Biomass and Bioenergy 96 (2017) 87–95

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Density, viscosity and specific heat capacity of diesel blends with rapeseed and soybean oil methyl ester

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ARTICLE INFO

Article history:
Received 1 April 2016
Received in revised form
13 November 2016
Accepted 16 November 2016
Available online 23 November 2016

Keywords:
Density
Viscosity
Specific heat capacity
Biofuel
High pressure

ABSTRACT

By 2020, the EU aims to have 10% of the transport fuel of every EU countries come from renewable sources such as biofuels. Fuel suppliers are also required to reduce the greenhouse gas intensity of the EU fuel mix by 6% in comparison to 2010. The thermophysical properties of biofuels are, therefore, required for the efficient design of every step in their production, distribution, and utilization. Despite of these needs, high pressure thermodynamical characterization of biofuels is not still exhaustive. Next generation injection systems work with pressure up to 300 MPa, but available measurements are limited to 200 MPa. Measurements extrapolation generally are not recommended at these pressure because it can hide freezing phenomena here documented at temperature of (20 and 30) °C. In this work, density and viscosity of pure and blended FAME (SME and RME) biofuels have been measured up to 300 MPa. Since the scope of the work is both to investigate cold start conditions found in engines and the thermal behaviour of fuels in tanks of cars, petrol station and dispenser, the temperature interval is limited to (0 −60) °C. In particular, it has been observed a partial freezing even for temperature up to 30 °C. Density and viscosity values were obtained by direct experimental measurements, while heat capacities have been calculated using density and speed of sound results previously obtained. At ambient pressure conditions, the uncertainty in density measurements was between 0.005% and 0.01% (k=2) and for viscosity measurements the uncertainty was between 0.2% and 1.3% (k=2). At elevated pressures the uncertainty in density measurements was 0.08% (k=2), while for viscosity and heat capacity it was 2% (k=2).

1. Introduction

Europe has defined ambitious targets for the development of biofuels with the aim of improving domestic energy security, improving the overall CO_2 balance and sustaining European competitiveness. In particular, European Directive 2009/28/EC on the promotion of the use of energy from renewable sources endorsed, in Article 3, a mandatory target of a 20% share of energy from renewable sources in overall European Community energy consumption by 2020 and a target of at least 10% of the final consumption of energy in transport. A deep understanding of the physical properties of biofuels will help to identify appropriate utilization areas and reduce the impact on climatic changes, but there is a lack of a sufficient amount of data to implement dedicated and accurate equations of state for simulations and practical approaches to composition dependent properties. For these reasons, the availability of thermophysical properties, such as density, viscosity and heat capacity of fuels and biofuel blends if of fundamental importance, especially, for legal purposes, for ensuring proper trade, enabling process control, ensuring proper operation and in developing new automotive applications, beside being input quantities needed to determine the process efficiency of injection, atomization, ignition, and combustion of fuel in the engine. For example, legal metrology considers density and its temperature dependence as crucial quantities to convert the measured volumes to a standard volume at 15 °C in order to ensure fair trade. The objective of this work is to provide traceable and reliable thermophysical data to help enable this major goals. As proof that the

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http://dx.doi.org/10.1016/j.biombioe.2016.11.009
0961-9534/

problem is still of importance, there are very recent published papers about these topics. For example, the work of Galle et al. [1] investigates the atomization processes using different biofuels and atomizing particles at different temperatures and for pressures up to 120 MPa. Results show how viscosity has a significant influence on atomization process. Furthermore, injection systems dealing with non-esterified oils are considered in the work of Vojtisek-Lom et al. [2], where biofuels were heated or cooled before being injected into the combustion chamber. The conclusion of this study is that viscosity, bulk modulus and density are fuel properties having the major impact on injection timing and emission control. Finally, Caresana [3] investigated the relation between injection conditions and emissions, finding that fuels physical properties are not the only quantities needed to describe the combustion process, but that the mechanics of the injection system plays its part. However, there is a general agreement that physical parameters are necessary for the optimization and the improvement of the combustion process to achieve a reduction in fuel consumption, pollutant emission and noise.

Despite the introduction of biofuels occurred years ago, their physical characterization is, mainly, focused at atmospheric pressure and as a function of temperature. Just for citing some works of recent years, the paper of Esteban et al. [4] shows density and viscosity measured between 10 °C and 140 °C at ambient pressure; Alptekin et al. [5] measured density at 15 °C for up to 75% biofuels blends and viscosity at 40 °C in the same samples. Among papers dealing with high pressure measurements, there is the interesting work of Habrioux et al. [6], where density is measured up to 100 MPa and speed of sound up to 200 MPa. The paper of Dzida et al. [7], focused on rapeseed oil methyl ester, extends the temperature range to 273 K, but with a maximum pressure limited to 100 MPa. The densities and viscosities of several biodiesel fuels from different feedstocks were measured between 5 °C and 100 °C by Laesecke et al. [8]. Viscosity measurements have been reported by Freitas et al. [9] up to 140 MPa starting from the temperature of 293.15 K in different soybean and rapeseed blends by means of a vibrating wire sensor. Instead, Paton et al. [10] used falling sinker viscometer up to 160 MPa. Also in present work, viscosity has been measured using this last method, but for pressure up to 300 MPa.

Considering that with increasing injection pressure the combustion processes become more efficient, next engines generation most probably will work at pressure between 200 MPa and 300 MPa [11]. For this pressure range there aren't direct measurements and extrapolations, obtained using lower pressure values, are not recommended, because it is expected that, depending on biodiesel composition, part of the fuel compounds can freeze.

Themophysical parameters of fossil fuels, which are used for volume measurement (for legal purposes) and for process control in engines (for industrial purposes [12]), cannot be readily transferred to biofuels. Specifically, the temperature and pressure dependence of key properties, such as density and viscosity, can be appreciably different from those of conventional hydrocarbon-based fuels.

2. Experimental

2.1. Materials

Pure mineral diesel (summer quality) was provided by Shell Deutschland Oil GmbH, Hamburg, Germany, while biodiesels rapeseed oil methyl ester (RME) and soybean oil methyl ester (SME) were provided by ADM Research GmbH, Hamburg, Germany. These components were used to prepare blends denoted in the usual way by Bx-RME or Bx-SME (where x represents the percentage volume fraction of the biofuel in the blend on the base of 15 °C). In addition to the pure B100-RME, B100-SME and B0 (summer diesel), the investigation covered the blends B5-RME, B5-SME, B10-RME, B10-SME, B15-RME and B15-SME. The blends were prepared gravimetrically at PTB and then sent to the partners at NEL, INRiM and LNE-CNAM. One SME tank showed precipitates in the liquid, it was therefore filtered before further usage.

Composition of the fatty acid methyl esters profile of the SME and RME samples has been determined by capillary gas chromatography in combination with flame ionization detection (GC-FID), carried out by JRC-IRMM (Institute for Reference Materials and Measurements). Obtained results are reported in Table 1, where the name of the determined fatty acid methyl ester, its concentration and the uncertainty associated to the measure is given. Measurement results are divided in two different classes: namely fully validated and not-fully validated. The fully validated values were obtained using methods validated on the basis of EURACHEM [13] and IUPAC [14] guidelines that have been tested both with reference test samples [15] [16] and with results obtained by other research institutes. The latter are measurements obtained on compounds that were not selected for comparisons. Expanded uncertainties (k=2) have been determined according to the Guide to the Expression of Uncertainty (GUM) [17], and it corresponds to a confidence interval of approximately 95%. For not-fully validated results, reported uncertainty values correspond with the standard deviation obtained by three independent measurements.

Certificate analysis of pure RME and SME, obtained according to DIN EN 14214-12710, are reported in Table 2. For the pure soybean and rapeseed oil methyl esters, together with blends B5, B10 and B15, the University of Rostock determined, by means of Karl-Fischer titration, that the water content did not exceed 0.024% by weight. All the investigated samples have been preserved in a dark room and the measurements have been carried out generally within three months since the opening of the tin.

2.2. Ambient pressure density measurements

PTB, LNE-CNAM and NEL made measurements of the density of the samples at ambient pressure. Comparisons were carried out in the temperature range between 0 °C and 50 °C.

At PTB, measurements of the density were carried out using an Anton Paar DMA 5000 oscillatory densimeter. The thermal insulation of the measuring cell of this densimeter was modified to enable measurements across an extended temperature range between −20 °C and +50 °C. Viscosity correction was considered negligible for the biofuels under study, since their viscosities were found generally to be below 10 mPa s. The samples were injected into the measuring cell by using glass syringes with steel needles. The volume of the syringes (12 ml) was chosen to be about 5 times larger than that of the measuring cell in order to be able to repeat the measurement and rinse the cell from parts of the samples which had been in contact with air at the opening of the needle during transfer from stock bottle to the densimeter.

Since fatty acid ester components of biofuels are capable of dissolving and penetrating plastic materials, the operating procedure generally excluded contact of the samples with plastics on the input side. The exit of the measuring cell was connected via a hose (about 0.5 m in length) with a bottle to collect used samples. A hole of 0.5 mm diameter was bored into the cover of this bottle for pressure relief during temperature changes, while the input side was closed by the syringe. This arrangement ensured that evaporation losses of the sample could not affect the measurement results. Calibration of the densimeter was carried out using pure water and the reference materials n-nonane and EF164, as provided by PTB. After injection of the sample, a temperature run was started at 50 °C. At each temperature step of 5 °C down to 0 °C, the sample