

THERMODYNAMIC PROPERTIES OF BIOFUEL COMPONENTS

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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 key thermodynamic properties such as the adiabatic coefficient of bulk compressibility (β_s), coefficient of thermal expansion (α_p), isothermal coefficient of bulk compressibility (β_T), isochoric (C_V) and isobaric (C_P) heat capacities, enthalpy (ΔH) and entropy (ΔS) difference, partial temperature derivative of enthalpy $(\partial H/\partial T)_P$ and entropy $(\partial S/\partial T)_P$, and the partial specific volume derivatives of internal energy $(\partial U/\partial V)_T$ (internal pressure) of 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

Thermophysical properties of the fuel components such as density, viscosity, heat capacity, and enthalpy play a fundamental role in mass and heat transfer. 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. Biofuel is a type of fuel derived from organic materials, such as plants and animal waste. It can be used as an alternative to fossil fuels in various applications, including transportation, heating, and electricity generation.

Common types of biofuels include:

1. Ethanol: Made from fermented plant sugars, often derived from corn or sugarcane.
2. Biodiesel: Produced from vegetable oils, animal fats, or recycled cooking oil through a process called transesterification.

Biofuels are considered renewable energy sources because they can be replenished over time. They can help reduce greenhouse gas emissions and dependence on fossil fuels, though their production can also have environmental impacts, such as deforestation or land-use changes.

Biodiesel primarily consists of fatty acid methyl esters (FAME), which are produced from the

transesterification of triglycerides found in vegetable oils, animal fats, or recycled cooking oils. During this process, the triglycerides react with an alcohol (usually methanol or ethanol) in the presence of a catalyst to form biodiesel and glycerin.

The main feed stocks for biodiesel include:

1. Vegetable oils: Such as soybean, canola, palm, and sunflower oil.
2. Animal fats: Such as tallow and lard.
3. Recycled oils: Used cooking oils from restaurants and food processing.

Biodiesel can be used in diesel engines either on its own or blended with petroleum diesel, making it a renewable alternative to traditional fossil fuels. Thus, 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 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, 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 (viscodensimeter) 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 accurately measure thermodynamic, acoustic, and transport properties of different types of natural and molecular liquids. Besides, the key derived thermodynamic properties for practical applications based on the measured data were calculated. There are limited and inconsistent thermodynamic properties data for methyl laurate and methyl stearate in the literature. We are provided the brief review of some of the works that are reported the density and speed of sound data for methyl laurate and methyl stearate.

EXPERIMENTAL AND MATERIALS

Materials

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].

Experimental Method

Several methods such as DSA5000M VTD, DMA 5000, and modified Sprengel pycnometers or tube techniques have been applied to accurately measure 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-densimeter) or pulse-echo speed of sound measurement cell with an uncertainty within (0.1 to 0.5) m·s⁻¹.

The working principle of an oscillation-type densimeter is based on the law of harmonic oscillation, in which a U-tube is completely filled with the sample under study and subjected to an electromagnetic force. The measurement of the frequency and duration of vibration of the tube filled with the sample, allows the determination of the density of the sample. This measuring principle is based on the Mass-Spring Model. The measuring cell consists of an oscillator formed by a hollow U-shaped tube made from glass or metal. The tube has double walls and space between them is filled with a gas with high thermal conductivity. In this space is also placed a platinum resistance thermometer (PRT) that allows the temperature measurement of the sample during the density measurements.

Density measurements with a VTD are based on the dependence of the period of oscillation of a unilaterally fixed U-tube on its mass. This mass consists of the U-tube material and the mass of the fluid

sample under study filled into the U-tube. Vibrating – tube is a technique to determine the density of liquids based on an electronic measurement of the frequency of oscillation, from which the density can be calculated. The well-known principle of vibrating-tube densimeters is based on the theory of vibration and material deformation of mechanical oscillator concerning a U-shaped tube of constant volume filled with a fluid sample. Stationary oscillations of the tube are maintained by the electromagnetic force, generated by means of a drive system, acting on the tube. The two branches of the U-shaped oscillator function as its spring elements. The input signal for the drive system is obtained from a pick-up system that converts mechanical oscillations of the tube into an electrical signal. If the sample volume inside the cell is constant, the oscillations are close to the resonant frequency

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m_0 + V_b \rho_b}} \quad (1)$$

of the tube and are related (function) to the density ρ_b of a fluid filled in; $m_b = \rho_b V_b$ is the sample mass. It is apparent that $\rho_b, m, V_b,$ and f depend on the measurement conditions, *i.e.* on the $T, P,$ and viscosity of the fluid. The period of the oscillation of the filled tube is

$$\tau = f^{-1} \quad \text{or} \quad \tau = 2\pi \sqrt{\frac{m + V_b \rho_b}{k}} \quad (2)$$

Applying the square of Eq. 2 we can obtain the working equation for this method as

$$\rho_b = A - B\tau^2 \quad (3)$$

where instrument constants (parameters) $A = \frac{m}{V_b}$ and

$B = \frac{k}{4\pi^2 V_b}$ in which the cell volume and the cell mass are involved as well as the spring constant k of the measuring cell are both functions of temperature and pressure. Usually the temperature and pressure dependences of the parameters A and B are determined using the calibration procedures with a minimum of two reference fluids such as water, air, nitrogen, benzene, and toluene whose PVT properties are well known and should be performed very carefully (Lemmon et al. 2010). Particularly, the instrument constant, as this follows from Eq. 3, The calibration

constant $B = \frac{\rho_1 - \rho_2}{\tau_2^2 - \tau_1^2}$, can be determined by measuring

the oscillation periods (τ_1^2 and τ_2^2) for two reference fluids with well-known densities (ρ_1 and ρ_2). The parameter B is approximately a linear function of temperature (slope is about 10^{-4} to 10^{-3} K⁻¹). The accuracy of the method is limited by the calibration procedure and depends on the uncertainty of the properties of calibrating fluid. The temperature in the measuring cell, where located the U-tube, was

controlled using a thermostat with an uncertainty of 10 mK and measured using the (ITS-90) PRT100 thermometer with an uncertainty 0.03 K. This densimeter (DMA4500) allows for a highly precise density measurements in the wide measuring range from (0 to 3000) kg·m⁻³ and at temperatures from (273 to 363) K. The uncertainty of the density measurements is 5×10⁻⁵ g·cm⁻³ (or about 0.005 %). The repeatability of density and temperature measurements are 1×10⁻⁵ g·cm⁻³ and 0.01 K, respectively. This type VTD has

been successfully used previously in our earlier publications to accurate measure of the density of various fluids (ionic liquids, hydrocarbons, and their mixtures with alcohols (Abdulagatov *et al.* 2008a-d; Schmidt *et al.* 2012).

During the oscillation of the U-tube, the sample shows the effect of damping of the oscillation, which is function of the sample viscosity. Correction related with influence of the viscosity can be estimated as (Segovia *et al.* 2009)

$$\rho_{cor} = \rho_{unc} [1 - (0.4482\sqrt{\eta} - 0.1627)10^{-4}] \quad (4)$$

where ρ_{cor} is the “corrected” and ρ_{unc} “uncorrected” densities. This correction for our geothermal samples is within (0.001 to 0.004) %. The total absolute uncertainty (kg·m⁻³) in density measurements caused by the viscosity and oscillation nodes move effects can be approximately estimated as $\Delta\rho_b \approx 0.05\sqrt{\eta}$, where η is the viscosity of fluid in mPa·s. The correction for the present geothermal samples is within from (0.03 to 0.06) kg·m⁻³ or (0.0035 to 0.006) %.

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].

Derived Thermodynamic Property Data

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. (5) and (6)

$$\rho(T) = \rho_0 + \rho_1 T + \rho_2 T^2 \quad (5)$$

$$u(T) = u_0 + u_1 T + u_2 T^2 \quad (6)$$

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 1).

Based on the measured density and speed of sound data together with the selected reported vapor-pressure data the derived key thermodynamic properties of methyl stearate have been calculated using well-known thermodynamic relations. The calculated values of the thermodynamic property data of methyl laurate are given in Tables 2.

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 stearate. Each 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 in our previous publications. The detailed quantitative comparison of

Table 1.

Values of fitting parameters (ρ_i) and (u_i) of the reference correlation eqs. (5) and (6) for density and speed of sound of methyl laurate and methyl stearate together with the deviation statistics

Sample	ρ_0	ρ_1	ρ_2	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 2.

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

$T(K)$	$Q_s \times 10^9 (Pa^{-1})$	$a_p \times 10^3 (K^{-1})$	$\left(\frac{\partial H}{\partial P}\right)_T \times 10^3 (m^3 \cdot kg^{-1})$	$\left(\frac{\partial U}{\partial V}\right)_T (MPa)$	$-\left(\frac{\partial S}{\partial p}\right) \times 10^6 (m^3 \cdot kg^{-1} \cdot K^{-1})$	$Q_T \times 10^3 (MPa^{-1})$	$V (MPa \cdot K^{-1})$	$C_V (kJ \cdot kg^{-1} \cdot K^{-1})$	$C_P (kJ \cdot kg^{-1} \cdot K^{-1})$
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

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.

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THERMODYNAMIC PROPERTIES OF BIOFUEL COMPONENTS

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