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Refractive index of biodiesel-diesel blends from effective polarizability and density

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ABSTRACT

The refractive index of blends of soybean biodiesel with low sulfur diesel and also with ultra-low sulfur diesel was determined in the full composition range. Measurements were carried out acording to ASTM D1218/12 standard at 589 nm with an uncertainty of 2.10^{-4}. The temperature ranges were from 288 K to 328 K for blends with low sulfur diesel and from 293 K to 323 K for blends with ultra-low sulfur diesel.

The experimental results of refractive index as a function of temperature and composition were satisfactorily fitted to linear models with an uncertainty lower than 5.10^{-4} for blends with low sulfur diesel and 4.10^{-4} for ultra-low sulfur diesel blends.

The density of the blends was measured according to the ASTM D1298/12 standard in the same temperature range and the agreement with models available in the literature was satisfactorily checked. The effective polarizability of the blends was defined from the Lorentz-Lorenz equation using refractive index and density values. The effective polarizability for low sulfur diesel and ultra-low sulfur diesel were (0.3307 ± 0.0005) cm^3/g and (0.3327 ± 0.0005) cm^3/g respectively, and independent of temperature. These results are in good agreement with the published values for pure hydrocarbons and crude oils. For soybean biodiesel, a value of (0.3110 ± 0.0002) cm^3/g was obtained. It was also found that the effective polarizability of soybean biodiesel-diesel blends follows a linear dependence with composition. From our results, it also follows that the effective polarizability is independent of temperature, within the studied range.

From the values of effective polarizability of the pure fuels, together with the blend density at each temperature, it is then possible to estimate the refractive index of biodiesel-diesel blends in the full range of composition and studied temperatures, with an RMS difference below 6.10^{-4}.

1. Introduction

World energy consumption has increased in recent years due to motorization and industrialization processes, and fossil fuels are used by most countries to satisfy this growing demand. These energy resources are finite, non renewable, their reserves are found only in certain regions and their combustion releases large quantities of contaminants to the enviroment [1]. Diesel fuel is particularly important, since it is used for automotive and railway transport of industrial and agricultural goods.

Due to these concerns and in order to perserve the environment, it is urgent to search for alternative, economically viable and carbon-neutral fuels that can be obtained from a large variety of renewable sources. Biodiesel (BD) is an alternative fuel obtained from the transesterification of vegetable oils or animal fats [2]; it is non-toxic, biodegradable, with lower carbon dioxide and particulate emissions than fossil fuels [3]. BD is used in internal combustion engines, usually blended with diesel fuel. In many countries the use of biodiesel-diesel blends is regulated.

The characterization of líquid biofuels, fossil fuels and their blends is made according to international standards (ASTM D6751/15 [4], EN 14214/13 [5], etc.) where several properties are included, together with their acceptable ranges.

There are also alternative properties that are useful for biodiesel and blends characterization, such as permittivity, conductivity and speed of sound [6–8]. In the literature, dielectric properties at low frequencies

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were successful used to characterize feedstocks [9], biodiesel and its blends with diesel [10–12], and to detect contaminants [13]. However, measurements of dielectric properties at optical frequencies (i.e. refractive index) offer several advantages for characterization [14]. Particularly in the visible range, the technique is fast, accurate, simple, non destructive, and requires small sample volume. At present, there are several manufactures [15] that supply a wide variety of automatic refractometers, both for laboratory and inline control applications. Refractometry is widely used in many industries for concentration monitoring, dosage and quality control [15–16] including chemical, pharmaceutical, food/ beverage, sugar/bioethanol production, pulp, paper and textile, lubricant agents, and semiconductors, particulary for "inline" process control applications. In recent years [14], this technique has also been applied in biodiesel technology [17–23], for instance, to monitor the transesterification reaction [24–26], and to estimate the viscosity [27] and density of biodiesel-diesel blends [28]. The refractive index of biodiesel-diesel blends was studied for biodiesel of different origin: rapeseed biodiesel at temperatures between 298 and 323 K [23], for soybean biodiesel at 298 K [29] and Canola oil at 293 K [22].

As usual, in this work the volumetric percentage of the biofuel in the blend is indicated as Bx. For instance, B10 corresponds to 10% (v/v) biodiesel in the blend.

2. Materials and methods

2.1. Samples

The blends of soybean BD with diesel fossil fuel were prepared from two types of commercial diesel fossil fuel: low sulfur diesel (LSD) and ultra-low sulfur diesel (ULSD). The pure fuel samples were provided by a local refinery and complied with the ASTM D975/16 standard [30]. The same refinery provided the soybean biodiesel, according to ASTM D6751/15 specifications [4], that they use to prepare the commercial blend. Two series of samples were prepared: soybean BD-LSD blends in 5% steps, called Series 1, and soybean BD-ULSD blends in 10% steps called Series 2, in the full range of compositions (from B0 to B100).

2.2. Equipment

The refractive index of all samples was determined using an Abbe-type refractometer (Warkzawa Model RL-3) with an accuracy of 2.10^{-4}, according to the ASTM D1218/12 standard [31]. A 589 nm sodium arc lamp was used as a light source, and the sample cell temperature was kept constant within ± 0.1 K by a termostatic bath. The refractometer was calibrated using deionized water and toluene.

Density measurements of the samples were made with hydrometers according to ASTM D1298/12 standard [32] for the different density ranges, in a thermostatic bath, LAUDA, stabilized within ± 0.1 K. The measurement uncertainty was 10^{-3} g/cm^3.

2.3. Measurements

Refractive index measurements were made on both Series, according to the ASTM D1218/12 standard [31]. For Series 1, the temperature range was from 293 K to 328 K in 5 K steps, while for Series 2 the temperature range was from 298 K to 328 K, also in 5 K steps.

Density measurements were made in the temperature range between 303 K and 323 K in 5 K steps. The studied samples were LSD and ULSD pure diesel (B0), B30 and B70 from both series and pure biodiesel (B100). Measurements were carried out according to ASTM D1298/12 standard [32].

3. Theory

At optical frequencies, permittivity is generally controlled by

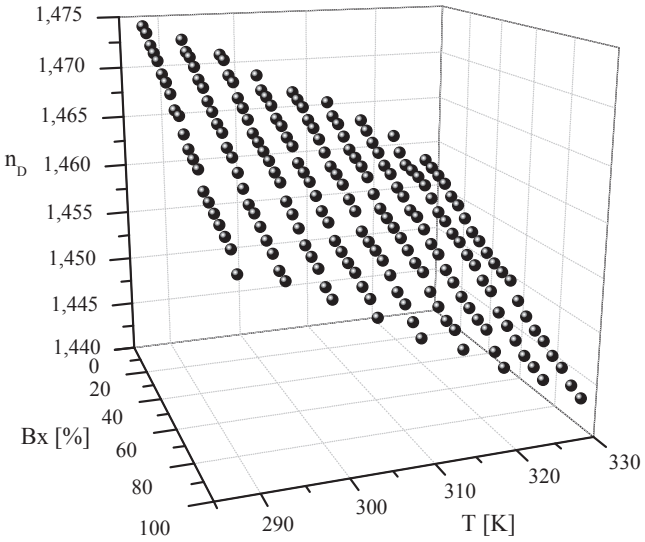

Fig. 1. Refractive index as a function of temperature and BD content (Series 1).

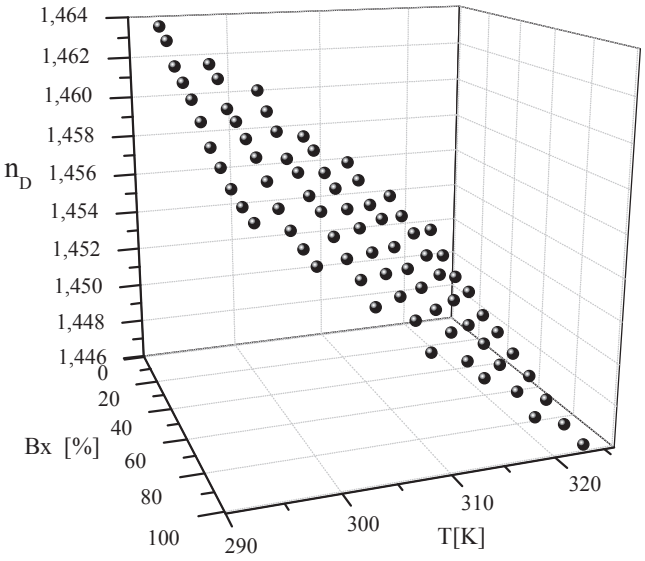

Fig. 2. Refractive index as a function of temperature and BD content (Series 2).

electronic polarization processes and refractive index measurements are commonly used to determine it [14]. In biodiesel, diesel fuel and their blends, the optical attenuation is small and the magnetic permittivity is practically equal to the vacuum value; therefore, the refractive index in the visible range can be written as:

$$n(\omega) = \sqrt{\varepsilon'(\omega)} \tag{1}$$

where $n(\omega)$ is the refractive index and $\varepsilon'(\omega)$ is the permittivity. Usually the refractive index is measured at the frequency, ω, corresponding to the sodium Na_D emission line (vacuum wavelength of 589 nm), indicated as n_D [14].

At optical frequencies, the Lorentz-Lorenz equation (Eq. (2)) is applied to estimate the polarizability, α, of pure substances as a function of refractive index, n, density, ρ, and molar mass, MW [33].

$$\alpha = \frac{n^2-1}{n^2+2} * \frac{MW}{\rho}\left(\frac{3}{4\pi N_A}\right) \tag{2}$$

where α is in cm^3, density in g/cm^3, molar mass in mol/g and N_A is the Avogadro constant, in mol^{-1}. Therefore, Eq. (2) may be written as:

$$\alpha = A*Rm \tag{3}$$