Fuel 165 (2016) 244–251

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Biodiesel density and derived thermodynamic properties at high pressures and moderate temperatures

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HIGHLIGHTS

- Viscosity and refractive index of sunflower oil and lard biodiesels at 0.1 MPa.
- Density of sunflower oil and lard biodiesels at high pressures.
- Correlation of high pressure density using the modified Tammann–Tait equation.
- Calculation of the isobaric thermal expansivity and the isothermal compressibility.
- Sunflower oil methyl esters are more dense than its ethyl esters.

ARTICLE INFO

Article history:
Received 17 June 2015
Received in revised form 25 August 2015
Accepted 14 October 2015
Available online 23 October 2015

Keywords:
High pressure density
Isothermal compressibility
Isobaric thermal expansivity
Sunflower oil biodiesels
Viscosity
Refractive index

ABSTRACT

Knowledge of the basic thermodynamic properties of biodiesel under different conditions is necessary because of its wide use as a substitute for fossil fuels. The viscosities and refractive indices of the methyl and ethyl esters of the fatty acids from sunflower oil were measured at atmospheric pressure and at temperatures 288.15–373.15 K and 288.15–343.15 K, respectively. The same properties were measured also for the methyl esters of the fatty acids from lard at atmospheric pressure and at temperatures 298.15–373.15 K and 298.15–343.15 K, respectively. The densities of the mentioned biodiesel samples were measured at temperatures up to 413.15 K and at pressures 0.1–60 MPa. The experimental density values were correlated using the modified Tammann–Tait equation. Based on the obtained results, thermodynamic behavior, such as the isothermal compressibility, the isobaric thermal expansivity, the internal pressure and the difference between the specific heat capacity at constant pressure and at constant volume, were calculated. The absolute average deviations between measured densities and those calculated using the modified Tammann–Tait equation of about 0.006% for all of the three examined samples confirm the accuracy of the modeling and reliability of the calculated derived properties.

1. Introduction

In past few decades more attention has been paid to production and using of biofuels, especially biodiesel, because of the significant disadvantages of the use of fossil fuels and their limited supplies. Biodiesel is usually produced by transesterification reaction, where triacylglycerols (TAGs) from a vegetable oil or animal fat reacts with a short-chain alcohol in the presence of a catalyst, commonly a base [1,2]. The products of the reaction are alkyl esters of the fatty acids from the starting raw material. Almost from the beginning of the use of diesel engines, there has been an idea of using vegetable oils or fats as a fuel but their high viscosity and low volatility can cause various operational problems in a diesel engine, so it is not recommended [1,3,4]. Precisely because of this, the transesterification reaction is performed in order to convert TAGs from oils and fats to fatty acid alkyl esters that have the kinematic viscosity much closer to that of petro-diesel [1,5]. Biodiesel should meet different quality standards in order to be accepted as a fuel for diesel engines; in Europe it is EN 14214 [6] for fatty acids methyl esters, while ASTM D6751 [7] is applied in the U.S.A. These standards set requirements regarding composition, stability, thermodynamic and combustion properties of the biodiesel.

Biodiesels are interesting mostly because of their use as alternative fuels for diesel engines, pure or mixed with a petro-diesel in various proportions, without significant corrections in engine design. Some of the reasons for replacing a petro-diesel with biodiesel are preferred reduction in the carbon monoxide, carbon

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http://dx.doi.org/10.1016/j.fuel.2015.10.050
0016-2361/

dioxide, unburned hydrocarbons and particulate matter emissions, although, in most cases, increasing the emission of the nitrogen oxides, compared to the use of petro-diesel [3,8,9]. Their important advantages over petro-diesel are renewability, non-toxicity, biodegradability, being sulfur free and having higher lubricity [3]. They also have higher cetane number, depending on the composition of the fatty acids alkyl esters, and therefore shorter ignition delays [1,8]. However, biodiesels contain about 10% oxygen by weight, leading to a lower calorific value and further to a greater fuel consumption [5,10]. Thanks to its favorable impact on the environment, the utilization of biodiesel instead of petro-diesel is recommended by a law in most countries. The directive of the European Union on replacing at least 10% of the petro-diesel with biodiesel or other renewable fuels in the transport sector by 2020 has increased the use of biodiesel and its blends with petro-diesel [11]. The biodiesels produced from animal fats have a higher melting temperature than those originating from vegetable oil, due to a significant share of saturated fatty acids, so as it cannot be used as a fuel in a diesel engine as pure. However, biodiesels derived from animal fats have higher calorific value and cetane number than those obtained from vegetable oils, and can be used in boilers for heat generation in their original form [12].

A pressure wave in the injector's feed pipe that is generated during the operation of the diesel engine can change the mass flow rate of the injected fuel [13]. The fuel injection and combustion are performed at high pressures and moderate temperatures and are affected by fuel volumetric properties, such as density and viscosity [14–16]. Therefore, knowledge of these properties, at various pressures and temperatures, is of utmost importance when using biodiesel. Density data of biodiesel that can be found in the literature are mostly measured at atmospheric pressure [17–19], and recently papers reporting densities of various fatty acids esters at high pressures have been published [14,20–23]. There are a few papers where biodiesels from sunflower oil and lard are examined [24], even though sunflower oil is among the most commonly used raw materials for biodiesel production. Densities of the methyl (SME) and ethyl (SEE) esters of the fatty acids from sunflower oil, at temperatures 288.15–413.15 K (at 16 isotherms), and of the methyl esters of the fatty acids from lard (LME), at the temperatures 298.15–413.15 K (at 14 isotherms) and at pressures 0.1–60 MPa, are presented in this work. Also, viscosities of SME, SEE and LME at temperatures up to 373.15 K and refractive indices of the same samples at temperatures up to 343.15 K, were measured at atmospheric pressure.

The experimental density values, at various pressures and temperatures, were modeled using the modified Tammann–Tait equation, an empirical model widely used for correlating of densities at high pressures. Based on the obtained parameters of the modified Tammann–Tait equation, the isobaric thermal expansivity, the isothermal compressibility, the internal pressure and the difference between the specific heat capacity at constant pressure and at constant volume, were calculated. The mentioned derived properties describe thermodynamic behavior of the samples, which is very useful for the calculations related to the injection of biodiesel in diesel engine.

2. Experimental section

2.1. Materials

The biodiesels examined in this work were synthesized by transesterification of sunflower oil with methanol and ethanol and lard with methanol. The transesterification reactions with methanol were carried out in a stirred batch reactor at temperature 333.15 K in molar ratio 6:1 (methanol: sunflower oil or lard) where KOH was used as a catalyst (1 mass% of the sunflower oil or lard mass). The transesterification with ethanol was conducted at 343.15 K in molar ratio 12:1 (ethanol: sunflower oil) with CaO as a catalyst (15 mass% of the sunflower oil mass). Fatty acid composition of the sunflower oil and lard used as a raw material, determined by using gas chromatography method [25] and the composition of the produced biodiesels, determined by using high-performance liquid chromatography method [26], are presented in Table 1. Some of the most important properties of the biodiesels are, also, given in Table 1 and compared to the values prescribed by standards [6,7]. Cetane number was calculated according to equation proposed by Knothe [27].

Table 1
Properties of the biodiesels and comparison with standard values [6,7].

Property	Unit	Limits		Test method	SME	SEE	LME
		Min	Max				
FAME content	% (m/m)	96.5	–	EN 14103	98.7	96.8	96.3
Density at 15 °C	kg/m^3	860	900	EN ISO 3675 EN ISO 12185	888.2	883.7	–
Viscosity at 40 °C	mm^2/s	3.5 1.9	5.0 6.0	EN ISO 3104 D 445	4.915	4.524	4.687
Cetane number	–	51 [6] 47 [7]	–		51	51	72
Water content	mg/kg	–	500	EN ISO 12937 D 2709	110	150	355
Acid value	mg KOH/g	–	0.50	EN 14104 D 664	0.42	0.40	0.46
Iodine value	$g\ I_2/100\ g$	–	120	EN 14111	120	120	56
Polyunsaturated (⩾4 double bonds) methyl esters	% (m/m)	–	1.00	EN 15779	0	0	0
Group I metals (Na + K)	mg/kg	–	5.0	EN 14108 EN 14109	<1	5	0.2
Linolenic (C18:3) acid ester	% (m/m)	–	12.0	EN 14103	0	0	0.24
Myristic (14:0) acid ester	% (m/m)				0.08	0.08	0
Palmitic (C16:0) acid ester	% (m/m)				8.03	8.03	28.63
Stearic (C18:0) acid ester	% (m/m)				3.26	3.26	16.98
Oleic (C18:1) acid ester	% (m/m)				29.27	29.27	43.52
Linoleic (C18:2) acid ester	% (m/m)				59.32	59.32	10.63
Monoglyceride content	% (m/m)				0.4	0.3	1.1
Diglyceride content	% (m/m)				0.9	2.5	2.5
Triglyceride content	% (m/m)				0	0.4	0.1