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Measurement, correlation and prediction of biodiesel blends viscosity

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HIGHLIGHTS

- Viscosity and refractive index experimental data for systems with biodiesel for temperature range 293.15–323.15 K.
- The accuracy of different models for viscosity calculations is presented.
- Correlative–predictive equations give better results than the ones predictive.
- Calculation of viscosity of biodiesel blends from the refractive index of the blends.

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ABSTRACT

The viscosity is one of the most important transport properties of a fuel, influencing especially the injection system, mainly at low temperatures when viscosity increases. Biodiesel is considered an alternative fuel for diesel engines, but some of its properties such as density and viscosity, have higher values than those of diesel fuel. In this paper, the viscosity of binary blends biodiesel + diesel fuel, biodiesel + benzene and biodiesel + toluene in the temperature range 293.15–323.15 K is presented. Experimental data were used to evaluate the accuracy of viscosity calculations with different models, both for blends of biodiesel with pure components (benzene or toluene) and for biodiesel with diesel fuel. The biodiesel + benzene and biodiesel + toluene blends were used as base of comparison, to better understand the behavior of biodiesel + diesel fuel blends. The Grunberg–Nissan, Wilke and McAllister equations were used to predict the blends viscosity from the viscosities of pure components and to correlate the experimental data. Also, the viscosity of the biodiesel blends was calculated from the refractive index of the blends or by the means of viscosity–temperature and viscosity–temperature–composition empirical correlative equations.

1. Introduction

High consumption of conventional fuels and environmental concerns had created urgent needs for alternative fuels. Transport sector uses a significant amount of petroleum-derived fuels. Even though new oil reserves were discovered in the recent years, non-renewable fuels could not meet the world energy demand in the long term. Fuels made from petroleum can be replaced with fuels from renewable sources (e.g. vegetable oils) because they have equivalent features with fossil fuels [1–3].

Vegetable oils have a high viscosity and their use in diesel engines causes different problems, such as low atomization, incomplete combustion, injector clogging and low oxidation stability due to polyunsaturated content [1]. To minimize or to avoid these problems, the vegetable oil were transesterified and thus was obtained biodiesel with better qualities than those of diesel fuel, like biodegradability, significant reduction of CO, SO_x, unburned hydrocarbons, volatile organic compounds and particulate matter emissions.

More than 95% of biodiesel is made today at industrial level from edible oils [4]. Six raw materials for biodiesel production dominate the entire world: rapeseed, sunflower, palm, cottonseed, soybean and peanut oils [5–8]. Biodiesel properties differ from one sample to another, due to esters varying composition determined by the type of feedstock. Biodiesel is a mixture of esters, while diesel fuel is a mixture of hydrocarbons.

Biodiesel is an alternative fuel for diesel engines, but some of its properties such as density and viscosity, have higher values than those of diesel fuel. Viscosity is one of the most important transport properties of a fuel, influencing especially the injection system, mainly at low temperatures when viscosity increases. Biodiesel and its blends with diesel fuel show similar viscosity–temperature dependence [2,9]. Some methods for predicting biodiesel and

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diesel fuel + biodiesel blends viscosity are presented in literature [2,10–16]. Blends of diesel fuel with 5–10% biodiesel are currently commercialized as fuel for diesel engines.

To be used in transport area, biodiesel and its blends with diesel fuel must fulfill standard requirements. The ASTM D975 (USA) and EN 590 (Europe) standards are used to evaluate the quality of diesel fuels and also are used in the case of diesel fuel + biodiesel blends with up to 5% biodiesel. For blends with 6–20% biodiesel content, the ASTM D7467 is used and for pure biodiesel, the ASTM D6751 (USA) and the EN 14214 (Europe) requirements must be fulfilled [17].

As a continuation of our studies on properties of biodiesel blends [18,19], the objectives of this work are to present new experimental data and to evaluate the accuracy of some equations for viscosity data correlation or prediction from pure components properties. For this purpose already used equations for biodiesel blends were tested (Grunberg–Nissan eqs.), also Wilke equation from petroleum domain and McAllister equation from classical thermodynamics of molecular mixtures, equations that have not yet been used for biodiesel + diesel fuel blends. Grunberg–Nissan (one parameter) and McAllister equations are semiempirical or theoretical-based models with one or two adjustable parameters, more difficult to use for complex blends of biodiesel + diesel fuel. Because the experimental determination of refractive index is simpler than of viscosity, the viscosity evaluation from refractive index data can be useful in many practical cases. An equation from petroleum domain was tested to correlate viscosity and refractive index for biodiesel blends.

Given the fact that biodiesel + benzene and biodiesel + toluene blends are not recommended as fuels for transport due to the toxicity of aromatic compounds, their data were used for comparison purposes to better understand the quality of viscosity data correlation of biodiesel + diesel blends. The biodiesel + benzene and biodiesel + toluene blends are simpler regarding their composition and components structure, compared to biodiesel + diesel fuel blends; they have no polar molecule and are miscible throughout the composition with biodiesel.

After our knowledge, properties of biodiesel + diesel fuel blends of different degrees of blending at different temperatures using biodiesel obtained from rapeseed oil and other types of vegetable oils have been investigated. There are a lot of studies referring to biodiesel + diesel fuel blends [18–28], but not all specifies the biodiesel type, its chemical composition and average molecular weight, fact which has been achieved in this study; the biodiesel + benzene and biodiesel + toluene blends have been less studied [29].

2. Material and methods

2.1. Materials

Biodiesel used in this study was synthesized by transesterification of commercially available rapeseed oil. Methanol with a purity of 99.5%, and potassium hydroxide 99% purity as catalyst, both of Czech origin (Lachi-ner), were used in the transesterification process. Binary blends with biodiesel were prepared using 99.7% purity benzene from Merck, 99.7% purity toluene from Merck and diesel fuel from a local company.

The vegetable oil (rapeseed oil) was converted into fatty acid methyl esters (biodiesel) by transesterification reaction. Molar ratio methanol/oil was 6:1 and the catalyst (KOH) was 1.5% by weight based on oil. The catalyst was dissolved in alcohol and the mixture was added over the oil sample. Transesterification reaction progresses at temperatures of 60 °C at atmospheric pressure, under continuous mixing for 2 h. The reaction was performed in a reaction vessel (500 ml) equipped with condenser, magnetic stirrer and thermometer. The mixture obtained was introduced into a separating funnel and kept for about 12 h to reach the two-phase separation, the crude biodiesel and glycerin. Biodiesel obtained after glycerol removal was washed with distilled water up to 50 °C. Biodiesel was washed with water to remove traces of unreacted methanol and catalyst. Biodiesel layer was separated from water. This process was repeated until the pH of washing water was the same as distilled water. At the end of the process, biodiesel was dried on calcium sulfate.

The methyl esters composition of the biodiesel samples was determined by gas chromatography using a Clarus 500 GC chromatograph equipped with a FID detector and the separation of esters was realized on a capillary column of high polarity, with polysiloxane as stationary phase. Isothermal separation was made at 210 °C using hydrogen as carrier gas flow of 20 ml/min. Fatty acid composition of the biodiesel is presented in Table 1.

Based on their chemical composition, the average molar mass of biodiesel samples was calculated using Eq. (1) [23]:

$$\overline{M_{Bio}} = \sum x_i \cdot M_i \quad (1)$$

where $\overline{M_{Bio}}$ represents the mean molar mass of biodiesel, M_i and x_i, the molar mass and molar fraction of i-th fatty acid methyl ester, respectively.

The mean molar mass of diesel fuel was determined using the cryoscopic method with benzene as solvent. The determinations were realized on an ice bath. The accuracy of the thermometer was ±0.3 °C. Three measurements of the melting point of diesel fuel + benzene solutions were made. The mean value was taking into account for diesel fuel molar mass calculation.

The properties of biodiesel and diesel fuel are presented in Table 2.

2.2. Kinematic viscosity and refractive index measurement

Blends of biodiesel + diesel fuel (Bio + D), biodiesel + benzene (Bio + B) and biodiesel + toluene (Bio + T) were prepared by volume fractions (v_1 – volume fraction of biodiesel) of 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75, 0.80, 0.85, 0.90 and 0.95. All components are completely miscible. The experimental uncertainty in volume fractions was estimated to be less than ±0.002.

The kinematic viscosity (η) was measured using an Anton Paar SVM 3000 viscometer calibrated with double distilled water and pure solvents. This viscometer is equipped with a Peltier thermostat whose accuracy is ±0.02 °C. The kinematic viscosity was measured in the temperature range 293.15–323.15 K at 5 K intervals with an accuracy of ±0.35%. The kinematic viscosity data reported here are means of triplicate determinations.

The refractive index was measured for temperature ranging from 298.15 K to 323.15 K. A refractometer Abbé, Atago 3T type coupled to a thermostated bath was used to measure the refractive index. The reproducibility of refractive index data was of 10^{-4} and the thermostated bath had an accuracy of ±0.05 °C.

3. Results and discussions

3.1. Experimental data

The experimental kinematic viscosity data (η) for biodiesel binary blends with diesel fuel, benzene and toluene, respectively, for

Table 1
Fatty acid compositions of biodiesel.

	Fatty acid mass percent					
	14:0	16:0	18:0	18:1	18:2	20:1
Biodiesel	0.21	25.89	3.11	59.80	10.60	0.39

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