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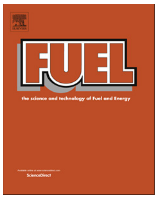

Full Length Article

Reid vapor pressure prediction of automotive gasoline using distillation curves and multivariate calibration

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ABSTRACT

Partial least squares regression (PLS) in conjunction with distillation curves (ASTM D86) were used successfully to predict the vapor pressure of automotive gasoline. The errors obtained in the calibration and validation models (0.71 and 0.69 kPa) were lower than those reported in the literature. In addition, the proposed method is inexpensive, reduces test time and is easy to implement, making it an alternative method for gasoline quality control. It does be possible because the distillation tests are already routinely performed by ANP as one of the evaluation parameter of the automotive gasoline quality.

1. Introduction

Automotive gasoline is a flammable liquid formulated by mixing hydrocarbons ranging from four to twelve carbon atoms, with boiling points between 30 and 220 °C, obtained by refining petroleum, involving direct distillation, cracking, reforming, isomerization and alkylation [1,2]. Its composition varies according to the method employed in its production and the chemical composition of the crude oil. In 2015 about 44.2 billion liters was sold in Brazil [3].

In this context, there is an increasing need for quality control of gasoline and the development of new technologies to ensure that the product meets the requirements of engines and does not produce emissions above legal levels [4]. According to the ANP (National Petroleum, Natural Gas and Biofuels Agency), various parameters are used in quality control of gasoline, such as distillation parameters, specific gravity, and octane numbers, among others [5]. Currently, the analyses of these parameters are carried out in Brazil using the ASTM (American Society for Testing and Materials) or NBR (Brazilian Association of Technical Standards) standard methods. A fuel must meet all the specifications to be considered of good quality.

An important physical-chemical parameter in assessing the quality of gasoline is the vapor pressure, because it is related to the fuel's volatility, which directly influences engine performance. In the production of fuel, vapor pressure is measured to indicate the requirements that must be met for the transport and storage of the product, in order to avoid accidents and minimize losses by evaporation. Fuels with high vapor pressure emit more volatile compounds and, after production and shipping fuel to service stations, this test can be applied to evaluate nonconformities related to adulteration caused by adding solvents. Takeshita et al. [4] noted that the addition of organic solvents at different ratios modifies the vapor pressure of gasoline, an effect that is more preponderant at 50% (v/v) and above.

The evaluation of vapor pressure is also required to assure proper engine performance, since fuels with low vapor pressures are harder to vaporize in the intake manifold, hindering the combustion process. On the other hand, fuels with high vapor pressure emit more volatile organic compounds, which can cause incomplete fuel vaporization and uncontrolled air/fuel ratio. Hence, the vapor pressure must be within an acceptable range [6]. In Brazil, ANP establishes a maximum of 69.0 kPa for the vapor pressure, at 37.8 °C, of automotive gasoline [5].

The volatility parameters, which affect the performance at low temperature, are typically determined by testing vehicles at high RPM. At high temperatures, the most common phenomena that affect fuel systems in vehicles are vapor lock and percolation. Vapor lock is the occurrence of a mass of vapor between the fuel tank and carburetor or fuel injection system. Percolation is the result of uncontrolled fuel vaporization, which can happen after a long period operating at high temperatures [6].

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Vapor pressure can be measured following ASTM D5191 [7]. The test conditions are carefully specified since the vapor pressure varies with temperature, the amount of dissolved air and the ratio between vapor and liquid in the container. In this method, the sample contained in a jar (filled to between 70 and 80% of capacity) is cooled to temperatures between 0 and 1 °C and subsequently inserted into the liquid chamber and the equipment is connected to the vapor chamber heated to 37.8 °C. The increased pressure in the vapor chamber is measured using a sensor transducer and a pressure indicator and the vapor pressure is registered on the display. This measure is defined as Reid vapor pressure (RVP) and can be expressed in kPa or psi.

Although the test based on ASTM D5191 be relatively quick (approximately seven minutes), it is desirable to have simpler and low cost methods for RVP determination. In this context, chemometric methods combined with distillation curves can provide important information about different gasoline quality parameters, reducing the number of tests to being performed and used as screening for more specific tests. The current literature demonstrates the predictive power of multivariate regression models for vapor pressure prediction of automotive gasoline [8–11]. Among the regression techniques available, the most widely used are partial least squares regression (PLS) and principal components regression (PCR).

Cooper et al. [8] correlated the results of vapor pressure obtained experimentally together with the Raman spectra of fuels to build a regression model using PLS. The authors found RMSEP values (root mean squares error of prediction) of 3.92 kPa. Using dispersive fiber-optic Raman spectroscopy with a CCD detector and near infrared, Flecher et al. [9] determined the vapor pressure of gasoline samples, finding RMSEP of 5.99 kPa. Besides PLS, Côcco et al. [10] associated near-infrared spectroscopy and the chemometric tool PCR to determine different chemical and physical parameters, including vapor pressure. For this property, the value of RMSEP obtained was 2.81 kPa.

Recently, several works have demonstrated the good potential of distillation curves in conjunction with PLS regression to forecast quality parameters, such as specific gravity and ethanol content [11], MON and RON in automotive gasoline [12], flash point [13], cetane number [13], biodiesel content [14], specific gravity [15] and kinematic viscosity [15] in diesel oil. In addition to these parameters, these models have the ability to discriminate the refinery of origin [16] and to detect adulteration by solvents [17].

Distillation is a method of separation based on the phenomenon of vapor-liquid equilibrium for mixtures. With the ASTM D86 method it is possible to evaluate the complexity of liquid blends, which is directly related to the volatility of the sample's components [18].

To simplify the analysis of gasoline through the use of a single test, thus reducing costs and increasing the number of samples that can be analyzed, this work describes the use of distillation curves from regular tests to evaluate the quality of gasoline, obtained according to ASTM D86 [18], in conjunction with multivariate calibration PLS for determination of the vapor pressure. We carried out manual distillations to obtain the composition of each fraction using infrared spectrometry with the purpose of showing the most important variables in predicting vapor pressure.

2. Experimental

2.1. Samples

To build the PLS model used in the determination of the vapor pressure of gasoline, 80 samples of premium and regular gasolines (both containing ethanol 25 % v/v) were obtained from service stations in the eastern region of the state of Minas Gerais (Brazil), which receives fuels produced by five different refineries. A study proposed by Aleme et al. [16] showed that gasolines produced by these refineries have different distillation curve profiles, due to their different chemical composition, related to the source of crude oil and the refining process thereof.

The samples were stored in polyethylene bottles, sealed and chilled to 8–15 °C to avoid evaporation of volatile components. All samples were subjected to the tests of physico-chemical parameters established by the ANP [5].

2.2. Materials and equipment

2.2.1. Vapor pressure analysis

Before starting the tests, the samples were transferred to 50 mL flasks, filled to between 70 and 80% capacity and sealed. The samples were cooled in an ice-water bath to a temperature between −5 and −7 °C. After reaching the proper temperature, the flasks were shaken and opened momentarily. This process was repeated three times.

Before the readings, the measuring chamber was cleaned with toluene and dried with *n*-pentane with the aid of a vacuum pump. After ensuring that the measuring chamber was completely dry, one of the valves was closed and a volume of 2.55 mL of air was introduced with a syringe, after which the valve was closed quickly to achieve pressure between 19.0 and 21.0 kPa. After one minute for stabilization, 2.05 mL of sample was and injected into the measuring chamber, with temperature of 37.8 ± 0.1 °C, using a syringe. The results were displayed in approximately three minutes, in kPa. The test was repeated three times for each sample. The reagent *n*-pentane (known volatility) was used to verify proper calibration of the instrument. The reagent was subjected to the same test conditions as the samples [7]. Moreover, the instrument calibration was checked daily using the reagent 2,3-dimethylbutane, according to ASTM D 5191, that has a similar vapor pressure value to Brazilian gasoline (57.1 ± 0.2 °C).

2.3. Experimental procedures

2.3.1. Distillation curves

The samples were analyzed in a Herzog HDA 627 automatic distiller according to the ASTM D86 standard [18]. For the distillation test, 100 mL of previously cooled gasoline was transferred to a specific distillation flask coupled to a sensor and heated to maintain the distillation rate between 4 and 5 mL min^{-1}. The distilled vapor was condensed and collected in a cooled beaker and the distillation curves (distillation temperature versus volume recovered), at 1% (v/v) intervals, were obtained after correcting temperature readings at atmospheric pressure to 760 mmHg and considering volume loss, according to ASTM D86 [18].

2.3.2. Manual distillation

A manual distillation system adapted to the specifications established by ASTM D86 was used for the analysis of distillation fractions of automotive fuel [18]. The samples were prepared by adding 25% (v/v) ethanol to regular gasoline, originally from the REGAP refinery. Most of the samples were originally from this refinery. The specifications used for the manual method were the same as those for the automatic method, with distilled fractions being collected every 10 mL. Five distillations of this gasoline were carried out, and each distillation fraction was mixed to increase the representation of the results. The solutions of the different percentages of recovered volume were cooled (from 8 to 15 °C) and later submitted to spectrometric analysis in a commercial infrared spectrometer to determine the composition of the distilled fractions.