Fuel 112 (2013) 163–171

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Detection and quantification of adulterants in gasoline using distillation curves and multivariate methods

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HIGHLIGHTS

- PCA applied to distillation curves enables the detection of gasoline adulterations.
- The most important fractions for the discrimination were the 4–40%(v/v) interval.
- This interval was related to the increase of paraffin and isoparaffin content.
- PLS-DA enables the detection and quantification of the solvent used in adulterations.
- The method produced highly accurate results and is suitable for routine analysis.

ARTICLE INFO

Article history:
Received 4 February 2013
Received in revised form 15 April 2013
Accepted 24 April 2013
Available online 24 May 2013

Keywords:
Adulteration
Gasoline
Distillation
Multivariate analysis

ABSTRACT

This study has shown that the use of distillation curves combined with PCA (Principal Component Analysis) and PLS-DA (Partial Least Squares Discriminant Analysis) provides a model with enough sensitivity to discriminate adulterated and unadulterated gasoline samples, as well as, the determination of the solvent used in adulteration with minimum percentage of 97% accuracy. PLS-DA provided the prediction of adulterants with low RMSEC (Root Mean Square Error of Calibration) and low RMSEP (Root Mean Square Error of Prediction) when compared to other methods. The great advantage is the possibility to apply the results of the distillation curves to routine analysis (ASTM D86), therefore not requiring various assays, speeding up the analytical process. In addition to its feasibility this method can be quite useful in fuel quality monitoring and inspection procedures whilst having low cost and good reliability.

1. Introduction

The end of government monopoly brought serious changes to retail and distribution of fuels in Brazil. One of the effects is the planned adulteration of fuel with the addition of controlled solvents, which have the objective of maintaining the product within the current specification [1]. This practice has occurred quite frequently despite the measures of Brazilian authorities through the ANP (Agência Nacional do Petróleo, Gás Natural e Biocombustíveis), which establishes technical specification through specific legislation regarding the minimum quality of fuels mainly guaranteeing the standardization of retail production [2].

The addition of solvents is one of the most common practices of adulteration of fuel due to the enormous difference in taxation between gasoline and solvents. The addition of illegal compounds to fuels can cause damaging and unpleasant issues to society such as environmental risk due to the emission of vapours and toxic gases, i.e. CO and NO_X, less durability to the vehicles' engine, as well as, unfair market competition of fuel prices causing a great loss to the State in tax revenues [3,4]. The most commonly used solvents include: ethanol in excessive amounts, diesel, kerosene, refined petrochemicals, toluene, xylene, hexane, among others [5].

Several physicochemical properties are monitored to ensure the quality of Brazilian gasoline through the ANP [2], and these tests include specific mass measurements, distillation analysis, octane analysis, among others. However, the current specifications were chosen largely based on the good functioning of the engine, rather than identifying an illicit addition of solvents. Even though they are capable of indirectly identifying a fraud of any type of solvent in any proportion of addition, which can lead to adulterated gasoline to be in conformity with the physicochemical assays [5].

In recent years the ANP, after numerous cases reported by the media, created means to protect the consumer against the harmful consequences caused by adulteration. The Agency invested in a Marking Solvents Program, where mandatorily every solvent commercialised throughout the country had the addition of a chemical marker, which was designed to have no impact on the applicability

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http://dx.doi.org/10.1016/j.fuel.2013.04.077

of the solvents when used individually. The presence of the marker in gasoline indicates that it has been adulterated with some kind of solvent, although it is a rather laborious process that requires laboratorial analysis, a tight logistic for the markers, and the monitoring process which becomes highly expensive [5]. It is very common to find gasoline in the Brazilian market with all the physical and chemical properties in accordance with the specifications of the ANP, but with the presence of traces of solvents [6].

A study carried out by LEC-UFMG (Laboratório de Ensaios de Combustíveis of UFMG) showed that in 2012 approximately 40% of the gasoline samples analysed were considered atypical [7]. Atypical samples are the ones that have a different profile than the majority of samples, though they are in accordance with the parameters established by the ANP. This can be attributed to careful and meticulous adulteration of fuel with the addition of solvents so that the final product stays in accordance with legal standards or a different origin from the one stated [8]. Therefore, new analytical methods must be developed to detect these adulterations. The methods are simple, fast and efficient in ensuring the quality and authenticity of commercial fuels and therefore highly recommended for routine analysis.

Currently the scientific literature has reported alternative methodologies in the detection of adulteration in gasoline. These methodologies use the employment of chemometric tools combined with several conventional techniques of gasoline analysis [1,3,5,9–17]. The large majority refer to studies using chromatographic [1,3,9] and spectroscopic [11–17] methods.

Wiedemann et al. [3] carried out a study to detect adulteration in gasoline samples using the results obtained through physicochemical properties and chromatographic data in the gas phase of samples combined with hierarchical clustering analysis (HCA).

Balabin et al. [13–16] used near infrared, different chemometric tools and artificial neural networks to predict different gasoline properties [13,14] and classify gasoline and gasoline fractions by source (refinery or process) and type [15,16]. The models have low errors and could be useful to detect anomalous gasoline samples.

In another study Monteiro et al. [17] used hydrogen nuclear magnetic resonance (^{1}H RMN) of retail gasoline and added solvents combined with principal component analysis (PCA) and hierarchical clustering analysis (HCA) to distinguish samples in conformity and not in conformity. The results indicated a tendency of noncomplying samples clustering with the increase of the content of solvent added.

Recent studies have shown the great potential of distillation curves, or a few specific points, for the analysis of different parameters of petroleum products [8,5,18–39], as refinery origin [24,25,27] enthalpy of combustion [21], specific gravity [26,31], kinematic viscosity [31], octane numbers [30], cetane index [32], flash point [32], ethanol content [26] and biodiesel [39]. The addition of solvents changes the properties related to the gasoline volatility and also distillation temperatures can change significantly for them to be detected by this assay [5,8,18,23,28,37,38].

The assay is carried out according to the ASTM D86 [40], which describes the distillation at atmospheric pressure of various petroleum products. The aim of this assay is to determine volatility characteristics verifying if the light and heavy properties of the fuel being produced are adequate and also to detect the contamination of other products. The ANP establishes that Brazilian fuel must have maximum temperature values of 10%, 50% and 90% of the recovered volume, as is for the final boiling point and residual volume [40]. The great advantage of this tool is the possibility to use the results from routine analysis reducing the number of assays, as well as, eliminating the demand for sample pre treatment. Therefore, distillation curves have become quite a useful tool for quality control of automotive fuel.

Gasoline is the second most consumed fuel in Brazil while diesel is the most consumed [2], approximately 39.7 billion litres in 2012. Hence, there is a great demand from society for high quality gasoline, which requires the development of methods for the detection of possible contaminants in fuel to support monitoring and surveillance programs.

In this work, distillation curves, a routine procedure in fuel analysis, combined with chemometric techniques of classification PCA and PLS-DA were employed to identify the adulteration of gasoline with solvents sold at fuel stations. Furthermore, multivariate calibration models were built using PLS in the prediction of the solvents added to automotive gasoline.

2. Experimental

2.1. Material

This study used 150 samples from common gasoline C collected at fuelling stations located in the eastern region of the State of Minas Gerais, Brazil, through the Fuel Quality Monitoring Program (PMQC-ANP). The origin of the samples was determined from the data provided in the invoices from the fuel stations at the moment of collecting the samples, since they come from different refineries from other states. The samples were stored in polyethylene flasks, sealed, and kept at 8 to 15 °C temperature range.

Four groups of doped gasoline samples were prepared using gasoline A (mixture of hydrocarbons without ethanol from the Gabriel Passos Refinery – REGAP – Petrobras) and 5 to 40% (v/v) of each one of the solvents, in 1% (v/v) steps, more the 45 and 50% (v/v) ones. The solvents used were kerosene, turpentine, thinner and rubber solvent (a mixture of aliphatic and aromatic hydrocarbons from C6 to C8). The ethanol concentration was kept at 25% (v/v) in all samples maintaining the same content of gasoline sold at fuel stations. Petrobras provided all solvents as well as the gasoline, except thinner, which was acquired through retail (Dissolminas 3500). These samples were used to identify the types of solvents used in automotive gasoline adulteration through statistical tools i.e. PCA and PLS-DA and also the PLS models built for quantification.

All samples were previously analysed through several physicochemical parameters established by the ANP [2] such as distillation temperatures equivalent to 10%, 50% and 90% of the recovered volume, final boiling point, residue volume (ASTM D86) [40], specific gravity (ASTM D4052) [41], octane numbers (MON and IAD) (correlated with ASTM D2699 and D2700) [42,43], contents of benzene (%v/v) (ASTM D6277) [44], anhydrous ethanol (NBR 13992) [45] and hydrocarbons (saturated, olefins and aromatics, correlated with ASTM D1319) [46]. An automatic distiller was used for the analysis (Herzog HDMA 627), a densimeter (Anton Paar 4500) and an automatic gasoline analyser (Petrospec GS1000) based in infrared spectrometry and multivariate analysis. From these results the samples were classified as in-conformity (in agreement with the specification) and nonconformity (not in agreement to at least one of the specifications).

Besides the aforementioned assays the analysis of the markers of solvents was also carried out. The detection of the solvents' markers carried out by the ANP was done by submitting the samples to chromatographic analysis. The marker is a product developed exclusively for the detection of adulterations and due to legal issues it is not possible to publish information on the marker neither standards required for the analysis nor the methodology used. However, it is possible to state that the analysis takes 20 min, besides having a high cost it can only be carried out by ANP authorized labs.