-1}, of the Five FAME Compounds Measured at 83 kPa[a]

Temperature/K	methyl palmitate	methyl stearate	methyl oleate	methyl linoleate	methyl linolenate
278.15	---[b]	---[b]	1462(1)	1472(2)	1485(2)
288.15	---[b]	---[b]	1425(1)	1434(2)	1448(1)
298.15	---[b]	---[b]	1389(1)	1398(1)	1411(1)
308.15	1338(1)	---[b]	1353(1)	1362(1)	1375(1)
313.15	1320(1)	---[b]	---	---	---
318.15	1303(1)	1317(1)	1318(1)	1327(1)	1340(1)
323.15	1285(1)	1299(1)	---	---	---
328.15	1268(1)	1282(1)	1284(2)	1293(1)	1306(1)
333.15	1250(1)	1265(1)	---	---	---
338.15	1233(1)	1248(1)	1250(2)	1260(1)	1272(1)

[a] The uncertainty of each measurement, discussed in the text, is the number in parentheses. [b] The measurement was not performed since the FAME is a solid at this temperature.

in the speed of sound measurement. As a conservative measure, we assume that the instrumental uncertainty is 0.1 % in the propagation of uncertainty.[16] Temperature is measured with an integrated Pt-100 thermometer with an estimated uncertainty of 0.01 K. Before each measurement, the instrument was calibrated with deionized degassed water at 293.15 K, and the reproducibility of the sound speed of water was within 0.01 % before and after measurements of the FAMEs. After each calibration, the instrument was rinsed at least five times with each of two solvents (acetone and n-hexane) and then maintained at 343.15 K for 1 h under a stream of forced room air to ensure that the measurement cells were thoroughly cleaned and dried.

Results

The density and speed of sound measurements are reported in Tables 3 and 4. Each density and speed of sound measurement was repeated four times for each of the five

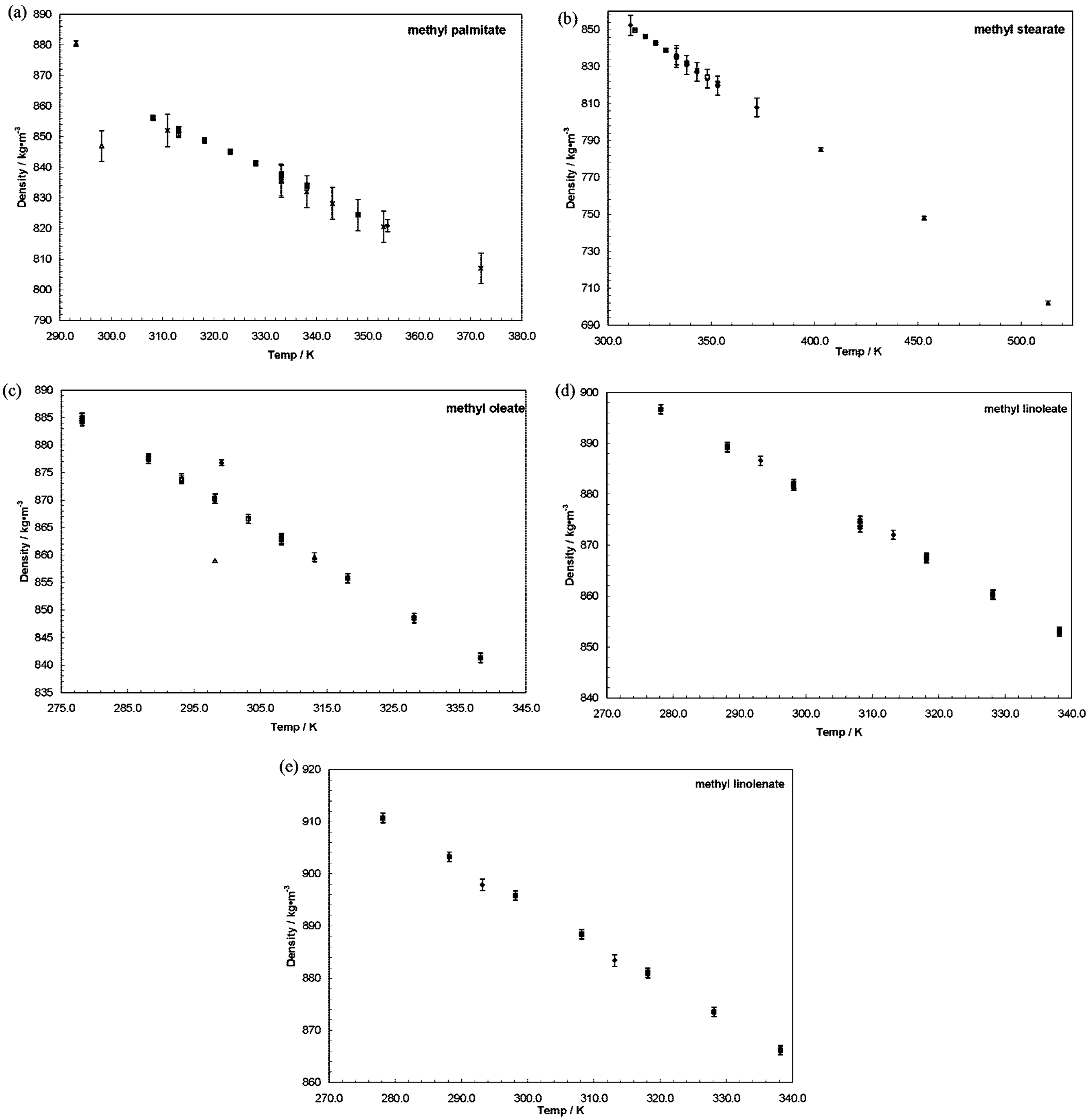

Figure 1. Graphical comparison of the densities of the five FAMEs studied herein with the previous literature data. For points where the error bars are not visible, the error bars are smaller than the symbols used. The data points correspond to: (a) ■, current work; ◆, Eykman 1919; ▲, Drake and Spies 1935; ○, Gros and Feuge 1952; □, Gouw and Vlugter 1964; △, Rusling et. al. 1969; ×, Bonhorst et. al. 1948; *, Gaikwad and Subrahmanyam 1988. (b) ■, current work; ◆, Bonhorst et. al. 1948; ▲, Boelhouwer et. al. 1950; ●, Gaikwad and Subrahmanyam 1988; □, Hosman et. al. 1949; ○, Gros and Feuge 1952; △, Gouw and Vlugter 1964; Rusling et. al. 1969; ×, Liew and Send 1992. (c) ■, current work; ◆, Bridgeman 1932; ▲, Gouw and Vlugter 1964; ●, Wheeler and Riemenschneider 1939; □, Keffler and McLean 1935; ○, Hammong and Lundberg 1954; △, Rusling et. al. 1969. (d) ■, current work; ◆, Gouw and Vlugter 1964. (e) ■, current work; ◆, Gouw and Vlugter 1964.

FAMEs. Methyl palmitate and methyl stearate have relatively high melting points (approximately (303 and 312) K, respectively) that precluded making measurements at temperatures below these melting points. The expanded total uncertainty (with a coverage factor of $k = 2$, incorporating both random and systematic uncertainty) in each measurement is given parenthetically after the significant figure to which it applies (for example, 856.1 $kg \cdot m^{-3}$ with an uncertainty of 0.9 $kg \cdot m^{-3}$ is shown as 856.1(9) $kg \cdot m^{-3}$).

The densities measured herein correlate well with, and also expand upon, previous measurements (except for the apparently outlying points collected by Rusling et al.[10] and Bridgman[1]). The densities of both the experimental work herein and previous measurements are shown in Figure 1, and the speeds of sound of both the experimental work herein and previous measurements are shown in Figure 2.

The density data collected in the current work are consistent with previous literature reports. The uncertainties

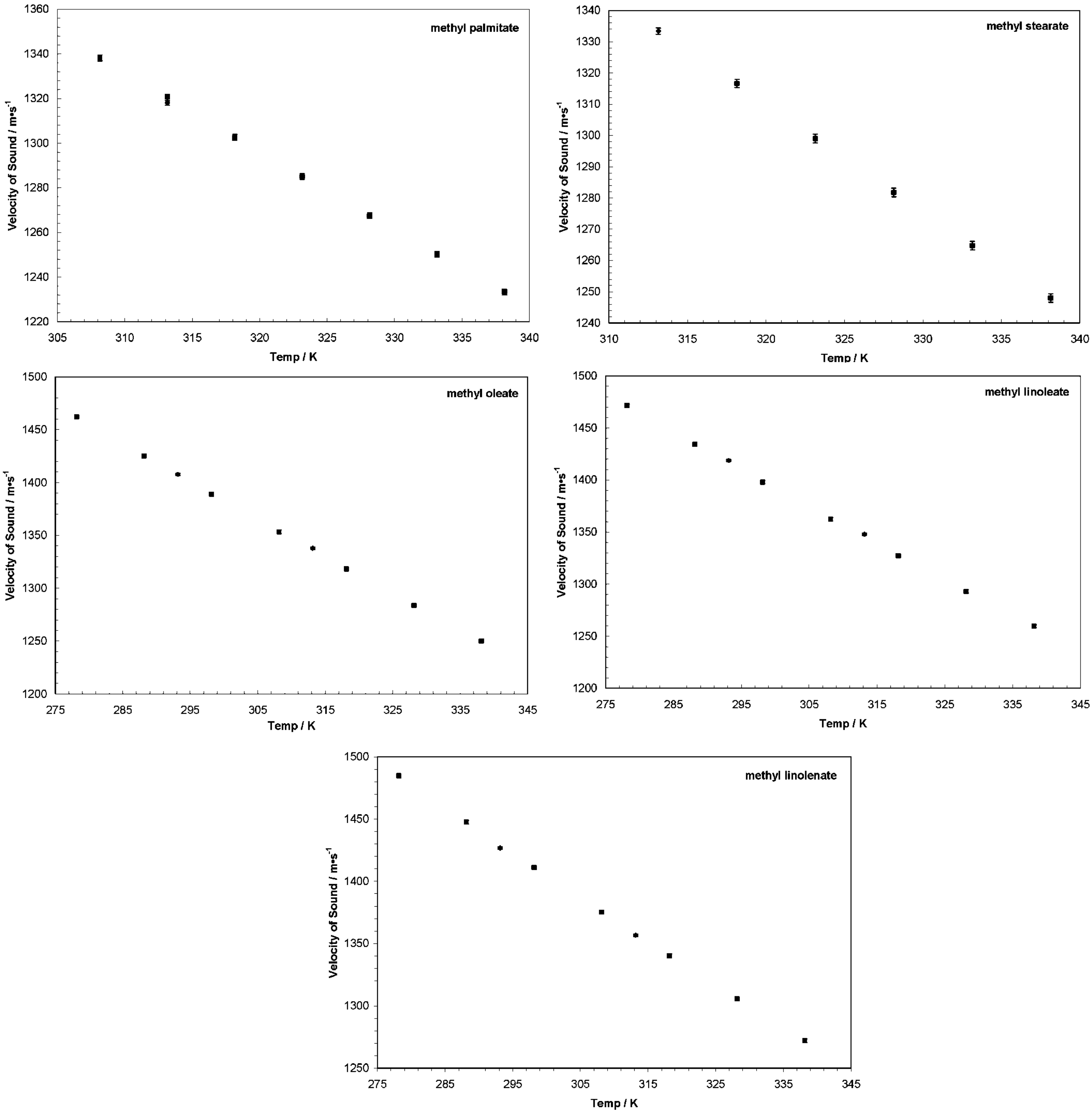

Figure 2. Graphical comparison of the speeds of sound of the five FAMEs studied herein with the previous literature data. For points where the error bars are not visible, the error bars are smaller than the symbols used. The data points above correspond to: ■, Gouw and Vlugter 1964; ◆, current work.

of the density data collected herein are lower in almost every case than those of the literature data, making them valuable for thermodynamic modeling. The speed of sound measurements made herein are consistent with what limited literature values are available and provide needed data for equation of state development. Additionally, the speed of sound measurements of these pure components will be useful for designing fuel injection timing in diesel engines fueled with biodiesel fuel.

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