Gasoline composition monitoring using ultrasonics

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Abstract. Monitoring the adulteration of fuels is a matter of interest as a means of protecting consumers, preventing fraud and protecting the environment. In Brazil, commercialized gasoline is a mixture of fuel with 27% anhydrous ethanol, called C gasoline. As a misleading practice, larger fractions of ethanol and organic solvents are used. Laboratory analyses are necessary to detect this irregularity, making inspection actions more difficult. Given the above, the article proposes using ultrasound to identify gasoline adulteration as an alternative method. Different samples were used: pure gasoline, gasoline with ethanol prepared for the study (gasoline C) and mixtures with kerosene. The study was based on measuring two monitoring parameters: propagation velocity and experimental attenuation. Ultrasound transducers with central frequencies 1 MHz and 5 MHz were used in the pulse-echo method. Paired comparisons (t-tests) were performed to assess whether the use of ultrasound was sensitive to changes in the medium with the addition of solvent. The experimental attenuation showed a statistical difference compared to gasoline without kerosene, proving to be a good parameter to be monitored. For the propagation speed, only the samples with 20% and 30% of kerosene and with the 1 MHz transducer proved adequate to the proposed method.

1. Introduction

In Brazil, gasoline commonly sold is called C gasoline, which corresponds to a mixture of 73% A gasoline (which is gasoline without the addition of any other component) and 27% anhydrous ethanol, according to legal specifications [1]. There are other authorized components, such as additives to reduce pollutant emissions, improve fuel efficiency, or even prevent vehicle damage.

Despite the rules for gasoline composition, misleading practices of adulterating this composition are observed, aiming to defraud and obtain improper profit. To evidence such practices, chemical analyses in the laboratory are required. At sale stations, it is only possible to determine the density and percentage of anhydrous ethanol in the gasoline sample collected.

Given the context presented, this article proposes using ultrasound to monitor gasoline composition as a simpler technique and with the possibility of wider use than conventional analyses. The addition of solvents to gasoline alters its physicochemical properties. With this, acoustic properties are also changed. And it is precisely on the correlation between acoustic parameters with physical-chemical properties that the work is based.

The effectiveness of this correlation has been the subject of interest in different areas, especially in the food industry. In the study by Boutkedjirta et al. [2] on olive oil, it is concluded that "there is a good correlation between the measured acoustic and mechanical parameters (an increase of the group velocity, phase velocity, density and a decrease of attenuation and viscosity according to the percentage of soya oil in the mixtures)".

The work proposed by Figueiredo et al. [3] uses gasoline as an object of study, where the phase velocity (speed of sound) and attenuation (or transmission loss) of ultrasound were assessed, differing, in the present case, the method used which was the transmission-reception method. In contrast, the one proposed here uses the pulse-echo method and different frequencies.

The velocity of sound wave propagation has a characteristic value for each medium. It may have variations caused by changes imposed on the medium, such as, for example, the change in fluid temperature capable of altering the density or viscosity of the medium. However, in general, the propagation velocity can be used to identify a given material.

In the study by Sharma and Gupta [4], this parameter was used to identify the adulteration of fuels, especially gasoline and diesel. In the specific case, the propagation velocity of the wave in the medium showed an increasing value with the increase of gasoline adulteration (with diesel) and a decreasing value with the rise in diesel adulteration (with kerosene). The common fact in all samples studied was the increase in velocity with the rise in specific mass. However, the fact is unjustified, requiring further theoretical and experimental investigation.

The propagation velocity has been determined experimentally as pure water for many media. In the publication, Underwater Acoustics – Technical Guides, from the National Physical Laboratory – NPL [5], the propagation velocity is presented as a function of temperature and, in a particular case, pressure. This information is useful when using reference values as a standard for comparison or even when determining the distance travelled by the sound wave.

From the knowledge of the distance (d), it is possible to obtain the propagation velocity (c) by measuring the ultrasound flight time in different media (t) by the relation:

$$c = \frac{d}{t} \tag{1}$$

Attenuation can be understood as any effect that causes a reduction in the amplitude of a sound wave. It can be caused by reflection, scattering, and heat dissipation. In a theoretical approach, it is considered an intrinsic characteristic of the material where the sound wave propagates. Thus, variations in the medium are expected to produce changes in attenuation. Proving the previous claim, Souza et al. [6] experimentally evaluated the changes in the attenuation coefficient of a tissue-mimicking material caused only by changes in temperature (between 19 °C and 37 °C). In this specific case, the temperature gradient promoted slight changes in molecular cohesion, sufficient to affect the impedance of the propagation medium.

In another study proposed by Figueiredo et al. [7], "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 concept of experimental attenuation (AT_E) adopted in the cited work, is transcribed for application in the present research and can be obtained as a function of the relationship with the loss of amplitude concerning deionized water, considered the reference medium.

$$AT_E = \frac{20 \log\left(\frac{V_{wat}}{V_A}\right)}{d} \tag{2}$$

Where:
V_{wat} – reference voltage amplitude (deionized water);
V_A – propagation medium voltage amplitude (medium under test);

d – distance travelled by ultrasound waveforms.

2. Materials and Methods

The first stage of the work consisted in the preparation of solutions for the study. From gasoline A, the regulated value of ethanol (27%) was added, obtaining gasoline C. Kerosene was the chosen solvent. The C gasoline thus produced was mixed with different concentrations of kerosene for further ultrasound time-of-flight determinations and signal amplitude measurement. Mixtures of gasoline C and kerosene were prepared in the following concentrations: 10%, 20% and 30%.

Ultrasound propagation velocities (c) were obtained in the different samples, as established by equation (1). Half of the flight time was used in applying the equation since pulse-echo was used. That is, the measured time corresponds to the round-trip interval of the sound wave. The signal amplitude determined the experimental attenuation according to equation 2.

A t test (paired comparisons) was performed between the C gasoline samples and the different kerosene-added preparations. To carry out the test, the following hypotheses were considered:

$$H_0: \mu_1 - \mu_2 = \Delta_0$$
$$H_1: \mu_1 - \mu_2 \neq \Delta_0$$

In this case, μ_1 corresponds to the mean of the C gasoline sample and μ_2 will represent the means of mixtures with kerosene, in each test. $\mu_d = \mu_1 - \mu_2$ is the average of the differences. To assess whether there is a difference in the addition of kerosene, $\Delta_0 = 0$ will be considered. A probability of 95% was adopted, and the t statistic was calculated, according to equation (3), where s corresponds to the difference standard deviation, n the number of elements in the data set:

$$t = \frac{|\mu_d - \Delta_0|}{s \cdot n^{-0,5}} \tag{3}$$

The t$_{critical}$ values for ν degrees of freedom, considering a two-tailed t-distribution were determined for comparison with t$_{calculated}$ values. t Tests were performed for propagation speed and experimental attenuation, as shown in section 3.
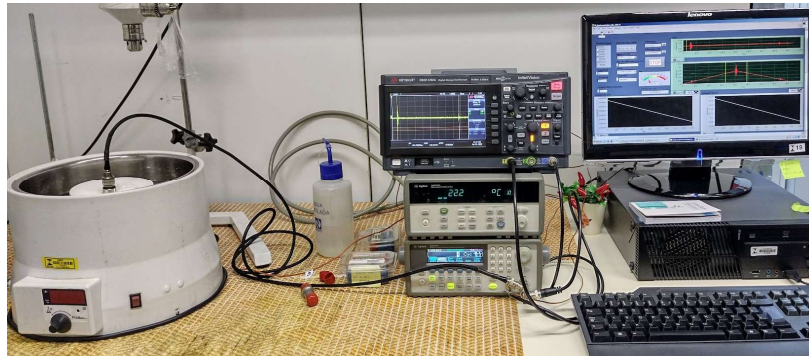

Figure 1. Experimental setup.

In all determinations, the experimental setup followed what is shown in figure 1.

The samples were placed in a glass container with a stainless-steel reflector target at the bottom. The distance (d) travelled by the ultrasound to the reflecting target was previously determined using deionized water as a reference since this propagation medium already has known acoustic parameters. Figure 2 summarizes the reported scheme.
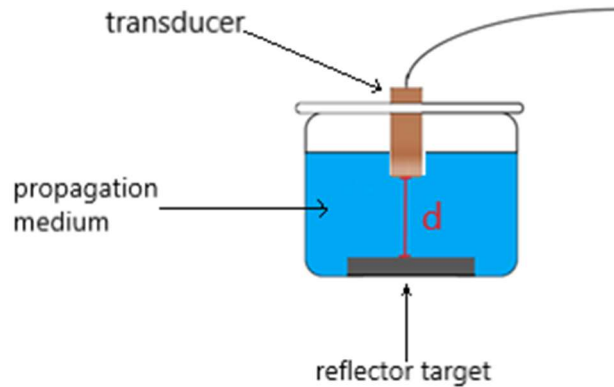
Figure 2. Detail of the positioning of the reflector target and transducer.

Measurements were performed at the laboratory's ambient temperature. A thermostatic bath was used only to condition the glass container and maintain thermal inertia. The ultrasound transducers were used in pulse-echo mode, excited by an Agilent Technologies signal generator, model 33250A. Olympus transducers of different nominal frequencies, specified in the result tables, were used. The data of the generated signals were digitalized by an oscilloscope Agilent Technologies, model DSO-X 3012A and the temperature data of the propagation medium was measured with thermocouple type K and Data Acquisition Agilent Technologies, model 34970A. A Labview™ routine was used to acquire the signals. Figure 3 shows an example of the Labview control panel for signal amplitude measurement.
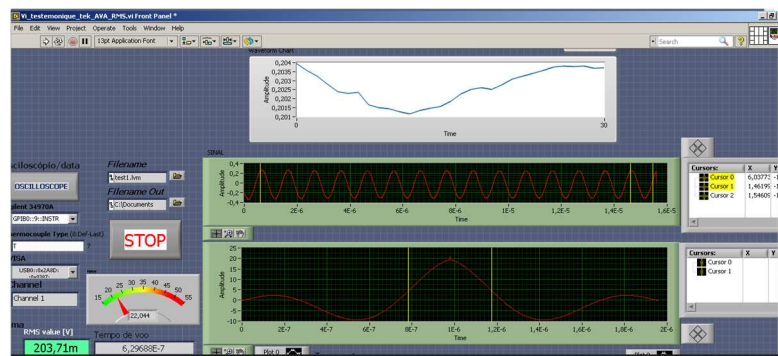

Figure 3. Labview™ panel.

3. Results

The results of determining the propagation speed and experimental attenuation of the samples are in table 1 below.

Table 1. Speed of propagation and experimental attenuation

	f (MHz)	A	C	10%	20%	30%
c ($m\ s^{-1}$)	1	1126.83	1160.14	1146.50	1118.55	1121.95
	5	1162.02	1154.01	1157.77	1168.15	1148.17
AT_E ($db\ cm^{-1}$)	1	1.51537	0.20042	0.79926	0.74652	0.86286
	5	1.86838	3.09951	4.43071	1.89634	1.95167

The results of the t tests (paired comparisons), comparing the propagation speed from samples with C gasoline (without the addition of kerosene) are presented in tables 2 and 3, for frequencies used, 1 MHz and 5 MHz.

Table 2. t Test – C Gasoline x Kerosene – 1 MHz – Propagation Speed.

Parameter	10%	20%	30%
$t_{calculated}$	1.67	4.09	4.43
$t_{critical}$	2.4	2.4	2.4

Table 3. t Test – C Gasoline x Kerosene – 5 MHz – Propagation Speed.

Parameter	10%	20%	30%
$t_{calculated}$	1.09	1.99	1.03
$t_{critical}$	2.4	2.4	2.4

The results of the t tests (paired comparisons), comparing the experimental attenuation from samples with C gasoline (without the addition of kerosene) are presented in tables 4 and 5, for frequencies used, 1 MHz and 5 MHz.

Table 4. t Test – C Gasoline x Kerosene – 1 MHz – Experimental Attenuation.

Parameter	10%	20%	30%
$t_{calculated}$	13.0	11.7	7.3
$t_{critical}$	2.4	2.4	2.4

Table 5. t Test – C Gasoline x Kerosene – 5 MHz – Experimental Attenuation.

Parameter	10%	20%	30%
$t_{calculated}$	29.2	16.9	50.8
$t_{critical}$	2.4	2.4	2.4

4. Discussion

The t Tests were performed to analyze the effect of adding solvent compared to the sample without addition (only C gasoline), as shown in tables 2, 3, 4 and 5. The adopted criterion establishes that the null hypothesis (H_0) is rejected when $t_{calculated}$ is greater than $t_{critical}$. H_0 states that there is no difference between means. Rejecting H_0 means that the data sets are not considered to be statistically equal. Thus, rejecting the null hypothesis is the expected result.

In tables 2 and 3 propagations speed comparisons are showed. In this specific case, it was observed that the null hypothesis is only rejected for kerosene concentrations of 20% and 30%, using the transducer with a central frequency of 1 MHz.

From a statistical point of view, there is a difference in experimental attenuation for all concentrations and regardless of the transducer used. In this case, all tests performed returned with the information to reject H_0.

It was observed that the attenuation of the ultrasonic signal is greater with a frequency of 5 MHz compared to 1 MHz. This fact can be used to help choose the most appropriate transducer.

5. Conclusion

Practically, there is an indication that ultrasound was somehow sensitive to the variation of the medium with the addition of solvent. It is observed specially for the experimental attenuation. Another aspect of

interest is the proposed method (pulse-echo), which proved to be adequate, being a more practical option due to the use of a single ultrasound transducer.

The proposal contained in the article represents the initial action of an experimental sequence that requires the investigation of other solvents at different concentrations. An evaluation of the uncertainties involved is proposed for proper validation of the method, in addition to determining the limits of detection and quantification.

As in other referenced works, it was proven that the alteration of physicochemical properties, such as the density, caused by the addition of substances different from the original results in a change in the acoustic parameters since the acoustic impedance of the medium also changes.

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