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Short communication

An ultrasonic method to appraise diesel and biodiesel blends

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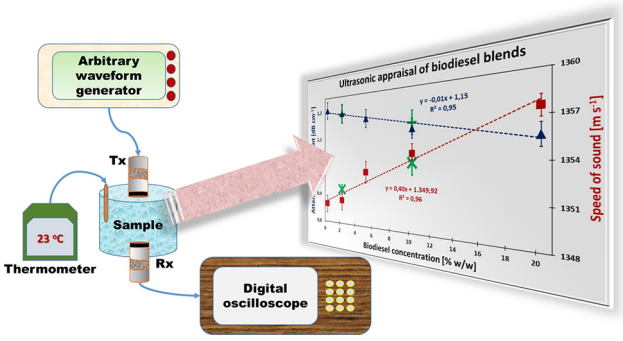
GRAPHICAL ABSTRACT



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ABSTRACT

Biodiesel is an evolution toward the attempt to substitute fossil fuel by renewable biomass. Typically, blends of diesel and biodiesel are commercialized instead of pure biodiesel for economic and technical reasons. It would be of interest for customers, regulations agencies, and dealers regarding custody transfer of biodiesel blends to have a rapid and reliable method to analyses the mixture on site and in real time. The aim of this research is to use a previously developed ultrasonic method to analyse mixtures of diesel and biodiesel. The samples were blends which proportion varied from 0% (pure diesel) to 20%. The ultrasonic quantities were speed of sound and ultrasonic attenuation. Those parameters were determined in a transmission/reception scheme. The measurement uncertainties were evaluated according to the Guide to the Expression of Uncertainty in Measurement (BIPM JCGM 100:2008). Complementary, commercial samples (B2 and B10) were obtained from a local supplier and evaluated accordingly. The expanded definitional uncertainty was 2.0 m s^{-1} for speed of sound and 0.032 dB cm^{-1} (p = 0.95). The method has shown capability to identify less than 4% of biodiesel in diesel blends for both parameters.

1. Introduction

Diesel is a petroleum derived product obtained with distillation ranging usually between 220 °C and 380 °C. This derivative has a set of properties which allows their use in machines driven by motors which operate on the diesel cycle. The scope of diesel-driven machines is very wide, as for instance sea vessels, automobiles, tractors, and power generating units as well [1]. On the other hand, the demand for renewable energy sources associated with the environmental conscience, joining economic and social development, has encouraged technical development of renewable energy source [2,3]. Biodiesel is an evolution in the attempt to substitute fossil fuel by green energy. It is

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obtained by reaction of vegetable oils or animal fat with alcohol and a catalyst, a process known as transesterification. The chemical reaction products are mixture of esters (biodiesel) and glycerol (propanetriol). The esters have physicochemical characteristics very similar to the diesel, as disclosed in an assortment of experiments conducted worldwide for a long while [4–9]. For economic and technical reasons, it is not usual to feed diesel engines purely with biodiesel. Typically, blends are defined by national regulations, as for the Brazilian regulation which allows ratios up to 20% of biodiesel in diesel [10]. Manufacturing fees are taxed according to the amount of diesel and biodiesel in the blend commercialized, so the evaluation of the final product became important further than the regulation accomplishment. Analytical chemistry methods are the most reliable and accurate to determine the amount of biodiesel present in diesel blends. However, they are not simple to use in the field nor are inexpensive to be widely spread. On the other hand, ultrasonic methods have been exploited for fuel analysis, as disclosed in recent papers [11,12]. A specific experimental research was conducted to evaluate the applicability of such method in the metrological evaluation of blends of diesel and biodiesel ranging from 0% to 20%. Measurement uncertainties were assessed in accordance with common practice for ultrasound and acoustics use, as defined in Refs. [13–17].

2. Material and methods

The experimental apparatus and measurement procedure were described in detail somewhere else [11,12]. Summarizing, the fuel samples were placed in a cylindrical glass recipient with 80 mm height and 35 mm diameter, with its extremities sealed with 12-μm thick plastic film (PVC). The sample were blends of diesel and biodiesel with mass concentrations of 0%, 2%, 5%, 10%, 20% and 100% of biodiesel produced from soybean oil. The samples were precisely determined (error $< 0.1\%$) with a gravimetric method and using a microbalance model CP224S (Sartorius, Germany). Complementary, local supplier commercial diesel samples for B2 and B10 were measured in the validated system in order to evaluate the method usefulness. The method was validated regarding the measurement capability with pure water at room temperature ($\sim 23\,^{\circ}C$ to $24\,^{\circ}C$). The ultrasound was generated with an arbitrary waveform pulser model 33250A (Agilent Technologies, CA, USA) and transmitted to the interrogated medium with the aid of a pair of piston-like plane transducers operating at 10 MHz (Panametrics-NDT Olympus Corporation, Japan). The excitation signals were 20-cycles sine bursts driven at 20 V peak-to-peak. The ultrasound was digitalized with an oscilloscope model DSO6032A (Agilent Technologies, CA, USA). The temperature was measured using a calibrated digital thermometer model 34970A (Agilent Technologies, CA, USA). The measuring instruments were remotely controlled with a dedicated homemade software developed in LabVIEW™ (National Instruments Corporation, Austin, TX, USA). Fig. 1 disclose an illustration of the experimental setup.

2.1. Experimental attenuation coefficient and speed of sound

Details about the rationale regarding ultrasonic attenuation measurement can be found in Refs. [18–21]. In a straightforward formulation, experimental attenuation coefficient AT_E for the diesel/biodiesel samples, expressed in [dB cm^{-1}], was calculated according to Eq. (1), in which V_{wat} is voltage measured with the water as propagation medium (reference signal), V_{sam} is the voltage measured with the sample, and x_e is the sample thickness or the transmission path length in centimetres. All voltages were measured in effective (RMS) [V].

$$AT_E = \frac{20log\left(\frac{V_{wat}}{V_{sam}}\right)}{x_e}\,[\mathrm{dB\ cm^{-1}}] \tag{1}$$

According to Eq. (1), AT_E is the excess ultrasonic attenuation in diesel/biodiesel samples relative to the attenuation in water. The sample thickness x_e was calculated as a function of the time of flight between the two transducers Δt_{wat}, measured in [s], and the speed of sound within the medium c_{wat} measured in [m s^{-1}], according to Eq. (2). The speed of sound was determined as function of the temperature, as disclosed in Refs. [22–24] and Eq. (3).

$$x_e = 100 \cdot c_{wat} \cdot \Delta t_{wat}\ [\mathrm{cm}] \tag{2}$$

$$c_{wat} = (1405{,}03 + 4{,}624 \cdot T - 0{,}0383 \cdot T^2)\ [\mathrm{m\ s^{-1}}] \tag{3}$$

The sample propagation velocity c_{sam} was calculated as described in Eq. (4), in which Δt_{sam} is the time of flight inside the tested samples.

$$c_{sam} = \frac{x_e}{\Delta t_{sam}}\ [\mathrm{m\ s^{-1}}] \tag{4}$$

Measurements were repeated five times at the frequency of 10 MHz, and the attenuation medium (water and blends samples) was changed between successive measurements.

2.2. Uncertainty model

Uncertainties were assessed in accordance to the Guide to the Expression of Uncertainty in Measurement (GUM) [17], as well as some recent papers for ultrasound applications [13–16,20,23,24]. Type A is derived from the experimental data as the standard deviation of the mean, while Type B components were collected from calibration certificates and operation manuals for every equipment or accessory. All measurements were repeated 5 times in repeatability conditions to assess the Type A measurement uncertainty component. To assure the repeatability condition, the attenuation medium (water or diesel/biodiesel samples) was changed between successive measurements.

Type A is the standard deviation of the mean for the five-repeated measurement undertaken to assess each result. Type B involve all other uncertainty sources, mainly derived from the mathematical model, the measuring system resolution and calibration certificate. The setup and the procedure used in this measurement were properly set to lead the

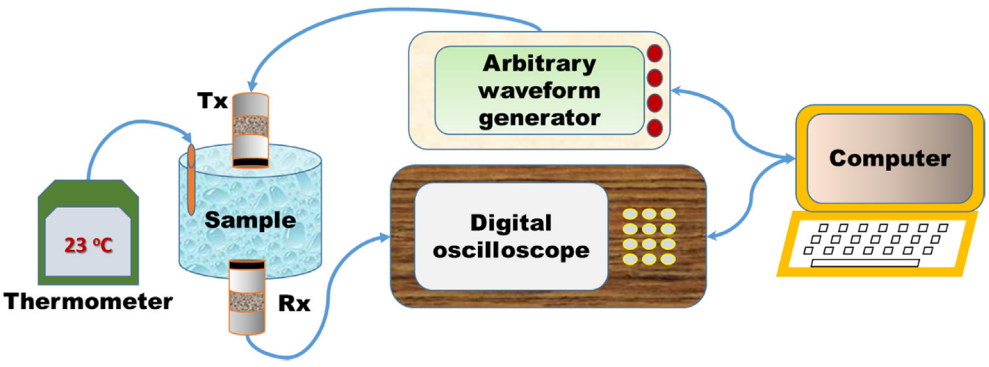

Fig. 1. Experimental setup, in which Tx represents the emission transducer whilst Rx is the reception transducer.