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Thermodynamic properties of biodiesel and petro-diesel blends at high pressures and temperatures. Experimental and modeling

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HIGHLIGHTS

- Viscosity of lower sunflower oil biodiesels and petro-diesel blends at 0.1 MPa.
- Density of sunflower oil biodiesels and petro-diesel blends at high pressures.
- Correlation of high pressure density using the modified Tammann-Tait equation.
- Calculation of the isothermal compressibility and the isobaric thermal expansivity.
- Correlation of viscosity at 0.1 MPa using Vogel-Tammann-Fulcher model.

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ABSTRACT

One of the solutions to greenhouse gases emission is the use of biodiesels, since their mixtures with petro-diesel can be used as fuel in existing diesel engines without additional corrections in engines' design. In order to estimate engine performance and increase its efficiency, it is necessary to know the basic properties of fuels under different operating conditions, and among the most important ones are density and viscosity. Therefore, the densities of pure petro-diesel, as well as densities of its blends with sunflower oil methyl and ethyl esters, in the ratio of 10 vol% and 20 vol% of the biodiesel, at temperatures 293.15–413.15 K and at pressures of 0.1–60 MPa, are presented here. Measurements were taken at an Anton Paar DMA HP densimeter. For the device calibration the classical calibration method with one reference fluid was applied. Also, for the same samples, the viscosities at 288.15–373.15 K and the refractive indices at 288.15–343.15 K at atmospheric pressure were measured. Measured densities decrease linearly as temperature rises along isobars and increase with pressure rise at a constant temperature for all examined samples. Refractive index, also, decreases linearly with temperature rise, while viscosity decreases exponentially with increase in temperature. Densities and refractive indices are higher for blends with sunflower oil methyl esters than with its ethyl esters, opposite to viscosity. Densities of blends increase linearly with rise in biodiesel share, while the increase of viscosity is exponential. Density data were fitted to the modified Tammann-Tait equation and the obtained results were used for calculation of derived thermodynamic properties such as the isothermal compressibility, the isobaric thermal expansivity, the internal pressure and the difference between specific heat capacity at constant pressure and the specific heat capacity at constant volume. The absolute average percentage deviations of the measured densities from those calculated using the modified Tammann-Tait equation were about 0.01%, for all studied samples, assessing positively the correlation procedure. The dependence of the measured and calculated properties of the blends on biodiesel amount was also examined.

1. Introduction

Harmful environmental impact of the fossil fuels use, as well as reduction of their reserves leads to enormous interest in alternative energy sources. Governments of many countries have been implementing measures, such as more stringent norms for exhaust gases and feed-in tariffs that encourage the use of renewable energy sources, in order to increase the replacement of fossil fuels by biodegradable and environment-friendly substitutes. One of solutions for transport sector is the use of biodiesel because it is miscible with petro-diesel in all portions and can be used in diesel engines without any correction in engine design [1–3].

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Biodiesel is a mixture of alkyl esters of long-chain fatty acids produced from vegetable oils or animal fats in transesterification reaction with alcohol, that meets relevant standards, EN 14214 [4] in Europe and ASTM D6751 [5] in the U.S.A. [1,6,7]. They are carbon neutral, less toxic and produce less greenhouse gases during combustion than petro-diesel [8–10]. Although they can be applied neat in new-generation diesel engines, their lower blends with petro-diesel are more favorable for common transport usage [11,12].

Biodiesel has higher density and viscosity than conventional diesel which affects the atomization process of fuels resulting in poorer combustion and reduction of the usable power delivered by an engine. For blends of biodiesel and petro-diesel with portion of biodiesel up to 20% the decrease of the output power of a diesel engine is significantly lower than for pure biodiesel [13,14]. Biodiesel also contains about 10% of oxygen leading to lower calorific value relative to petro-diesel. It causes higher mass consumption of biodiesel per unit of work done by engine, however for lower biodiesel and petro-diesel blends that increase was not so noticeable [13,14]. The same conclusion can be derived for thermal efficiency of an engine which decreases as percentage of biodiesel increases but for mixtures with up to 20% of biodiesel it is very similar to that of a pure petro-diesel [11–14]. As for exhaust gases emission, which is the most important reason for biodiesel use, emission of CO, as well as exhaust gas temperature, is reduced by replacing part of petro-diesel with biodiesel due to more complete combustion. Still, for higher biodiesel blends the emission of CO can increase relative to petro-diesel probably because of aforementioned worse fuel atomization [11–14]. CO_2 emission decreases with rise in biodiesel share in blends but at the same time amount of NO_x gases increases so there must be found optimal portion of biodiesel [11,13]. CO_2 gas is used by plants in process of photosynthesis meaning it is not so important in terms of atmospheric pollution and therefore attention should be paid on reduction of NO_x emission favoring petro-diesel and biodiesel blends with lower share of biodiesel.

In order to promote the use of renewable energy sources the European parliament and the Council of the European Union adopted Directive 2009/28/EC which established mandatory national target of raising the share of energy from renewable sources in transport sector up to 10% in Community energy consumption by 2020 [15]. The most manageable way to achieve that goal, beside electricity or hydrogen, is to increase the use of biodiesels because of all listed above [3]. Blending of petro-diesel with biodiesels has already become practice in the most developed European countries that even standard for automotive fuels EN 590/2009 [16] allows adding up to 7% (v/v) of biodiesel in petro-diesel without a special emphasis.

In accordance with the aforementioned, lower biodiesels and petro-diesel blends with biodiesels share up to 20 vol% are studied in this work.

Density and viscosity of fuel have great influence on fuel atomization and combustion in diesel engines that occurs at elevated pressures and temperatures, as well as derived thermodynamic properties, such as the isothermal compressibility and the isobaric thermal expansivity [17–19]. Consequently, the knowledge of fuel density and viscosity at various conditions is of utmost importance for prediction and improvement of an engine performance.

The influence of different substitutes for conventional diesel, particularly biodiesel and its mixtures with petro-diesel and/or alcohols, on diesel engine's performance and design has been the subject of numerous studies in last decades [1,9–13,20–22]. With an aim to study the use of biodiesel in diesel engines or to study its stability, storage, transport or miscibility of various fuels, many research groups have made an effort to propose the optimal model for prediction of the fuel's volumetric and transport properties [23–29]. For that reason reliable data at various conditions of pressure, temperature and composition are necessary. There is a number of papers presenting the data of thermodynamic properties for pure biodiesel and petro-diesel fuels over wide ranges of pressure and temperature [17–19,30–36], while their blends are mostly studied at atmospheric pressure and in a narrower ranges of temperature [23,24,28,37–42]. Only a few works give relevant viscosity and density data at high pressures and temperatures [17,43]. The common conclusion for biodiesel blends with petro-diesel is that both densities and viscosities decrease with increase in temperature and pressure drop, and that biodiesel and its blends with petro-diesel are more dense and viscous than pure petro-diesel.

Besides soybean oil which is commonly used in biodiesel production in U.S.A. and rapeseed oil in Europe, there are many vegetable oils and animal fats that can serve for this purpose, such as sunflower oil, palm oil, jatropha oil, cottonseed and corn oil [38]. Sunflower oil is a good choice because of its large oil content and possibility to be cultivated between harvests [44]. Still, there are only a few studies of sunflower oil biodiesels and its blends with petro-diesel at atmospheric pressure [38,44–46] while, to the best of our knowledge, the densities at high pressures have not been published before. Most of the literature data at atmospheric pressure are given only at 288.15 K for density and 313.15 K for viscosity [38,45] which is required for comparison with standards [4,5,16] and some of papers don't present the composition of a studied biodiesel. Parente et al. [44] have published densities and viscosities only for sunflower oil methyl esters and petro-diesel blends at atmospheric pressures and temperatures from 293.15 to 373.15 K over the whole composition range, while Rajagopal et al. [46] did the same at temperatures 303.15–318.15 K. Therefore, densities of pure petro-diesel and its blends with sunflower oil methyl esters containing 10 vol% of biodiesel (ED90SME10) and 20 vol% of biodiesel (ED80SME20) and with sunflower oil ethyl esters, 10 vol% of biodiesel (ED90SEE10) and 20 vol% of biodiesel (ED80SEE20) were measured in the temperature range 293.15–413.15 K (at 11 isotherms) and at pressures 0.1–60 MPa and presented here. Viscosities of all mentioned samples at temperatures 288.15–373.15 K and its refractive indices at temperatures 288.15–343.15 K, were measured at atmospheric pressure.

Density data, determined over wide ranges of pressure and temperature, were correlated using the modified Tammann-Tait equation and obtained parameters were used in order to calculate the isothermal compressibility, the isobaric thermal expansivity, the internal pressure and the difference between the specific heat capacity at constant pressure and the specific heat capacity at constant volume. The dependence of measured and derived thermodynamic properties on biodiesel share in blends were examined using Kay's mixing rule [47] or rule proposed by Grunberg and Nissan [48].

2. Experimental section

2.1. Materials

The biodiesels used for the preparation of the mixtures examined in this work were synthesized by transesterification of sunflower oil with methanol (SMEs) and ethanol (SEEs). Basic information about the transesterification reactions, as well as the composition of the sunflower oil used as raw material and of the produced biodiesels, are given in our previous paper [19]. The studied petro-diesel was EuroDiesel produced in compliance with the European standard EN 590 [16] by NIS Petrol Serbia.

2.2. Apparatus and procedure

Densities, ρ, of the examined samples at atmospheric pressure were measured using an Anton Paar DMA 5000 digital vibrating