

Using gas chromatography to determine the amount of alcohols in diesel fuels

V. Hönig^{1,*}, J. Táborský¹, M. Orsák¹ and R. Ilves²

¹Czech University of Life Sciences Prague, Faculty of Agrobiological Sciences, Department of Chemistry, Kamýcká 129, 16521 Prague 6, Czech Republic

²Estonian University of Life Sciences, Institute of Technology, Kreutzwaldi 56, EE51014 Tartu, Estonia.

*Correspondence: honig@af.czu.cz

Abstract. The European Union tries to reduce carbon dioxide production and reduce fossil fuel consumption. One way to achieve this goal is adding biofuels to regular motor fuels. Biofuels also decrease the production of other harmful substances. This paper evaluates the identification of n-butanol and isobutanol in diesel fuel. The application of n-butanol to diesel fuel is currently being considered. Alcohols blended into diesel fuel have been shown to have a positive impact on solid particle production, smoke emission, etc. Bioethanol and biobutanol can be easily produced from waste products as second-generation biofuels. The experimental part of the paper focuses on the identification of n-butanol and isobutanol in diesel fuel, as it has been previously used for detecting bioethanol additions in diesel fuel. Test samples with the following composition were prepared: 10% of ethanol in diesel fuel; 5%, 10%, 20% of n-butanol in diesel fuel; 5% of n-butanol and 5% of isobutanol in diesel fuel; 10% of n-butanol and 10% of isobutanol in diesel fuel. This paper deals with the use of gas chromatography (GC) in the evaluation of motor fuels. GC analysis can provide a sort of a fuel ‘fingerprint’ that shows the approximate distillation profile and can reveal the presence of other foreign fractions. Regular evaluation procedures using gas chromatography for the determination of a diesel fuel’s quality unfortunately do not exist at the moment. As it is shown, GC could provide very valuable information in fuel quality assessment, making it the method of choice for this procedure.

Key words: GC–FID, n-butanol, isobutanol, boiling point.

INTRODUCTION

The European Union is one of the main actors in the struggle for reducing the emission of greenhouse gases. The main producers of greenhouse gases in the European Union are the energy, transport and industry sectors (Nigam and Singh, 2011). The key to reducing greenhouse gas emissions is the introduction of renewable energy sources into the field of energy and industry. In the transport sector, the efficiency of combustion in engines must be improved and the use of biofuels must be significantly increased (Dukulis et al., 2009; (Dukulis & Birkavs, 2013).

The growing transport load raises several fundamental problems that need to be solved in an optimal manner by the modern society. From the perspective of long-term sustainability in transport, we are presented with two major problems—fossil fuel consumption and carbon dioxide production. A possible solution to both these problems

is biofuel. Bioethanol and biobutanol are easy to manufacture compared to traditional fossil fuels (Demirbas, 2011; Da Costa Filho, 2014).

Diesel Flexi–Fuel vehicles with the respective marking are an equivalent of FFVs (Flexible–Fuel Vehicle) designed for burning high ethanol blends. There is also an alternative in the form of E–diesel, which is used mainly for heavy goods vehicles and agricultural machinery. Another option is O2 Diesel™ that can be used in unmodified engines within the existing infrastructure according to the manufacturer. This fuel is mainly available in the southern and south-eastern part of the United States.

Bioethanol has a low calorific value; however, in diesel fuel it causes a number of problems. Yet, it is also possible to use other alternative alcohols. Biobutanol can be produced from the same sources as bioethanol, and it has a more positive impact on the quality of the fuel (Hönig et al., 2014; Mařík et al., 2014). Cultures of *Clostridium acetobutylicum* are used to produce biobutanol in the form of n-butanol (butan-1-ol). Researchers also focus on the blue-green algae strain of *cyanobacteria* that produce biobutanol in the form of isobutanol (Mosier et al., 2005; Patáková et al., 2010; Pointner et al., 2014).

The contamination of diesel fuel in the tank due to residual gasoline is a common phenomenon. In the evaluation of diesel with the help of GC–FID it was found that there are also cases where diesel fuel contains other non-standard additives with different boiling points. The presence of undesirable admixtures in diesel fuel is explained by the fact that the fuels are not taxed and their import has not been checked (Lissitsyna et al., 2012; Hložek et al., 2014).

There are no standard procedures for using gas chromatography to determine the quality parameters of diesel fuels. However, GC procedures for simulated distillation could represent the standard of distillation. The results cannot be confused with the classic distillation test corresponding to EN ISO 3405. Nevertheless, gas chromatography provides very valuable information in the evaluation of diesel fuel.

This paper deals with the addition of bioethanol, n-butanol and isobutanol to diesel fuel and their identification through gas chromatography. This method may also identify impurities, such as gasoline; light fuel oil, etc. (Sarafraz–Yazdi et al., 2012).

Conventional gas chromatography is used to obtain the so-called fingerprint of the chromatogram. The device is comprised of a flame ionization detector (FID), simple linear temperature program, and chromatographic column with a nonpolar stationary phase (Mostafa & Górecki, 2013).

A commercially available fused-silica capillary column with the stationary phase of the polydimethylsiloxane (PDMS) type with a length of 5–30 m and an internal diameter of 0.2 to 0.53 mm may be used. For dispensing the sample, a standard heated injector with a divider (split/splitless injector) is generally used (Biedermann & Grob, 2012; Blasé et al., 2015; Caruso et al., 2011).

The quantities of individual substances (ethanol, isobutanol, n–butanol) are calculated according to the following formula (1):

$$c_i = \frac{P_i}{P_s} \cdot c_s \cdot k_i \quad (1)$$

where: c_s – concentration of internal standard ($\mu\text{g ml}^{-1}$); c_i – concentration of analysed component ($\mu\text{g.ml}^{-1}$); P_i – area of respective peak (mm^2); P_s – peak area of internal

standard (nonane [mm²]); k_i – the coefficient calculated from the respective calibration curve.

MATERIALS AND METHODS

Diesel fuel samples complying with EN 590 that do not contain fatty acid methyl esters were used for laboratory tests. Test n-butanol and isobutanol were p.a. (LachNer, Ltd.), isooctane p.a. (Lachema Brno) in quality. Ethanol corresponded to the standard prEN15379. Nonane (puriss grade, certified reference material, Slovak Institute of Metrology) was used according to an internal standard.

Test samples were prepared with the following composition (all figures in % vol.):

1. ethanol in diesel fuel: 10%;
2. n-butanol in diesel fuel: 5%, 10%, 20%;
3. isobutanol and n-butanol in diesel fuel: 5% and 10% (each component).

The volume percentage was calculated from the measured quantities of the individual substances before mixing. Samples were stored in dark brown glass bottles with the volume of 20 ml. For the purpose of GC measurement the test samples were dissolved in isooctane, and nonane was added to all samples according to an internal standard. Samples were mixed according to the following scheme: 1,000 μ l of isooctane + 10 μ l of diesel fuel + 10 μ l of nonane. Diluting samples with a suitable solvent, in this case isooctane, has improved the separation efficiency in the chromatographic column.

The Varian 3300 gas chromatograph equipped with a fused silica capillary column DB-5 and a flame ionization detector was used for measurement. The device's parameters and measurement conditions are shown in Table 1. Evaluation was carried out pursuant to an internal standard. Hydrocarbon nonane was used as the internal standard.

Calibration curves for ethanol, n-butanol and isobutanol were measured using standard solutions of these substances in isooctane at three concentration levels (1,000 μ l of isooctane + 2 μ l or 5 μ l or 10 μ l of respective alcohol + 1 μ l of nonane in each of the three vials).

All calculations were performed automatically using the chromatographic software, which is also specified in Table 1.

Table 1. Parameters of gas chromatograph with FID detector

Chromatograph	Varian 3300
Analytical column	DB-5, 30 m x 0.25 mm ID, film thickness 0.25 μ m
Spray technique	manual; sample volume 1 μ l, split ratio 1:20
Carrier gas	nitrogen 1 ml min ⁻¹
Temperature program	50°C (3 min), gradient 8°C min ⁻¹ , 260°C (5 min)
FID detector	hydrogen 30 ml min ⁻¹ , air 300 ml min ⁻¹
Software for data collection	Star Chromatography Workstation vs. 4.51

RESULTS AND DISCUSSION

It is important to know the area below the peak of the measured substance and the area of the internal-standard nonane to calculate the concentrations of n-butanol and isobutanol in diesel. The numbers above the peaks of the chromatogram are the values of retention time (in minutes) pertaining to the measured substances. The retention times of the measured substances are compared with the retention time of standards for ethanol, n-butanol and isobutanol. Quantity is identified from the area below the peaks.

Figs 1–6 are chromatograms of fuel samples, where: R is detector response (V); t_R is retention time (min).

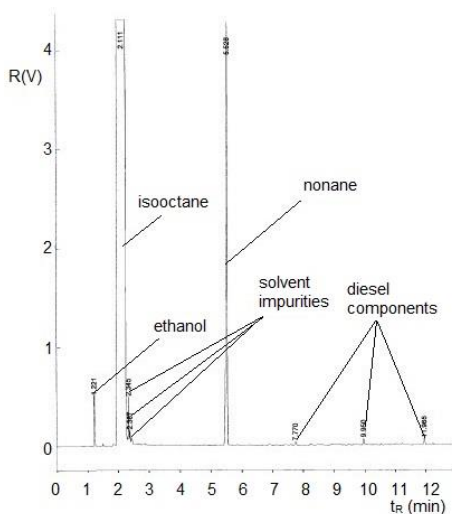


Figure 1. Diesel fuel with 10% vol. of ethanol.

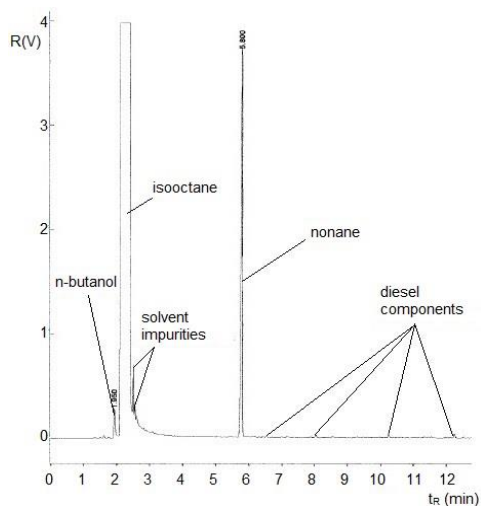


Figure 2. Diesel fuel with 5% vol. of n-butanol.

Chromatograms of normal commercial diesel fuel (without FAME) with the addition of ethanol and n-butanol (Figs 1, 2, 3, 4) have strong peaks of these substances with retention times in the interval of 1–2 min in the case of these measurement conditions.

Alcohols, nonane (internal standard) and isooctane (solvent) are observable in Figs 1–6. The chromatograms also indicate solvent impurities and diesel fuel components. All chromatograms were terminated after 12 min. Constituents of diesel fuel, a blend of hydrocarbons, have different boiling points. Therefore, some components were eluted even further for about 20 min.

Chromatographic records of clean diesel fuel may vary. Variability mainly depends on the refinery from which the fuel originates and also on the class of diesel fuel. Composition depends on seasons and the geographical conditions of the market to which the diesel fuel is distributed.

Therefore, a chromatographic ‘fingerprint’ also reflects the immediate limitations of a specific refinery. Despite the abovementioned differences, the chromatograms of commercial diesel fuels used in a moderate climate are rather similar.

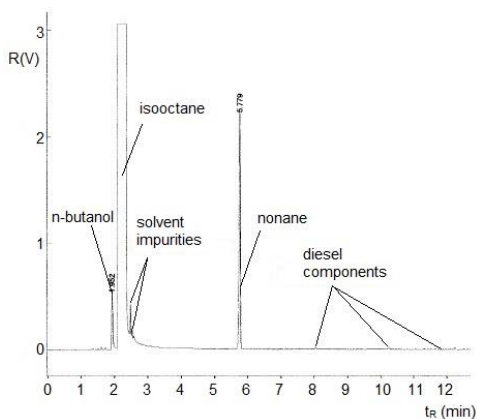


Figure 3. Diesel fuel with 10% vol. of n-butanol.

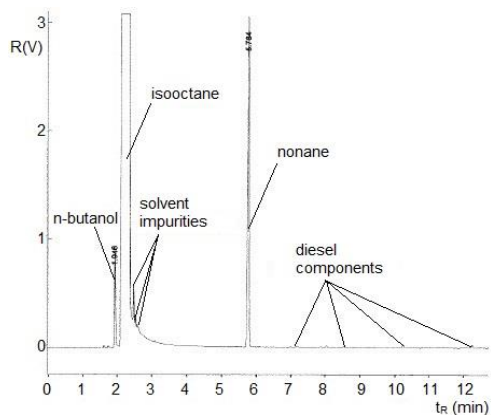


Figure 4. Diesel fuel with 20% vol. of n-butanol.

A nonpolar column is used in the GC-FID ‘fingerprint’ analysis (separated according to the boiling points of substances) so the arrangement of the gas-chromatographic system meets the basic requirement for simulated distillation. Classic simulated distillation requires special software for both analysing the calibration blend and evaluating the results to determine the relations between boiling points and retention time.

Gas chromatography allowed us to identify the simultaneous presence of n-butanol and isobutanol in diesel fuel (Figs 5 and 6); the peaks of both substances are well separated. The retention time of isobutanol is approximately 1.64 min under these measurement conditions.

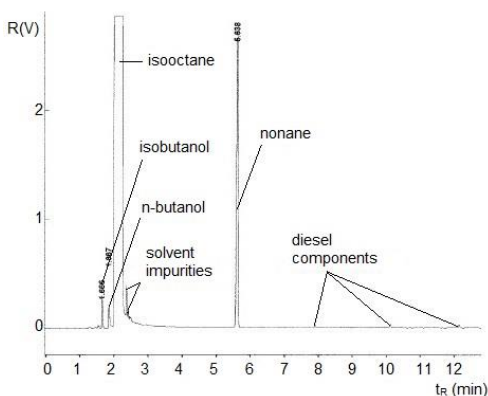


Figure 5. Diesel fuel with 5% vol. of n-butanol and 5% vol. of isobutanol.

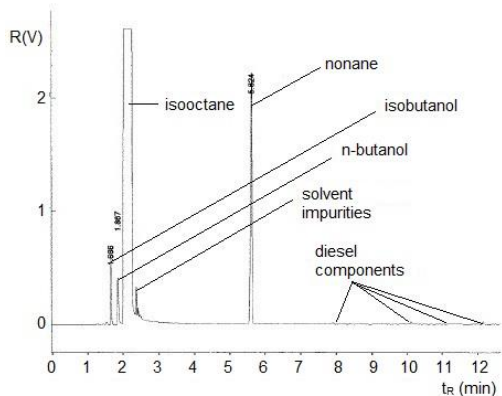


Figure 6. Diesel fuel with 10% vol. of n-butanol and 10% vol. of isobutanol.

Diesel fuel GC-FID allows estimating the flashpoint of the sample.

Gas chromatography identifies the presence of alcohol or gasoline in diesel fuel and quantifies the approximate alcohol concentration starting from about 0.1% vol. (Table 2) on the basis of peak areas (Figs 1–6).

Table 2. Measured concentrations of ethanol, n-butanol and isobutanol in diesel fuel

Fuel	Measured concentration of alcohol (% vol.)
Diesel fuel + ethanol 10% vol.	10.12
Diesel fuel + n-butanol 5% vol.	5.13
Diesel fuel + n-butanol 10% vol.	12.45
Diesel fuel + n-butanol 20% vol.	23.93
Diesel fuel + n-butanol 5% vol. + isobutanol 5% vol.	5.23 + 5.49
Diesel fuel + n-butanol 10% vol. + isobutanol 10% vol.	11.69 + 11.57

All values were calculated from three GC measurements as the arithmetic mean. Deviations of the measured values from the reference values may have occurred due to variations in detector response or the sorption of some components of the sample in the injection chamber. The variability of measured values can be improved by using the auto-sampler and devices with electronic gas flow control.

CONCLUSIONS

The regular evaluation of diesel fuel quality according to EN 590 does not allow gaining a thorough overview of the fuel's composition. On the other hand, GC–FID analysis is able to closely characterise the fuel's petroleum fractions and boiling ranges. It also allows detecting and quantifying the presence of other components in the diesel fuel and provides information about their approximate distillation profiles.

The regulatory adherence to dosing alcohols would require regular monitoring. A simple analytical method for the determination of bioethanol, isobutanol and n-butanol in diesel fuel using GC–FID was developed and verified.

Gas chromatography equipped with FID detection is a good method of choice for assessing the quality of diesel fuel and it can provide a wealth of useful information. This analytical technique shows the fuel's distillation profile and its fatty acid methyl esters content. In spite of using regular evaluation methods, GC–FID can also detect the presence of other compounds of interest like bioethanol, n-butanol and isobutanol that are already being considered as potential future additives to diesel fuel. The presented method has proven to have acceptable accuracy for the quantification of various alcohols. Therefore, gas chromatography analysis can provide a range of additional data to complement regular fuel evaluation and help to narrow selection parameters.

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