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Biofuel ethanol adulteration detection using an ultrasonic measurement method

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ABSTRACT

Hydrous ethanol is a worldwide used biofuel. According to Brazilian regulations, the concentration of ethanol in hydrous ethanol can be accepted at a maximum concentration of 93.8% and a minimum of 92.6% by mass. The aim of this study is to identify the possible changes in hydrous ethanol fuel using ultrasonic attenuation and propagation velocity. The experiments were performed in the Laboratory of Ultrasound of the Brazilian National Institute of Metrology (Inmetro). The experiments and uncertainties in the methodology were evaluated according to the Guide to the Expression of Uncertainty in Measurement, JCGM 100:2008. The test samples used in this study were mixtures of ethanol and water with ethanol concentrations varying from 89.84% to 93.71% by mass; and a commercial fuel ethanol bought from a local distributor. The correlation coefficient between ethanol concentrations and ultrasonic propagation velocity was 0.99 (in modulus), and the maximum combined uncertainty was 0.60 m s^{-1}. Considering attenuation, the correlation coefficient was 0.97, and the maximum combined uncertainty was 0.085 dB cm^{-1}. However, its signal is not stable resulting an unreliable parameter. Within the tested concentration range, the highest concentration that is statistically different ($p < 0.002$, $\alpha = 5\%$) from 92.60% is 92.25%, considering propagation velocity as parameter. To validate the methodology, a commercial ethanol fuel was tested using the proposed method as well as the gas chromatography analytical method (gold standard). Result was statistically identical for propagation velocity when compared to the gold standard.

1. Introduction

Fuels produced from biomass have a high energy potential, and one of the main advantages is the reduction of greenhouse effect gas emissions. These fuels may be a safe fuel source, may gradually reduce the dependence on ex-submersed biomass such as petroleum, and may also help in developing a strategic reserve [1–4]. However, the profit margins at all stages of the fuels trade are relatively low. To increase the profit margin, some owners of the gas stations or the distributors illegally adulterate fuels.

Hydrous ethanol is a renewable fuel and its production technology is available in Brazil. For this kind of biofuel, the most common adulteration method is the addition of water in amounts bigger than those specified in the formula of hydrated ethanol fuel, resulting in an off-specification product that is thereby unsuitable for use as a fuel. The immediate victim of adulteration is the consumer who supplies his car with the adulterated fuel. However, the adulteration practice is interest of all, as this leads to a reduction of tax revenue and damages the whole society. Due to several problems in ensuring the quality of biofuel used in Brazil, it is necessary to use a robust, accurate and non-destructive method, such as ultrasound, that can be applied in the process line.

Ultrasound has been used recursively in several stages of a chemical process: to accelerate the reaction [5]; to separate the compounds [6]; and to identify and analyze compounds [7]. Ultrasound is also suitable for other related activities such as flow measurement, as a physical principle of process execution. However, from the metrological point of view, there is still some work to be done. Metrology is essential to support and demonstrate scientifically the advantages and applications of ultrasound in sonochemistry and to control chemical processes.

The physical properties of a medium can be determined from the measurement of acoustic parameters as well as from other parameters, such as propagation velocity, impedance, attenuation

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and scattering. Using ultrasound, it is also possible to calculate density, viscosity, degree of homogenization of a mixture, and concentration of solid particles in a liquid [8]. At present, the chemical industries, such as the petrochemical and pharmaceutical industries, have a considerable demand for measuring instruments that perform the characterization and discrimination of liquids with high sensitivity and precision. Additionally, automation of the processes often requires "in line" measurements. For this purpose, the use of ultrasound technique can be applied to the process line [9,10].

The aim of this paper is to provide a fast, inexpensive and feasible method to identify the possible fuels adulteration through ultrasonic measurements of attenuation and propagation velocity, using the methodology implemented in the Laboratory of Ultrasound (Labus) of the Brazilian Institute of Metrology (Inmetro) [11]. The uncertainties were assessed according to the Guide to the Expression of Uncertainty in Measurement (GUM) [12].

2. Material and methods

The samples used for measuring the attenuation were poured into a glass cylinder of 80 mm height and 35 mm diameter, and its bottom was sealed with a PVC film. The reference sample contained only distilled water, and the sample to be analyzed contained a mixture of ethanol and water with ethanol concentration range from 89.84% to 93.71% by mass. These concentrations were accurately assessed using the gas chromatography analytical method. The reason for selecting this concentration range was the Brazilian regulation [13], which states that the Hydrated Ethanol Fuel must contain an alcoholic concentration between 92.6% and 93.8%.

In a transmission/reception scheme, an arbitrary waveform generator model 33250A (Agilent Technologies, CA, USA) was used to excite the transmission transducers with 20 V peak-to-peak 20 cycle ultrasonic sine bursts for each tested frequency. The signal from the reception transducer was digitized with an oscilloscope model DSO6032A (Agilent Technologies, CA, USA). One pair of of 15 MHz-central frequency transducers (Panametrics-NDT Olympus Corporation, Japan) was used to generate and capture the ultrasonic signal. Fig. 1 illustrates the measurement setup, and an example of the used waveform is presented in Fig. 2. Software was developed in LabVIEW™ 8.5 (National Instruments Corporation, Austin, TX, USA) to automate the measurements as well as to calculate propagation velocity, attenuation and related uncertainties. The temperature was measured using a calibrated digital thermometer, model 34970A (Agilent Technologies, CA, USA).

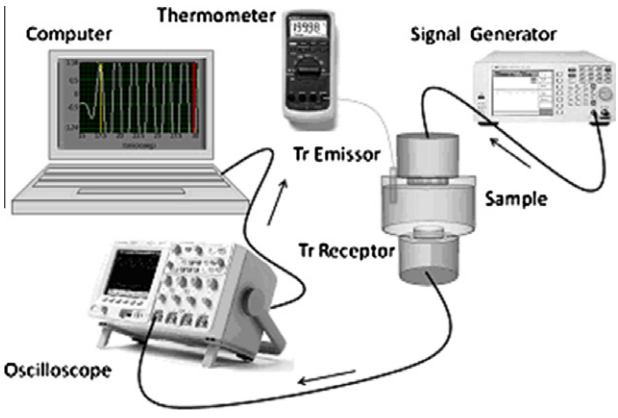

Fig. 1. Illustrative figure with the experimental setup, where "Tr Emissor" is the emitting transducer, "Tr Receptor" is the reception transducer, "Sample" is the container for samples of attenuations mediums, "Signal Generator", "Computer", "Thermometer" and "Oscilloscope" are accessories measuring instruments.

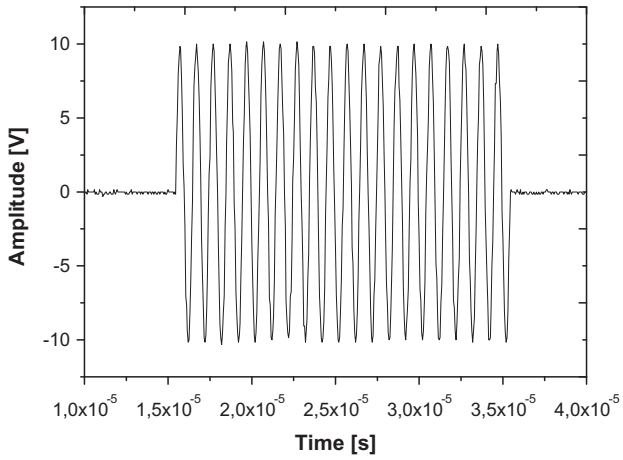

Fig. 2. Example of waveform used in the experiments.

The experiments were performed with the samples of water, ethanol/water and a commercial fuel at room temperature (22–23 °C). Each sample was analyzed in five repetitions to assure the statistical significance of the experimental data.

Illustration of the experimental setup, where "Tr Emissor" is the emitting transducer; "Tr Receptor" is the reception transducer; "Sample" is the container for samples of attenuations mediums; and "Signal Generator", "Computer", "Thermometer" and "Oscilloscope" are the measuring instruments.

2.1. Experimental attenuation

Experimental attenuation (AT_E) for the ethanol/water sample was calculated according to Eq. (1), where V_{wat} is the water attenuated waveform effective (RMS) amplitude (reference signal), V_A is the sample ethanol/water attenuated waveform RMS amplitude (sample signal), and x_e is the sample thickness or the transmission path length in centimeters.

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

According to Eq. (1), AT_E is the excess ultrasonic attenuation in ethanol/water sample relative to attenuation in water. The sample thickness x_e (Eq. (2)) was calculated as a function of the transmission delay Δt_{wat}, in s, measured with the oscilloscope using water as the attenuation medium and the propagation velocity in pure water c_{wat}, in $\mathrm{m\ s^{-1}}$, which was corrected for the temperature according to [14] (Eq. (3)), where T is the temperature, in °C. A precise manual linear stage was used to move the transmission transducer away and back to the same position to adjust the distance when the ethanol/water sample was used.

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

$$\begin{aligned} C_{wat} = {} & 1.40238744 \times 10^3 + 5.03836171T - 5.81172916 \\ & \times 10^{-2}T^2 + 3.34638117 \times 10^{-4}T^3 - 1.48259672 \\ & \times 10^{-6}T^4 + 3.16585020 \times 10^{-9}T^5\ (\mathrm{m\ s^{-1}}) \end{aligned} \tag{3}$$

Measurements were repeated five times at the frequency of 15 MHz, and the attenuation medium (water and ethanol/water samples) was changed between successive measurements.

All measurement system was previously validated with an expanded experimental uncertainty of 0.016 dB, which is equivalent to 0.18% of expanded experimental uncertainty.

2.2. Propagation velocity of the ethanol/water sample

Propagation velocity C_A was calculated according to Eq. (4).

$$C_A = \frac{x_e}{\Delta t_A} \ (\mathrm{m\ s^{-1}}) \tag{4}$$

where x_e is the same distance of the transmission path length of water, in (m), and Δt_A is the transmission delay with the ethanol/water sample as the attenuating medium, in (s).

2.3. Uncertainties models

Type A uncertainties were calculated for the experimental attenuation, and Type B uncertainties were assessed for every repetition. To combine both Type A and Type B uncertainties for a single frequency, the highest value of Type B was selected. Uncertainty in the experimental approach was calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM) [12].

2.4. Statistical tests

Statistical tests were performed to validate the method. A one-tailed t-test ($\alpha = 5\%$) was used to evaluate statistically the closest concentration, which is lower than the experimental concentration closest to the lower limit according to the regulation (92.60% for hydrous ethanol). A sample of commercial fuel was tested using the analytical gold standard (gas chromatography) and the proposed method. A two-tailed t-test ($\alpha = 1\%$) was performed in each pair of results.

The set of data (concentration and ultrasonic parameters) were used to perform a linear regression in the range of concentration from 89.84% to 93.71%.

3. Results

Using the parameters as defined in Eqs. (1) and (4), the experimental results for attenuation and propagation velocity at different fractions of dilution of ethanol are given in Table 1.

The concentration values given in Table 1 were determined using a gas chromatograph with a combined uncertainty of 0.010% (gold standard). A linear regression was applied to that set of data, both for attenuation and for propagation velocity. However, the results arising from the attenuation measurements were not repeatable and lead to high uncertainties (Fig. 3). Because of that the validation was conducted only with the propagation velocity as ultrasonic parameter.

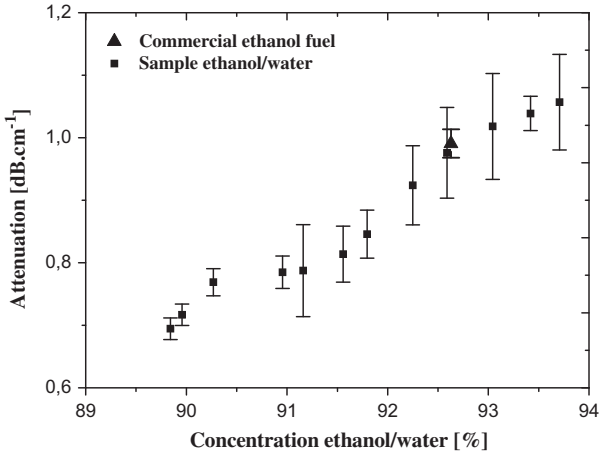

Fig. 3. The scatter plot between attenuation and different concentrations of ethanol/water with respective combined uncertainties. The triangle represents commercial fuel. Correlation coefficient between attenuation and the ethanol/water concentration was 0.97 with a maximum uncertainty of 0.085 dB.

Using ultrasonic propagation velocity as a dependent variable, the measured value is 1216.03 m s^{-1} (uncertainty of 0.15 m s^{-1}) resulted in a calculated concentration of the commercial ethanol 92.59% and uncertainty of 0.022%. The sample concentration was also measured with a gas chromatograph, what lead to a "real" value of 92.63%. A statistical test was applied to compare this "real" value of the concentration of the commercial ethanol, measured using the gold standard, and the concentrations calculated using propagation velocity parameter of the proposed method. The result was statistically identical ($\alpha = 1\%$).

Fig. 4 shows the scatter plot between propagation velocity and different concentrations of ethanol/water with respective combined uncertainties. The triangle represents commercial fuel. The correlation coefficient between attenuation and the ethanol/water concentration was 0.99 with a maximum uncertainty of 0.60 m s^{-1}.

4. Discussion

Two ultrasonic parameters were measured for different concentrations of ethanol and water. The concentration range (89.8–93.7%) was selected to cover the permissible dilution range (92.6–93.8%), as per Brazilian regulation, for hydrous ethanol to be used as biofuel. The upper limit of the tested range is slightly

Table 1
Experimental results for attenuation and propagation velocity at different fractions of ethanol dilution and commercial fuel, and their respective uncertainties (@ 15 MHz). The values present in the first column (concentration (%)) were measured in a gas chromatograph with an uncertainty of 0.010%.

Concentration (%)	Temperature (°C)	Attenuation		Propagation velocity	
		Average (dB cm^{-1})	Combined uncertainty (dB cm^{-1})	Average (m s^{-1})	Combined uncertainty (m s^{-1})
89.84	22.8	0.694	0.017	1236.08	0.59
89.96	22.6	0.717	0.017	1234.58	0.28
90.27	22.4	0.769	0.022	1231.52	0.22
90.96	23.0	0.785	0.026	1229.31	0.31
91.16	22.2	0.787	0.074	1225.68	0.60
91.56	22.6	0.814	0.045	1223.70	0.18
91.80	22.6	0.846	0.038	1221.33	0.23
92.25	22.6	0.924	0.063	1218.084	0.096
92.59	22.8	0.976	0.073	1216.23	0.54
93.04	22.8	1.018	0.085	1213.759	0.067
93.42	22.5	1.039	0.027	1211.35	0.24
93.71	22.4	1.057	0.077	1206.15	0.18
92.63	22.7	0.991	0.023	1216.03	0.15

The last row of the table is referring to the commercial ethanol.

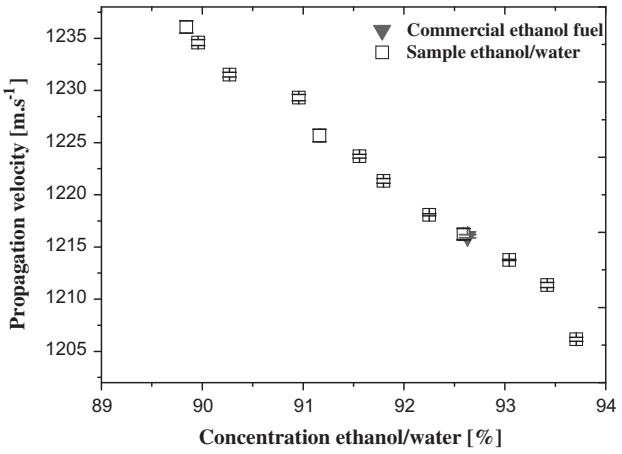

Fig. 4. The scatter plot between propagation velocity and different concentrations of ethanol/water with respective combined uncertainties. The triangle represents commercial fuel. The correlation coefficient between propagation velocity and the ethanol/water concentration was 0.99 with a maximum uncertainty of 0.60 m s^{-1}.

lower than 93.8%, but it is not that side of the range that is most important for adulteration concerns.

Statistical tests confirmed the sensitivity of the method. The results show that the propagation velocity have statistically different outcomes for the concentrations closer to and lower than the permissible limit (92.6%) specified in Brazilian regulation, the lower concentration was statistically 92.25%, which differs from 92.59% ($p < 0.02$, $\alpha = 5\%$). This result indicates that this parameter seems to be reliable to detect concentration within the permissible limits imposed by the Brazilian regulation.

Experimental attenuation (dB cm^{-1}) shows a maximum combined uncertainty of 0.085 dB cm^{-1} and a correlation coefficient of 0.97. However, its signal is not stable, so results were not reliable enough to consider this parameter a good one for determining the adulteration of fuel ethanol.

Ultrasonic propagation velocity leads to maximum combined uncertainty of 0.60 m s^{-1} and a correlation coefficient of 0.99 (in modulus). These uncertainties are larger as compared to the other analytical instruments, such as the gas chromatograph (uncertainty, 0.010%). However, a *t*-test shows that the concentration of a commercial ethanol fuel tested, using the proposed method as well as the gas chromatography analytical method (gold standard), is statistically identical for propagation velocity when compared to the gold standard ($\alpha = 1\%$). In addition, the proposed method is faster in obtaining the results and can be easily set up to use outside of the laboratory.

In this study, the experiments were conducted in a laboratory under controlled temperature conditions with a variation of less than 1.2 °C. The liquid temperature has a remarkable influence on the viscosity, which is one of the main parameters that affect attenuation and propagation velocity. Therefore, for outdoor application, precaution should be taken to avoid basic errors due to temperature variation. Moreover, other parameters should be take into account considering outdoor application as, for example, the ultrasound signal stability and transducers alignment.

As ethanol and water has a very low attenuation that increases with frequency, a relatively high ultrasonic frequency of 15 MHz was selected for the experiments. The instability of ultrasonic propagation at high frequencies can lead to higher uncertainties, and, thus, extra precaution should be taken in the experimental setup. Alternatively, low frequencies would lead to low sensitivity in the attenuation curve.

5. Conclusion

According to the measurement realized in the present work, ultrasonic propagation velocity was found to be useful to identify adulteration in ethanol fuel. The efficiency of this methodology is demonstrated by the low experimental uncertainties and the high correlation coefficient. On the other hand, considering the experimental setup used in this work, attenuation could not be considered a good parameter for identify adulteration. Improvements in the experimental setup are necessary to get more accurate attenuation measurements.

The described methodology can be used as a tool to identify fuel adulteration, and the assessment can be performed "in line", as far as some measurement conditions requirements are fulfilled. One should keep in mind that the proposed method is to be used as a survey, and precision of the method is not comparable to other analytical methods used in chemistry.

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