EXPERIMENTAL STUDY OF THERMODYNAMIC PROPERTIES OF BIOFUEL COMPONENTS

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ABSTRACT

The density (ρ) and speed of sound (u) of two main components of biofuels, methyl laurate and methyl stearate, were measured at temperatures from (283 to 353) K and from (313 to 353) K at atmospheric pressure, respectively. An Anton Paar DSA 5000 M sound-speed analyzer, has been used to simultaneously measurements of the density and speed of sound of the methyl laurate and methyl stearate as the primary components of biodiesel fuel. The measured values of density and speed of sound were used to calculate other derived thermodynamic properties such as adiabatic coefficient of bulk compressibility, coefficient of thermal expansion, isothermal coefficient of bulk compressibility, isochoric and isobaric heat capacities, enthalpy and entropy difference, partial temperature derivative of enthalpy, entropy, and the partial specific volume derivatives of internal energy (internal pressure), of the methyl laurate and methyl stearate as a function of temperature. The overall uncertainties (at the 95 % confidence level) of the reference correlations of the density and speed of sound of methyl laurate and methyl stearate are 0.025 % and 0.045 %, respectively.

Keywords: density, speed of sound, methyl esters (FAMEs), methyl laurate and methyl stearate.

INTRODUCTION

Biofuel, mainly derived from vegetable oils or the fermentation of plant material, have gained importance over the last few decades as more sustainable and environmentally friendly alternatives to fossil fuels. Biodiesel consist of the alkyl monoesters of fatty acids from vegetable oils and animal fats and can be used in existing diesel engines without modification [1]. The properties that have the

greatest effect on the fuel injection timing are the speed of sound, the isentropic bulk modulus, and the viscosity [1,2]. The injection timing changes are causing different exhaust emissions, for example, NO_x emissions increase with advanced timing. The main purposes of the present study are to measure of the density and speed of sound and derived values of adiabatic compressibility, $\beta_S = \dfrac{1}{u^2 \rho}$, of two main constituents of biodiesel (methyl laurate and methyl stearate), at temperatures from melting point to 353 K and atmospheric pressure of (101.325 kPa). There is great scientific interest in study of the thermodynamic properties of main components of biofuels. The thermodynamic properties of biofuels are varying from one biomass feedstock to another. Methyl laurate and methyl stearate are the primary components of biodiesel fuel. The measurements were performed using an Anton Paar DSA 5000 M sound-speed analyzer (viscodensemeter) for the simultaneously measurements of the density and speed of sound temperature range from (283.15 to 353.15) K and atmospheric pressure. This technique was successfully used previously [3-13] to accurate measure thermodynamic, acoustic, and transport properties of different type of natural and molecular liquids. Besides, the key derived thermodynamic properties for practical applications based on the measured data were calculated.

EXPERIMENTAL DATA

There are limited and inconsistent thermodynamic properties data for methyl laurate and methyl stearate in the literature. we are provided the brief review some of the works that are reported the density and speed of sound data for methyl laurate and methyl stearate. Several methods such as DSA 5000M VTD, DMA 5000, and modified Sprengel pycnometers or tube techniques have been applied to accurate measure of the density of methyl laurate and methyl stearate with an uncertainty of (0.05 to 0.1) kg·m⁻³. Reported speed of sound data were measured using Anton Paar DSA 5000 M sound-speed analyzer (visco-densemeter) or pulse-echo speed of sound measurement cell with an uncertainty within (0.1 to 0.5) m·s⁻¹.

EQUATIONS OF STATE AND CORRELATIONS

Correlation equations for density and speed of sound of methyl laurate and methyl stearate at atmospheric pressure, ρ_0, were developed by several authors using own experimental data. As a part of previous studies [3-7], in the present work the thermodynamic (density) and acoustic (speed of sound) properties of the two FAMEs (methyl laurate and methyl stearate) were studied. Another objective of the present study was to calculate other key derived thermodynamic properties of methyl laurate and methyl stearate such as adiabatic coefficient of bulk compressibility, coefficient of thermal expansion, thermal pressure coefficient, isothermal coefficient of bulk compressibility, isochoric and isobaric heat capacities, enthalpy and enthalpy difference, partial pressure derivative of enthalpy, entropy, and partial derivatives of internal energy (internal pressure) based on the measured density and speed sound and the reported thermal pressure coefficient data. The measured density and speed of sound data as a function of temperature together with reported data at atmospheric pressure were used to develop wide - ranged reference correlation equations. The reference correlation equation for density $\rho_0(T)$ (see below Eq. 2) can be used to develop Tait type equation of state to predict high - pressure PVT data as

$$\frac{\rho - \rho_0}{\rho_0} = c \, ln\left(\frac{B+P}{B+P_0}\right) \tag{1}$$

where $\rho_0(T)$ is the temperature dependence of the density as atmospheric pressure P_0=101.15 kPa. Also, other derived caloric properties (C_V, C_P) can be used as a reference data for calculation of other

thermodynamic properties from *PVT* equation of state at high pressures, since the calculations are based on the well-known thermodynamic relations by integrating.

EXPERIMENTAL

The samples (methyl laurate and methyl stearate) were purchased from a commercial supplier with stated purities greater than or equal to 99 wt %. The density and speed of sound of the methyl laurate and methyl stearate at atmospheric pressure (101.325 kPa) at elevated temperatures have been simultaneously measured with a sound-speed analyzer DSA 5000 M (digital VTD, Anton Paar Instrument, Austria) [8-13].

RESULTS AND DISCUSSION

Density

Density measurements were performed at atmospheric pressure of 101.325 kPa as a function of temperature from (283 to 353) K for methyl laurate and from (313 to 353) K for methyl stearateEach density measurement was repeated 5 times for both samples. The average absolute deviations AAD between the present density and the majority of reported data are within 0.03 % (for methyl laurate) and 0.02 % (for methyl stearate).

Speed of Sound

Measurements of the speed of sound of the same FAMEs samples were performed at atmospheric pressure (101.325 kPa) as a function of temperature over a same temperature range as in density experiment, namely, from (283 to 353) K for methyl laurate and from (313 to 353) K for methyl stearate (Table 1). The detailed quantitative comparison of the present measured speed of sound data for methyl laurate and methyl stearate (deviation statistics) with the reported data sources are provided in our publication [13].

Table 1.

Measured densities (ρ), speed of sound (u) and derived values
of adiabatic coefficient of bulk compressibility (β_S) of methyl stearate
and methyl laurate as a function of temperature (T)[a]

T/ K	ρ / kg·m^{-3}	u / m·s^{-1}	$\beta_S \times 10^9$ / Pa^{-1}	T/ K	ρ / kg·m^{-3}	u / m·s^{-1}	$\beta_S \times 10^9$ / Pa^{-1}
	Methyl stearate				**Methyl laurate**		
313.15	850.17	1335.18	0.6598	283.15	877.64	1390.31	0.5895
318.10	846.60	1318.09	0.6799	288.15	873.70	1371.09	0.6088
323.15	842.92	1297.53	0.7047	293.15	869.76	1351.87	0.6291
328.10	839.22	1281.88	0.7252	298.15	865.82	1333.35	0.6497
333.09	835.54	1262.72	0.7506	303.15	861.87	1314.82	0.6712
338.08	831.87	1245.77	0.7746	313.15	853.97	1277.46	0.7176
340.07	830.40	1239.01	0.7844	323.15	846.06	1241.74	0.7665
343.12	827.74	1230.75	0.7976	333.15	838.13	1206.25	0.8200
348.06	824.36	1213.33	0.8240	343.15	830.08	1171.06	0.8785
353.15	821.24	1196.13	0.8511	353.15	822.56	1138.13	0.9385

[a]Standard uncertainties u are: $u(T)$=7.5 mK; $u(\rho)$=0.0025 kg·m^{-3}; $u(u)$=0.05 m·s^{-1}; $u(P = 101.325 \text{ kPa})$= 0.51 kPa; $u_r(\beta_S)$=0.11 %.

Critical assessment reported density and speed of sound data. Primary data selection

In the present work, we have critically assessed all of the reported data for their internal consistence (see above) to carefully select primary data to fit correlation models. The selected primary density and speed of sound data for methyl laurate and methyl stearate together with the present data were fitted to eqs. (2) and (3)

$$\rho(T) = \rho_0 + \rho_1 T + \rho_2 T^2 \qquad (2)$$

$$u(T) = u_0 + u_1 T + u_2 T^2 \qquad (3)$$

All 42 (for methyl laurate) and 25 (methyl stearate) primary speed of sound data deviates from the values calculated from reference correlation eq. (3) within less than 0.1 %, except two data points where the deviations are within 0.12 % and 0.15 % at temperatures of 323.15 K and 333.15 K, respectively (Table 2). The derived thermodynamic properties of methyl stearate calculated and are given in Tables 3.

Table 2.

Values of fitting parameters (ρ_i) and (u_i) of the reference correlation eqs (2) and (3) for density and speed of sound of methyl laurate and methyl stearate together with the deviation statistics

Sample	ρ_0	ρ_1	$\rho_2 \times 10^4$	AAD, (%)	Bias, (%)	St.Dev, (%)	St.Err, (%)	Max.Dev, (%)
Methyl laurate	1097.89608	-0.768915	-0.359156	0.03	0.00	0.04	0.00	0.11
Methyl stearate	1138.61037	-1.087851	5.330402	0.02	0.00	0.03	0.00	0.11
Sample	u_0	u_1	u_2	AAD, (%)	Bias, (%)	St.Dev, (%)	St.Err, (%)	Max.Dev, (%)
Methyl laurate	2784.93874	-6.000006	0.003785	0.04	0.00	0.06	0.01	0.18
Methyl stearate	3016.93713	-7.028059	0.005302	0.05	0.00	0.06	0.01	0.15

Table 3.

Derived, from the present density (ρ) and speed of sound (u) measurements, values of the key thermodynamic properties of methyl stearate

T (K)	$\beta_S \times 10^9$ (Pa^{-1})	$\alpha_P \times 10^3$ (K^{-1})	$\left(\frac{\partial H}{\partial P}\right)_T \times 10^3$ (m$^3\cdot$kg^{-1})	$\left(\frac{\partial U}{\partial V}\right)_T$ (MPa)	$-\left(\frac{\partial S}{\partial P}\right)_T \times 10^6$ (m$^3\cdot$kg$^{-1}\cdot$K^{-1})	$\beta_T \times 10^3$ (MPa^{-1})	γ_V (MPa$\cdot$K^{-1})	C_V (kJ$\cdot$kg$^{-1}\cdot$K^{-1})	C_P (kJ$\cdot$kg$^{-1}\cdot$K^{-1})
313.15	0.6598	0.8868	0.8495	349.09	1.0431	0.7953	1.1151	1.774	2.138
318.10	0.6799	0.8845	0.8490	344.40	1.0449	0.8167	1.0830	1.788	2.148
323.15	0.7047	0.8821	0.8484	338.24	1.0467	0.8425	1.0470	1.810	2.164
328.10	0.7252	0.8796	0.8478	333.84	1.0483	0.8642	1.0178	1.825	2.175

333.09	0.7506	0.8771	0.8473	327.83	1.0500	0.8909	0.9845	1.842	2.189
338.08	0.7746	0.8746	0.8468	322.66	1.0515	0.9161	0.9547	1.857	2.197
340.07	0.7844	0.8735	0.8466	320.58	1.0521	0.9263	0.9430	1.865	2.203
343.12	0.7976	0.8719	0.8463	318.11	1.0529	0.9402	0.9274	1.875	2.210
348.06	0.8240	0.8693	0.8458	312.60	1.0543	0.9676	0.8984	1.892	2.222
353.15	0.8511	0.8666	0.8454	307.28	1.0556	0.9956	0.8704	1.910	2.234

[a]Standard uncertainties u are: $u(T) = 0.01 K$; $u_r(\beta_S) = 0.008\%$; $u_r(\alpha_P) = (0.05 - 0.10)\%$; $u_r(\beta_T) = (0.2 - 0.4)\%$; $u_r(C_V) = (2 - 3)\%$; $u_r(C_P) = (3 - 4)\%$. The values of γ_V were calculated from reference[13] and Tait-type equations of state.

CONCLUSIONS

The density and speed of sound of two FAMEs (methyl laurate and methyl stearate) have been measured over a temperature range from melting points to 353 K at atmospheric pressure. New wide - ranging reference correlations for density and speed of sound of methyl laurate and methyl stearate at atmospheric pressure were developed. The correlations based on the present measured and the critically assessed reported density and speed sound data (primary data). The correlations are applicable over the temperature range from melting point (278.15 K for methyl laurate and 310.95 K methyl stearate) to 353 K, although reasonable safety extrapolation to high temperatures (up to 453 K) is possible. The overall uncertainty of the reference correlations of the density and speed of sound of methyl laurate and methyl stearate are 0.03 % and 0.02 % (for density) and 0.04 % and 0.05 % (for speed of sound), respectively. The measured values of density and speed of sound for the methyl laurate and methyl stearate samples together with reported thermal pressure coefficient, $\gamma_V = \left(\dfrac{\partial P}{\partial T}\right)_V$, data were used to calculate other key thermodynamic properties such as, β_S, β_T, α_P, $\Delta H, \Delta S$, C_P, C_V, $\left(\dfrac{\partial H}{\partial T}\right)_P$, $\left(\dfrac{\partial H}{\partial P}\right)_T$, $\left(\dfrac{\partial U}{\partial V}\right)_T$, and $\left(\dfrac{\partial S}{\partial T}\right)_P$.

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