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High pressure physicochemical properties of biodiesel components used for spray characteristics in diesel injection systems

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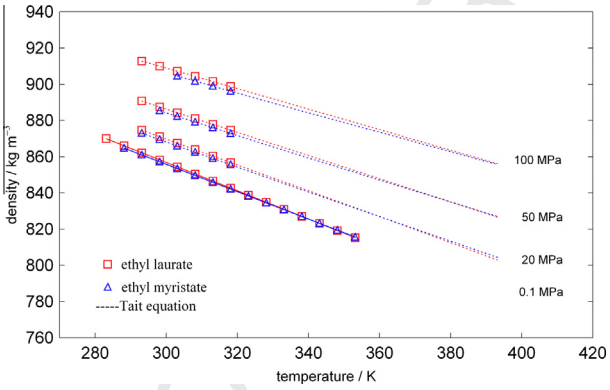
HIGHLIGHTS

- Density isotherms cross each other.
- Differences between densities increase with increasing pressure.
- Thermal expansivity is independent of temperature at high pressure.

GRAPHICAL ABSTRACT



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ABSTRACT

The two components of biodiesel derived from coconut oil or babassu oil such as ethyl laurate and ethyl myristate are studied. The speeds of sound were measured within the temperatures from 293 to 318 K and at pressures from 0.1 MPa to 101 MPa. The densities and heat capacities were measured under atmospheric pressure in the temperature range from 283 to 353 K and 286 to 341 K, respectively. The densities, isobaric heat capacities, isentropic and isothermal compressibilities, and isobaric thermal expansions as functions of temperature and pressure have been calculated using the experimental results. The results obtained show that the densities of ethyl myristate are lower than that of ethyl laurate below intersection temperature while at higher temperatures the densities ethyl myristate are higher than that of ethyl laurate. Moreover, analysis of the temperature dependence of density of esters under test using the Tait equation shows that the intersection temperature probably moves toward higher temperatures with increasing pressure. Additionally, for a given temperature, the differences between densities of the ethyl esters under test increases with increasing pressure. The isobaric thermal expansivity is approximately independent on temperature at pressures higher than 80 MPa and 60 MPa for ethyl laurate and ethyl myristate, respectively.

1. Introduction

The most common fatty esters contained in biodiesel are those of palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. This holds for biodiesel feedstock, such as soybean, sunflower, and rapeseed. However some tropical oils, such as coconut oil or babassu oil contain significant amounts of shorter chain saturated acids, such as lauric acid, myristic acid, caprylic acid, and capric acid [1,2]. Saturated fatty esters possess higher CN and better oxidative stability than their unsaturated counterparts. Using thermal efficiency data, it was originally suggested that ethyl esters of

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monounsaturated or short-chain saturated fatty acids should make good alternative fuels and that they should be evaluated in long-term engine tests [3]. If saturated fatty acids are preferred due to their greater oxidative stability, esters of decanoic acid appear advantageous because they offer a compromise between cold flow and cetane number. Moreover, by having accurate knowledge of the influence of the molecular structure on the properties determined, the modification of the fatty ester composition can be applied for improving biodiesel fuel properties. Important fuel properties of biodiesel that are influenced by the fatty acid profile and, in turn, by the structural features of the various fatty esters include ignition quality, heat of combustion, cold flow, oxidative stability, exhaust emissions, lubricity, viscosity and density. Fuel density affects the mass of fuel injected into the combustion chamber and thus, the air–fuel ratio. This is because fuel injection pumps fuel by volume not by mass and a denser fuel contains a greater mass in the same volume. Thus, the changes in the fuel density will influence engine output power due to a different mass of fuel injected [4]. Isobaric thermal expansion and compressibility, characterize how temperature and pressure affect density. As the propagation of sound is an adiabatic process, the acoustic method gives the most reliable values of the adiabatic compressibility [5]. The interest in this material constant has been increased in the last years due to the development of the common rail system in the diesel engines. In the common rail engines, the fuel is injected into the combustion chamber under pressure up to 250 MPa. The injection is very rapid, thus approximately adiabatic. Therefore, the adiabatic compressibility is particularly useful in the estimation of the fuel injection timing [6–8].

In the present paper, we report experimental speeds of sound in ethyl laurate and ethyl myristate measured within the temperatures from 293 to 318 K and at pressures from 0.1 MPa to 101 MPa, as well densities and heat capacities measured under atmospheric pressure in the temperature range from 283 to 353 K and 286 to 341 K, respectively. The densities and isobaric heat capacities at pressures up to 100 MPa were calculated from experimental data according to the suggestion of Davis and Gordon [9]. To this end, a slightly modified procedure of Sun et al. [10] was applied. We aimed this work mainly at comparison of effects of pressure and temperature on density, adiabatic compressibility, and isobaric thermal expansion of ethyl laurate and ethyl myristate. Furthermore, we tried to find out whether the differences in the material constants of the studied fuels are significant from the practical point of view. Data similar to those reported in this work have been used in calculations of other thermodynamic parameters, in simulations, and as a reference material for tests of performance characteristics of diesel engines [6–8,11–14].

2. Experimental section

2.1. Materials

Ethyl laurate from Aldrich, minimum 0.98 (GC) mass fraction purity, and ethyl myristate from Aldrich, 0.99 (GC) mass fraction purity have been used in this work. The content of the main component was checked by gas chromatograph and was found to be 0.995 mass fraction.

2.2. Ultrasonic speed measurements

The speed of sound in liquids under test has been measured at atmospheric and higher pressures using two measuring sets designed and constructed in our laboratory [15,16]. Two measuring vessels of the same acoustic path and construction have been used, one of them designed for measurements under atmospheric pressure, the other one for measurements under elevated pressures. The measuring set applies the pulse-echo-overlap principle. In the acoustic cell, a single transmitting–receiving ceramic transducer operating at 2 MHz frequency was applied together with and an acoustic mirror. The pressure was applied by a hand-operated hydraulic press connected with the chamber by a system of high-pressure capillary tubes and valves. The pressure was stabilized to within 0.03 MPa and was measured with a strain gauge measuring system (*Hottinger Baldwin System P3MD*) with accuracy better than 0.15%. During the measurements, the temperature is stabilized within the limits of ±0.01 K by a Haake DC 30 temperature controller, and measured using an Ertco Hart 850 platinum resistance thermometer (traceable to a NIST standard) with an uncertainty of ±0.05 K and resolution of 0.001 K.

The uncertainty of the speed of sound measurements was estimated to be 0.03% at atmospheric pressure, 0.04% under pressures up to 60 MPa and 0.05% under pressures from 60 MPa to 101 MPa. Other details of the high-pressure device and the method of the speed of sound measurements can be found in a previous papers [15,16].

2.3. Density measurements

The densities at atmospheric pressure were measured using a vibrating tube densimeter Anton Paar DMA 5000. The uncertainty of the density measurements was 0.05 kg m^{-3}, whereas the repeatability was estimated to be better than 0.005 kg m^{-3}.

2.4. Specific heat capacity measurements

The specific isobaric heat capacity was measured by a high sensitivity differential scanning calorimeter Micro DSC III, manufactured by Setaram and based on the Tian–Calvet principle. The uncertainty of the isobaric heat capacity measurements was ±0.15%. More details of the measurement procedure can be found in [17].

3. Measurement results

The ultrasonic speeds in compressed liquids were measured at temperatures from 293 to 318 K in about 5 K steps and under pressures up 101 MPa. The experimental values are listed in Table 1. The densities were measured under atmospheric pressure in the temperature range from 283 to 353 K in 5 K steps. The experimental values are collected in Table 2. The specific isobaric heat capacities were measured at atmospheric pressure and at temperatures from 286 to 341 K in about 0.02 K steps. In this way, ca. 3400 experimental points have been collected for each liquid. Therefore the values of isobaric specific heat capacity every 5 K are collected in Table 3.

The dependencies of the speed of sound, density, and isobaric specific heat capacity on temperature at atmospheric pressure were approximated by the following polynomials of the type:

$$y = \sum_{j=0}^{2} b_j T^j, \qquad (1)$$

where y, is the speed of sound; u_0, density; ρ, or isobaric specific heat capacity; C_p, at atmospheric pressure p_0; b_j are the polynomial coefficients ($b_j = c_j$ for the speed of sound, $b_j = \rho_j$ for the density, and $b_j = h_j$ for the isobaric specific heat capacity) calculated by the least squares method. The backward stepwise rejection procedure was used to reduce the number of non-zero coefficients. The coefficients and standard deviations from the regression lines are given in Table 4. The standard deviations are much smaller than the measurements accuracy.

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