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Ultrasonic attenuation and sound velocity assessment for mixtures of gasoline and organic compounds

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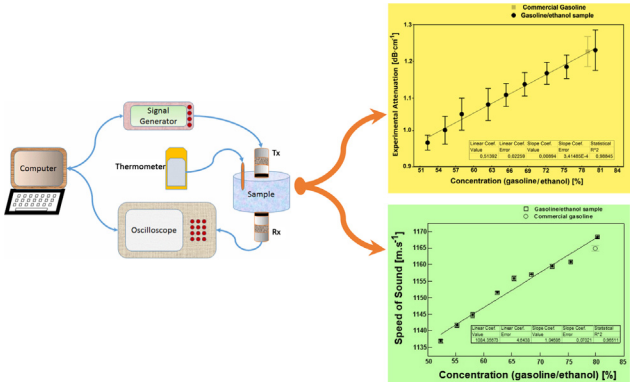
HIGHLIGHTS

- Fuel adulteration is an important issue worldwide.
- Ultrasound has been proved to be an important rapid and reliable measurement tool for measuring fuel characteristics.
- Ultrasonic propagation velocity could detect organic compounds in gasoline.
- The results disclosed may be used in field applications.

GRAPHICAL ABSTRACT



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ABSTRACT

The paper presents an experimental method that can be used to identify the possible adulteration in gasoline using ultrasonic attenuation and the ultrasonic propagation velocity. The experiments and measurement uncertainties were assessed according to the Guide to the Expression of Uncertainty in Measurement, JCGM 100:2008. The test samples were mixtures of gasoline and different chemical products: ethanol with gasoline concentrations varying from 52.3% to 80.3% in mass; a ternary mixture of gasoline, ethanol, and hexane, a ternary mixture containing gasoline, ethanol, and toluene; a ternary mixture of gasoline, ethanol, and turpentine; pure gasoline; and commercial gasoline purchased from a local supplier. For the ethanol mixtures, the correlation coefficient between the gasoline concentrations and the ultrasonic propagation velocity was 0.96, and the maximum combined uncertainty was 0.81 $m{\cdot}s^{-1}$. With regard to attenuation, the correlation coefficient was 0.99, and the maximum combined uncertainty was 0.066 $dB{\cdot}cm^{-1}$. Regarding the mixture of gasoline and ethanol, the quantification limit range for a typical maximum concentration (E25 or 75% of gasoline plus 25% of ethanol) was between 73.8% and 76.2%, with expanded uncertainty 0.62 $m{\cdot}s^{-1}$ (coverage probability p = 0.95), considering the propagation velocity as the parameter. In the case of gasoline adulteration with organic solvents, the results were not conclusive, mainly because of the ultrasonic physical-chemical properties of those products and the blends of gasoline and ethanol. Nevertheless, adulteration with those chemicals was easily identifiable for pure gasoline.

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1. Introduction

Gasoline is most often produced by the fractional distillation of crude oil. The crude oil is separated into fractions according to the different boiling points of hydrocarbons with various chain lengths. The fractional distillation process yields approximately 25% of straight-run gasoline from each barrel of crude oil. Although gasoline and ethanol blends are commercially available in many countries, their mass compositions are typically strictly regulated. Nevertheless, adulteration or dissimilar blends must be investigated, confirmed, and prosecuted by the authorities. Gasoline is a mixture of volatile and inflammable liquid hydrocarbons. These hydrocarbons contain different structures in different proportions and their molecules generally have between four and thirteen carbon atoms and a boiling point between 50 and 225 °C [1,2]. In many countries, gasoline is commercially available as a mixture of pure gasoline and anhydrous ethanol. In Brazil, for instance, type C gasoline is the most usual and is commonly known as "common gasoline". This type comprises a mixture of 75% of pure gasoline and 25% anhydrous ethanol (E25), with an allowable variation of one percentage point. Despite regulation and constant surveillance, gasoline is often adulterated worldwide with the addition of ethyl alcohol and paraffinic and aromatic hydrocarbons. The adulteration with paraffinic solvents, in particular, is not easily detected, because these compounds are within the temperature range of the distillation of gasoline.

To ensure the quality of gasoline worldwide, it is necessary to use a robust, accurate, and non-destructive method that can be applied in the distribution line. Ultrasound has been used extensively in several stages of chemical processes, for instance, to accelerate reactions [3], to separate the reaction by-products [4], and to identify and analyse chemical mixtures [5]. Additionally, methods using ultrasound have been proposed to identify fuel adulteration [6,7]. Viscosity has also been measured with the aid of ultrasonic systems, as reported in [8–10]. In [11], ultrasonic methods for monitoring aluminium hydrolysis were compared with regular pH-metry and exhibited interesting performance. Recently, the use of ultrasound has been proposed for the detection of oil and grease in water, providing remarkable findings [12]. Alcohol and carbohydrates composition can be determined by ultrasonic frequency analyses [13]. A comprehensive review of the use of ultrasonic parameters was presented by Kaatze and colleagues in [14], in which different ultrasonic methods were evaluated regarding their applicability to physicochemical analyses.

It is important to note that the use of ultrasound to analyse chemical mixtures is essentially the same, regardless of whether their contents are fuel or other compounds. Specifically, the phase velocity (speed of sound) and attenuation (or transmission loss) of ultrasound are assessed using the transmission reception or pulse echo methods (or both). The distinctiveness of an ultrasound application typically concerns the compounds of interest, mainly owing to their viscosity and density. The ultrasonic characteristics of gasoline, anhydrous ethanol, and most of the organic solvents present more similarities between them than with those of, for instance, diesel or water. The study reported in this paper investigated binary and ternary mixtures of gasoline, anhydrous ethanol, turpentine, hexane, and toluene. The research was based on a metrological approach and the uncertainties were determined according to the Guide to the Expression of Uncertainty in Measurement (GUM) [15].

2. Materials and methods

The samples were mixtures of gasoline and anhydrous ethanol with concentrations ranging from 52.3% to 80.3% in mass, pure gasoline, commercial gasoline, and mixtures of gasoline and organic solvents (hexane, turpentine, and toluene). The 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).

For the ultrasonic parameter measurement, distilled water was used as the reference sample. The temperature was measured during all the measurements and ranged between 22.2 °C and 23.1 °C.

The measurement setup is schematically illustrated in Fig. 1. The transmission reception method was used with two transducers. The transmitting transducer was excited by an arbitrary waveform generator, model 33250A (Agilent Technologies, CA, USA), which generated 20 cycles of sinusoidal waves of 20 V peak-to-peak at 15 MHz. The transmitted signals were captured by the reception transducer and digitalised using an oscilloscope, model DSO6032A (Agilent Technologies, CA, USA). The pair of transducers had 15 MHz central frequency (Panametrics-NDT Olympus Corporation, Japan) and were placed 10 mm apart. The temperature was monitored by a calibrated digital thermometer, model 34970A (Agilent Technologies, CA, USA). Each sample was analysed five times under conditions of repeatability.

2.1. Ultrasonic parameters

The experimental quantities of interest were the ultrasonic attenuation and the ultrasonic propagation velocity. The procedure is described in detail in [7] and the fundamentals of the approach are presented here. In this study, ultrasonic attenuation is not considered as an intrinsic property of the liquid under test (LUT), but as an experimental quantity comprising different physical phenomena that induce amplitude loss; namely, absorption, scattering, diffraction loss, and impedance mismatch. The propagation medium plays a key role in the behaviour of the ultrasonic wave. If the ultrasound propagates in media with different acoustic impedances, the interface provides an impedance mismatch that interferes with the propagation. This results in an amplitude variation that is not only caused by absorption, but also by different physical characteristics. This issue is addressed in detail in [16,17].

Another important aspect is diffraction loss. As discussed in [17–20], the positioning of large-aperture emission and reception transducers in close proximity minimises diffraction loss due to the edge effect, even in the near-field region. This was applied in the present experimental procedure, as the wavelength was smaller than one hundredth of the transducer's diameter, and the emission reception distance was smaller than 10 mm. According to Fay [21] and international standard [22], the level of diffraction correction that is applied to the amplitude of a signal emitted and received by finite-aperture transducers depends on the effective radiation radius, the distance between the transducers, and the wavelength. The experimental procedure was designed to maintain the difference between the diffraction loss in the intervening water and the diffraction loss in all studied LUTs below 0.1%.

A suitable ultrasonic measuring scheme can detect if any acoustic wave has not undergone nonlinear loss during the propagation from the emitter transducer to the receiver. This is unlikely when the propagation distances are small. Furthermore, the amplitude (particle displacement) is also of concern if nonlinearities must be avoided. In the present experimental arrangement, the output ultrasonic pressure amplitude was sufficiently small to avoid nonlinear distortion, according to [20,23].

In summary, if the same intervening path is used between the transmitting and the receiving ultrasonic transducers for both LUTs (fuel mixtures) and the reference medium (water) and the same signal is applied in the generating and measuring systems, the receiving amplitude difference is due to the excess attenuation that is related to different amplitude loss mechanisms (absorption,