Determination of ethanol Concentration in Gasoline using refractometry method

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Although a definitive decision has been made to gradually transition from propulsion by combustion engines to other forms, dominated by electric drives, there are sectors that still cannot do without conventional means of propulsion. One of these sectors is agriculture. In the context of economic or legislative measures and political arrangements and their changes, it is currently not possible to predict any longer-term trends in the consumption of petroleum fuels, biofuels or electricity. What is certain, however, is that the agricultural sector will be a significant consumer of its products in the form of biofuels for powering mobile vehicles. The actual consumption figures of bioethanol for the production of mixed fuel are around 100,000 tonnes per year (Bufka et al., 2022). The design measures for operating combustion engines on bio-components are described in great detail and have been used for a long time, but the problem is the constant demands placed on the resulting concentrations of limited pollutants. Until now, the control strategies of combustion engines with feedback on the proportion of oxygen will not be sufficient, because, for example, the amount of NOx pollutants is subject to Zeldovich's law, which unambiguously classifies the combustion temperature as a significant parameter. Optimisation of the combustion method and especially the adequate regulation of emission systems will rely on the determination of one's own fuel. Simply put, it will be necessary to determine the concentrations of the components even before the actual formation of the mixture. It is necessary to realise that in a real vehicle, fuels of different composition are mixed in the vehicle's tank. There are many ways to determine the concentration of, e.g., ethanol in automobile gasoline, one of the authors (Žák M., Marek, V., 2016) built it on the basis of monitoring the electrical conductivity of the double gate according to the topic of the study by (Rocha M.S., Simoes M.J.R., 2005). The concentration can also be determined in other ways, for example, it is possible to test the viscosity of the mixture (Kumbár V., Dostál P., 2014), but these methods are analytically demanding and necessarily require the precise measurement of other necessary quantities, e.g., temperature (Trost D. et al., 2021). The set goal of the experiment was to confirm, or to disprove the hypothesis that establishes the possibility of determining the concentration based on testing the optical properties of the mixtures, as is customary in other ethanol processing industries. If gasoline is a mixture of carbonaceous substances containing mainly chains with lengths of C4 to C10, it can be concluded from Table 1 that the refractive index of such a mixture could be around 1.45. From a comparison with ethanol's refractive index of 1.36, it can be seen that the mutual difference is significant. Based on this consideration, a method was proposed for determining the content of ethanol in a mixture with gasoline based on the change in the refractive index.

Table 1 – Refractive index of some liquids at a temperature of 20 °C

Chemical substance	Chemical formula	Refractive index
water	H_2O	1..33299
ethanol	C_2H_6O	1.36143
propane-1-ol	C_3H_8O	1.38556
propane-2-ol	C_3H_8O	1.37720
butane-1-ol	$C_4H_{10}O$	1.39930
pentane-1-ol	$C_5H_{12}O$	1.41000

cyclopentane	C_5H_{10}	1.40645
cyclohexane	C_6H_{12}	1.42623
benzene	C_6H_6	1.50112
toluene	C_7H_8	1.49693
acetone	C_3H_6O	1.35868

Materials and methods

The method of determining the refractive index is based on the fact that if a beam of monochromatic radiation passes through an interface separating two different media differing in density, there is partial reflection and partial passage of the beam through this interface. The environment into which the beam enters imposes a certain "resistance", the size of which depends on the density of the environment, which is a reflection of the qualitative and quantitative composition. A refraction, or refraction, of a light beam occurs through the interface, which changes its direction and speed. If the direction of the incident beam is perpendicular to the surface, only the speed of propagation changes, not the direction. Changes occur only at the interface, where light propagates in a straight line inside the environment. The index of refraction *n* is therefore the ratio of the propagation speed in the medium according to Equation *(1)* where the beam leaves c_1 and it enters the medium c_2.

$$n = \frac{c_1}{c_2} \text{ [-]} \qquad (1)$$

Where c_1 is the velocity of the propagation in the leaving medium [m.s^{-1}], c_2 is the velocity of propagation in the medium into which the beam enters [m.s^{-1}].

It follows from the above that the refraction index is only a relative quantity, so it was necessary to introduce a base to which the refraction index will relate. This environment is a vacuum, in which the speed of the light beam is the largest and is c_0 =2.997925.108 m.s^{-1}. The so-called absolute refraction index can thus be obtained by passing a beam from a vacuum into a given environment.

$$n_0 = \frac{c_0}{c_2} \text{ [-]} \qquad (28)$$

, where c_0 is the speed of light in a vacuum [m.s^{-1}], c_2 is the speed of propagation in the medium into which the beam enters [m.s^{-1}].

The technical means for determining the refractive index (RI) is a refractometer. For the purposes of the experiment, an ATAGO digital refractometer was used, which is commercially available (the technical specifications are shown in Table 2)

Table 2 – Technical parameters of the ATAGO PAL-RI refractometer

Refractometer ATAGO PAL-RI	
Measuring range	1.3306 – 1.5284 RI 5 - 45 °C
Distinction	0.0001 RI 0.1 °C
Measurement accuracy	± 0.0003 RI ±1°C

Due to the practical use of the results of the experiments, the samples were prepared from fuels that came from the distribution network of gas stations, with sampling occurring in the summer and winter months. Commercial fuel, which is distributed without the content of bio-components and is declared by the manufacturer to have a zero concentration (analytically verified), and 98.5% denatured bioethanol were used as components of the reference mixtures. At the same time, samples of the fuel mixtures were also prepared, which were composed of volume fractions of automobile gasoline and fuel labelled E85, this method of "preparation" will be dominant in normal operations. The samples (20 test samples) were mixed from the bases, which were subjected to tests, while emphasis was placed on performing the test in such a way that no error was introduced due to the evaporation of the lighter hydrocarbon fractions (non-linear function of time). The results were subjected to a statistical investigation in the software Statistica v14.

Results and discussion

The initial result was a comparison of the E85 samples distributed in the summer and winter periods. By comparison, a deviation was found, while the summer batch showed an actual ethanol content of 85%, the winter batch only showed an ethanol content of 80%. The results of the measurement of the sample standards are presented in Table 3, the descriptive statistics, and the results are shown graphically in Fig. 1.

Table 3 – Descriptive statistics of the fuel mixtures by the concentration

Concentration	Average	95% confidence interval	95% confidence interval	Median	Lower quartile	Upper quartile	Standard deviation
0	1.422895	1.422279	1.423511	1.423200	1.421600	1.423800	0.001316
15	1.413438	1.413132	1.413743	1.413400	1.412750	1.414200	0.000955
25	1.407563	1.407292	1.407833	1.407600	1.406900	1.408150	0.000846
40	1.398258	1.397940	1.398575	1.398200	1.397500	1.398850	0.000994
55	1.388938	1.388756	1.389119	1.388900	1.388550	1.389400	0.000566
70	1.379930	1.379811	1.380049	1.379950	1.379600	1.380200	0.000371
85	1.371703	1.371609	1.371796	1.371650	1.371500	1.371950	0.000292

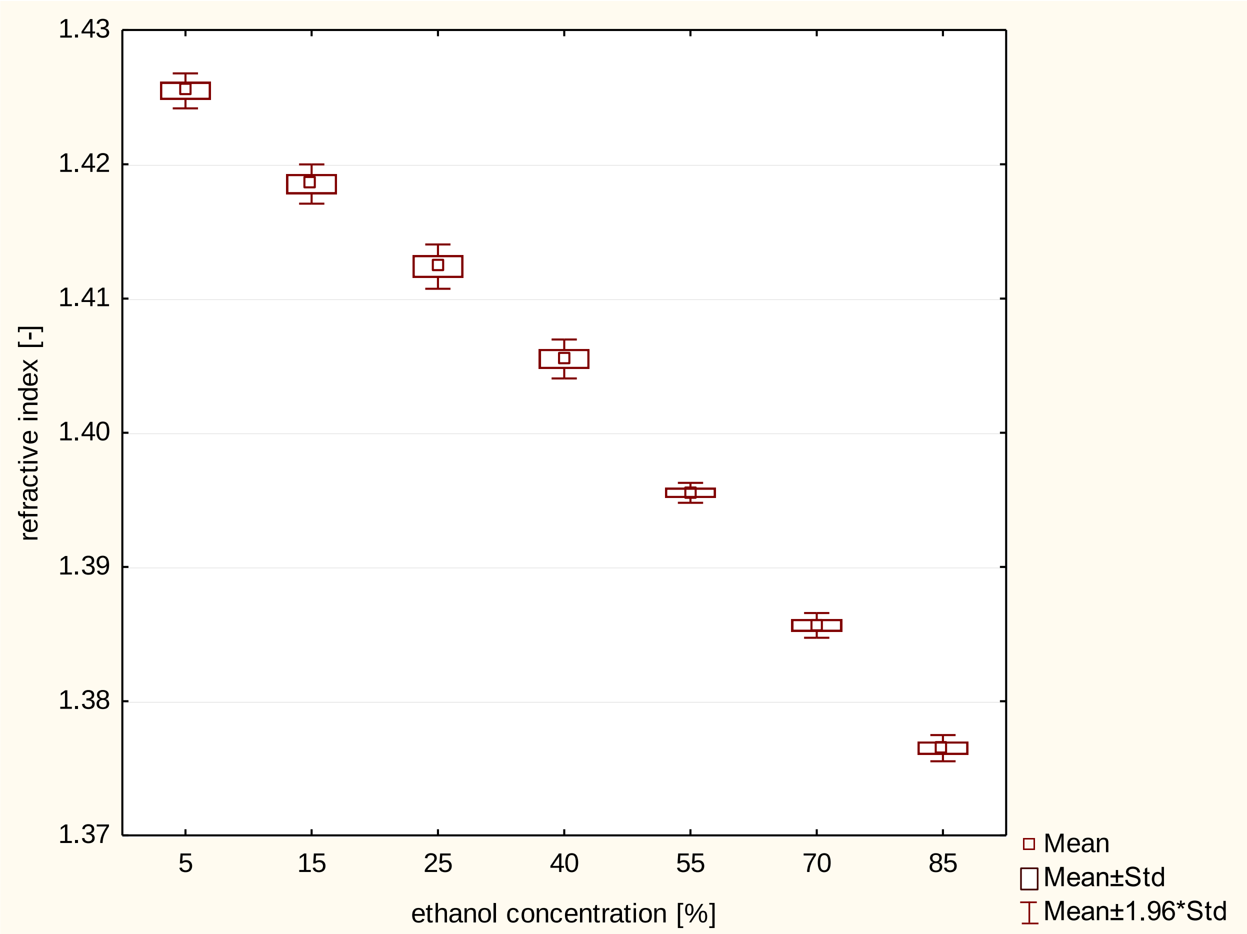

Fig. 1 – Refractive index depending on the ethanol concentration mixed with gasoline

However, it was observed from the analysis of variance (ANOVA) that the distribution of the measured data does not correspond to the assumption of homogeneity, for this reason, the data were subjected to a paired t-test in order to confirm that the individual concentrations will be reliably distinguishable (see Table 4).

Table 4 – Paired t-test results of the refractive index by the concentration

Compared concentrations		Average K1	Average K2	t-test	Degrees of freedom	Calculated level of significance
K1	K2					
0	**15**	**1.42290**	**1.41344**	**31.776**	**58**	**0.000**
0	25	1.42290	1.40756	54.663	58	0.000
0	40	1.42290	1.39826	81.079	58	0.000
0	55	1.42290	1.38894	140.113	58	0.000
0	70	1.42290	1.37993	193.130	58	0.000
0	85	1.42290	1.37170	236.483	58	0.000
15	**25**	**1.41344**	**1.40756**	**29.113**	**78**	**0.000**
15	40	1.41344	1.39826	69.655	78	0.000
15	55	1.41344	1.38894	139.515	78	0.000
15	70	1.41344	1.37993	206.793	78	0.000
15	85	1.41344	1.37170	264.215	78	0.000
25	**40**	**1.40756**	**1.39826**	**45.091**	**78**	**0.000**
25	55	1.40756	1.38894	11.,668	78	0.000

25	70	1.40756	1.37993	189.136	78	0.000
25	85	1.40756	1.37170	253.311	78	0.000
40	**55**	**1.39826**	**1.38894**	**51.540**	**78**	**0.000**
40	70	1.39826	1.37993	109.301	78	0.000
40	85	1.39826	1.37170	162.173	78	0.000
55	**70**	**1.38894**	**1.37993**	**84.141**	**78**	**0.000**
55	85	1.38894	1.37170	171.020	78	0.000
70	**85**	**1.37993**	**1.37170**	**110.211**	**78**	**0.000**

From the results of the paired t-test of the refractive index (Table 4), where all the data were evaluated, it is clear that the differences between the individual concentrations are highly significant. The most important information, however, is the difference between neighbouring concentrations, the results of which are highlighted in red in the table. A trend line was fitted to the measured data, shown also with its equation and determination index in the graph in Figure 2. Due to the high determination index (R2 = 0.9978), it was decided that a linear trend line is sufficient to describe the data.

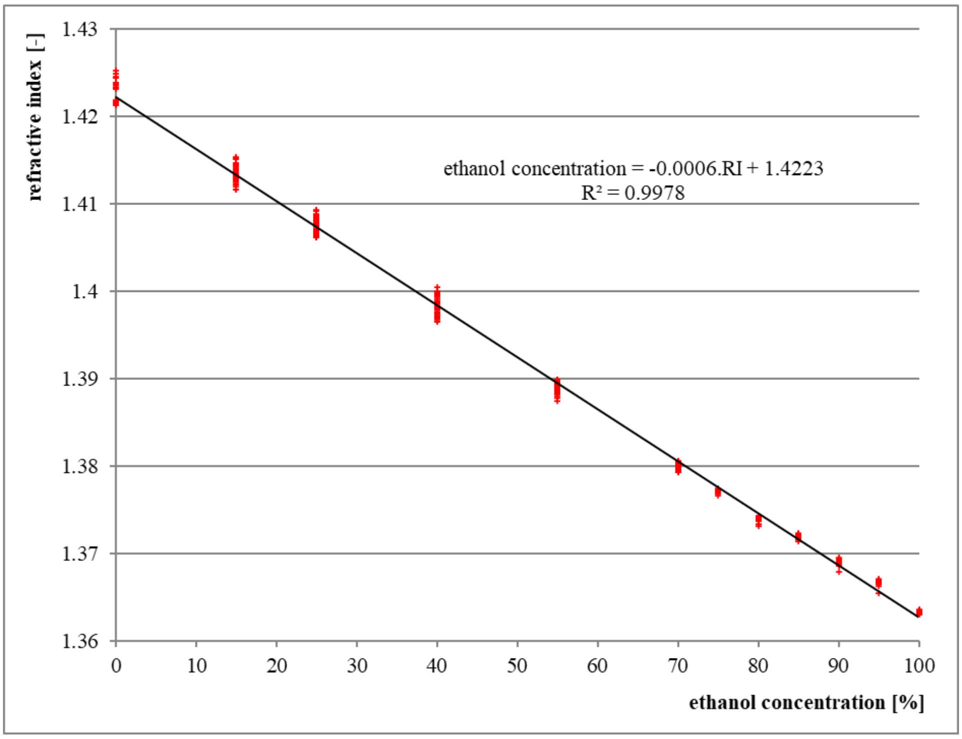

Fig. 2 – Linear trend line for the measured refractive index data

Conclusions

Based on the assessment of the results obtained by the experiment, it can be clearly stated that the determination of ethanol concentration in automobile gasoline is very reliable and can be used not only for the quick and effective detection for general detection, but especially for internal combustion engine control systems. Here, a significant advantage is the possible determination of a relatively accurate concentration and for the subsequent correction with a simple function with a linear prescription. These conclusions are supported by the statistical investigation illustrated above. The stated method of measurement, or respectively, the used method means that there need not be complex changes in the combustion process control. The technical implementation can consist of a simple device integrated into the system that continuously monitors the refractive index according to the detected dependence. In addition, the course of the regression function shows that a digital refractometer does not need to be used for the external orientation tests, and, if the measurement preparation time is respected (due to the evaporation of lighter fractions of gasoline), a manual optical refractometer will also be possible to use for the measurement.

Literature

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Summary

The article opens with a hypothesis that is able to distinguish the ethanol concentration in a fuel mixture based on the change in the refractive index. This hypothesis has been confirmed by an experiment monitoring the effect of ethanol content of fuel in automotive gasoline. The method has been verified on fuel standards and samples taken from the distribution network, also taking into account the influence of the transition between winter and summer fuels. The statistical investigation showed the tightness of the functional prescription and the reliability in determining the ethanol concentration.

Key words: ethanol, flex-fuel, refractive index, biofuel.

Souhrn

V úvodu článku je uvedena hypotéza, že koncentraci ethanolu ve směsném palivu lze rozlišit na základě změny indexu lomu. Tato hypotéza byla potvrzena experimentem sledujícím vliv podílu ethanolu v palivu u automobilových benzinů. Metoda byla ověřena na etalonech i vzorcích paliv odebraných z distribuční sítě, a to i při vlivu přechodu mezi zimními a letními palivy. Statistické šetření ukázalo těsnost funkčního předpisu a spolehlivost při určení koncentrace ethanolu.

Klíčová slova: ethanol, flex-fuel, index lomu, biopalivo.