



Measurement and prediction of high-pressure viscosities of biodiesel fuels



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HIGHLIGHTS

- New experimental η data for 3 biodiesels (293.15–393.15 K; 0.1–140 MPa).
- A correlation was proposed to predict the experimental data with OARDs of only 3.9%.
- Biodiesel + diesel mixtures η were predicted with OARDs of just 3.3%.

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ABSTRACT

Nowadays common rail injection systems use high pressures to pump the fuel, even if at these conditions the liquid viscosity increases substantially over atmospheric levels. For the proper operation of these injection systems the knowledge of fuels high-pressure viscosities becomes crucial to optimize the engine performance. This work reports new experimental data of high-pressure viscosities for three biodiesels (soybean, rapeseed and their binary mixture) measured at temperatures from 293.15 K to 393.15 K and pressures from atmospheric up to 140 MPa, and proposes a correlation capable of describing the experimental data. The predictions results are excellent for the biodiesels studied, presenting overall average relative deviations (OARD) of only 3.9% in the entire ranges of pressures and temperatures studied. This correlation was also extended to describe the viscosities of biodiesels mixtures with diesel with an OARD of just 3.3%.

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1. Introduction

Biodiesel is a mixture of alkyl esters obtained from vegetable oils, animal fats or greases by a transesterification reaction [1,2]. It has been generally considered an adequate alternative fuel for diesel engines as it offers several benefits capable of overcoming the worrying issues related to the environmental quality, energy security, economy growth and social services linked to the use of petroleum fuels, especially in oil-importing countries. Beyond being renewable and biodegradable, biodiesel can be blended in any proportion with petrodiesel to be used in diesel engines with no modification and its combustion emits less greenhouse gases [3–9]. The advantages of biodiesel have incentivized the conception of novel approaches for its production and processing to obtain a fuel with high quality. In this perspective, the study of the

thermodynamic properties of biodiesels becomes crucial as they provide strategic information about the procedures one must modify or reformulate to improve the quality of the biodiesel, such that its properties conform with the regulatory standards of the Norm CEN EN 14214 [10] in Europe and the Norm ASTM D6751 in United States of America [11].

Among the most important properties of a fuel, viscosity connotes the fluidity and also affects the quality of the fuel atomization in diesel engines. When using the old mechanical fuel injection systems, higher viscous fuels will certainly block the pump elements, and tend to form large droplets leading to poor fuel atomization and consequent poor engine performance and exhaust emission. Lower viscous fuels, on the opposite, will provoke fuel leakage and cause the fuel pressure to rise more slowly inside the pump [12]. These problems are minimized in the modern “common rail injection systems” that basically use high pressures (up to 200 MPa) to pump the fuel and avoid leakages [12,13]. At this point, the prior knowledge of high-pressure viscosities of

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Table 1
FAMES composition of the biodiesels studied, in mass percentage.

Methyl esters	S	R	SR
C10:0		0.01	
C12:0		0.04	0.03
C14:0	0.07	0.07	0.09
C16:0	10.76	5.22	8.90
C16:1	0.07	0.20	0.15
C18:0	3.94	1.62	2.76
C18:1	22.96	62.11	41.82
C18:2	53.53	21.07	37.51
C18:3	7.02	6.95	7.02
C20:0	0.38	0.60	0.46
C20:1	0.23	1.35	0.68
C22:0	0.80	0.35	0.46
C22:1	0.24	0.19	0.12
C24:0		0.22	

biodiesels becomes crucial for previewing the engine performance and the quality of emissions.

Most data available in the literature report the temperature dependency of viscosity for biodiesel fuels at atmospheric pressure. Only a few works have focused on measuring and predicting the high-pressure viscosities of biodiesel fuels and their blends with petrodiesel [12–16]. Therefore, this work aims to report new experimental data of high-pressure viscosity for three methylic biodiesels (soybean, rapeseed and their binary mixture) measured at temperatures from 293.15 to 393.15 K and pressures from atmospheric to 140 MPa, and to propose a correlation capable of predicting them and their mixtures with petrodiesel.

2. Experimental section

2.1. Biodiesel samples: synthesis and analysis

The three biodiesel samples here studied: Soybean (S), Rapeseed (R) and their binary mixture (SR) were synthesized in our laboratory by a transesterification reaction of the respective vegetal oils following the procedure described by Pratas et al. [17]. Shortly, the alkaline-catalyzed transesterification reaction was adopted. The molar ratio of oil/methanol used was 1:5 with 0.5% sodium hydroxide by weight of oil as catalyst. The reaction was performed at 55 °C during 24 h under methanol reflux. The reaction time chosen was adopted for convenience and to guarantee a complete reaction conversion. Raw glycerol was removed in two steps, the first after 3 h reaction and then after 24 h reaction in a separating funnel. Biodiesel was purified by washing with hot distilled water until a neutral pH was achieved. Then biodiesel was dried until the EN ISO 12937 limit for water was reached (less than 500 mg/kg of water).

Capillary gas chromatography was used to determine the composition in methyl esters of the biodiesel samples. A Varian CP-3800 with a flame ionization detector in a split injection system with a Select™ Biodiesel for FAME Column, (30 m × 0.32 mm × 0.25 μm), was used to discriminate between all the methyl esters in analysis inclusively the polyunsaturated ones. The column temperature was set at 120 °C and then programmed to increase up to 250 °C, at 4 °C/min. Detector and injector were set at 250 °C. The carrier gas was helium with a flow rate of 2 mL/min. The FAMES composition of the biodiesels is presented in Table 1.

2.2. Measurement of high pressure viscosity

Experimental measurements of high-pressure viscosities of biodiesels were made using a vibrating-wire instrument [18,19] developed in the TERMOCAL laboratory. This viscometer is capable

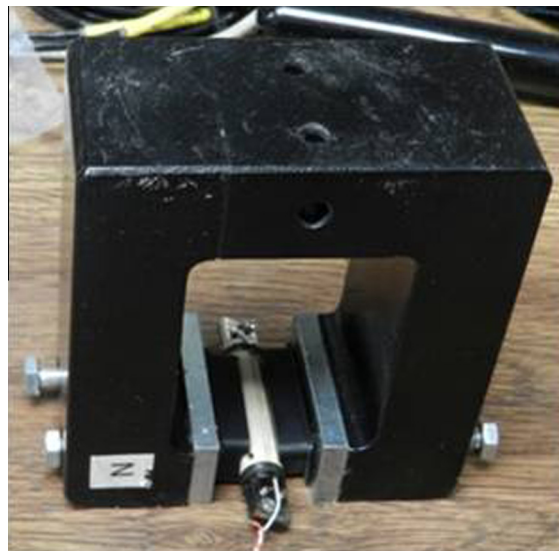


Fig. 1. Picture of the vibrating wire sensor and magnet.

of operating at temperatures between 273.15 K and 423.15 K and at pressures up to 140 MPa. Calibration was performed by means of measurements in vacuum, air, and toluene. The estimated uncertainty of the results is 1% in viscosity. The vibrating wire viscometer has been designed to operate in the viscosity range 0.3–30 mPa s. The main part of the equipment is a sensor with a tungsten wire (length 50 mm and nominal radius 75 μm) anchored at both ends [20], placed inside a pressure vessel, with an external magnetic field orientated in a direction perpendicular to the wire length using magnet placed around the vessel (it can be seen in Fig. 1).

The theory of vibrating-wire viscometer is based on transverse vibration of a stretched wire, which is used to measure the viscosity of the fluid that surrounds the vibrant wire. The oscillations are driven across to induce an alternating current through the wire. The circulation of a constant sinusoidal current through the wire, in combination with the constant magnetic field, generates the vibration of the wire. The electromotive force (EMF) generated through the wire can be measured with a lock-in amplifier (Stanford Research Systems SR830 DSP), which can also provide a constant amplitude sinusoidal drive voltage.

The resonance curve was fitted to the rigorous theoretical model which relates the resonance characteristics of the wire to its physical characteristics as well as the density and viscosity of the surrounding fluid. This experimental resonance curve contains the voltage contribution from the wire motion and the electrical contribution from the effectively stationary wire, and V (the complex voltage sampled by the computer) is expressed as:

$$V = V_1 + V_2 \quad (1)$$

where V_1 is the voltage induced by the wire motion and V_2 is the voltage arising by virtue of passing a current through the impedance of the wire. Both terms are given in Eqs. (2) and (3), respectively.

$$V_1 = \frac{\Lambda \tilde{f}}{f_0^2 - f^2(1 + \beta) + if^2(\beta' + 2\Delta_0)} \quad (2)$$

$$V_2 = a + bi + cfi. \quad (3)$$

Λ is the amplitude, f is the drive frequency, f_0 and Δ_0 are the resonance frequency and logarithmic decrement in vacuum, β and β' are the additional mass of the fluid and the damping due to the

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