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Determination of hydrogen content, gross heat of combustion, and net heat of combustion of diesel fuel using FTIR spectroscopy and multivariate calibration

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ABSTRACT

The precise determination of the heat of combustion is of great importance for trading automotive diesel. The net heat of combustion (NHC) of fuel is related to the hydrogen elemental composition of fuel as obtained by elemental analysis. Heat of combustion expressed as gross heat of combustion (GHC) and net heat of combustion (NHC) have been predicted from data obtained by proximate analysis (density, ash, water and sulphur content) (ASTM D4868). GHC was obtained using bomb calorimetry (ASTM D240). The results of ASTM D4868 and ASTM D240 were found in good agreement. GHC and NHC fall within the relatively narrow range 45.24–46.08 and 41.91–43.27 MJ/kg, respectively. GHCs of tested diesel samples are, on average, about 7% greater than NHCs. The present paper also present a simple analytical method for determination of hydrogen content, GHC, and NHC of automotive diesel fuel using FTIR spectroscopy and partial-least squares calibration (PLS-1). PLS-1 had a high prediction power for prediction of hydrogen from FTIR spectra of diesel samples. The spectral ranges used in calibration were 400–670 and 2846–2970 cm^{-1}. On the other hand, classical least squares calibration (CLS) was found invalid for determination of hydrogen content in diesel. The results obtained by the proposed analytical method were almost to those obtained by ASTM D4868 and ASTM D240. PLS-1 method, offers a simple and reliable analytical method for quantification of hydrogen content in diesel samples without running expensive analysis like those carried out using carbon, hydrogen, and nitrogen (CHN) instruments.

1. Introduction

Petroleum diesel fuel is derived from crude oil by fractional distillation at temperature range 170–350 °C at normal pressure. Diesel fuel is a very complex mixture of thousands of individual compounds with carbon numbers between 9 and 23 (number of carbon atoms per hydrocarbon molecule). Most of these compounds are members of the paraffinic, naphthenic or aromatic class of hydrocarbons. These three classes have different chemical and physical properties. The different relative proportions of the three classes are one of the factors that make one diesel fuel different from another. It influences fuel properties and affects its performance.

Fuels are evaluated, in part, based on the amount of energy or heat that they release per unit mass or per mole during combustion of the fuel. Such a quantity is known as the fuel's heat of combustion or heating value. The heat of combustion of a substance is the heat evolved when that substance is converted to its final oxidation products by means of molecular oxygen [1].

The heat of combustion of diesel is an important parameter for the planning and the control of generators using this type of fuel. The so-called gross heat of combustion (GHC) or 'higher heating value', also called gross calorific value, is the enthalpy of complete combustion of a fuel with, for instance, all carbon converted to CO_2, and all hydrogen converted to H_2O.

The fuel can be either liquid or solid, and contain only the elements carbon, hydrogen, nitrogen, and sulphur. The products of combustion, in oxygen, are gaseous carbon dioxide, nitrogen oxides, sulphur dioxide, and liquid or gaseous water. There exists two different values of specific heat energy for the same batch of fuel. One is the high (or gross) heat of combustion (GHC) is given for standard conditions (1 atm, 25 °C) and the other is the low (or net) heat of combustion (NHC). GHC is the quantity of energy released when a unit mass of fuel is burned in a constant volume enclosure, with the products being gaseous, other than water that is condensed to the liquid state. NHC is the quantity of energy released when a unit mass of fuel is burned in a constant pressure, with all of the products, including water, being gaseous. GHC is measured in a bomb calorimeter for fuels. The difference between the GHC and NHC values is significant, about 8% or 9%. While in the USA GHC is generally used, NHC is more common in European

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countries [2]. Because engines exhaust water as a gas, the NHC is the appropriate value to use for comparing fuels.

The NHC value of diesel corresponds to a heating value in which the water remains a vapour and does not yield its heat of vaporisation. Thus the energy difference between the two values is due to the heat of vaporisation of water, and

$$\mathrm{GHC} = \mathrm{NHC} + (m_{\mathrm{water}}/m_{\mathrm{diesel}})h_v \quad (1)$$

where m_{water} is the mass of liquid water in the combustion products, and h_v is the latent heat of vaporisation of water (40.8 kJ/mol).

The precise determination of the heat of combustion is of great importance for trading automotive diesel due to the fact that the heat of combustion is the most important parameter for determining the price of the automotive diesel to be paid the supplier by the user of the diesel fuel. Numerous empirical equations have been published to relate the NHC of fuel to the hydrogen elemental composition of fuel as obtained by elemental analysis (ASTM D240) (ASTM stands for American Standard for Testing and Material) [3]. Heat of combustion values have also been predicted from data obtained by proximate analysis (density, ash, water and sulphur content) (ASTM D4868) [4].

Recently, multivariate calibration has been applied for analysing many chemical systems including wastewater, foods, drugs formulations, and fuels without the need for separation of solutes prior their analysis as the case in chromatographic analyses [5–7]. Multivariate calibration is an effective calibration method in which the chemical information (absorption, emission, electrical etc.) of a set of standard mixtures recorded at different variables (wavelengths) are related to the concentration of the chemical compounds present in the mixtures [5]. The popular calibration way used in chemical analysis is the univariate calibration in which the chemical information of a set of solution recorded at one variable (i.e., wavelength) is related to the solute concentration in the solution. The most applied chemometric methods are Classical Least Squares (CLS), Inverse Least Squares (ILS), Principal Component Regression (PCR), Partial-Least Squares (PLS) and Net-Analyte Signal (NAS) [8]. In this work, the possible application of CLS, PCR and PLS-1 for determination hydrogen content in diesel samples will be investigated. The content of hydrogen in the samples was previously quantified with the aid of carbon, hydrogen, and nitrogen (CHN) analyser.

Therefore, the aim of this work was to determine GHC and NHC using bomb calorimetry (ASTM D240) and from data obtained by proximate analyses (density, ash, water and sulphur content) (ASTM D4868), respectively. The present paper also outlines a simple analytical method for determination of hydrogen content, GHC, and NHC of automotive diesel fuel using FTIR spectroscopy and PLS-1. Determination of hydrogen content in diesel fuels by FTIR/PLS-1 has never been discussed.

2. Experimental

2.1. Collection of diesel samples

Jordanian diesel samples were collected from different service stations in the Amman, Jordan area over a 2-week period and stored in brown glass bottles in the refrigerator at 3 °C. To ensure reproducibility of the analysis, the samples were analysed in duplicate over a 2-day period. Also important to note is that the composition of the diesel will depend not only on the Jordanian refinery, but also on the residual level in the tank when filled. Therefore, each diesel sample is chemically unique because of the inherent differences in the tank levels when filled. The unique chemical composition is useful in comparisons, as two samples that are statistically similar are more likely to originate from the same source.

2.2. Heat of combustion

2.2.1. Calibration

Prior to sample testing with the oxygen bomb calorimeter, the thermal mass of the system had to be defined. The bomb calorimeter was calibrated using the method described below by combusting a known mass, m, of standard benzoic acid which has a known heat of combustion of 26.453 kJ/g. Ten benzoic acid samples of size around one gram were tested. The calibration factor for the bomb calorimeter, C, was calculated from the benzoic acid calibrations as

$$C = \frac{(m \times 26.453\ \mathrm{kJ/g})}{(T_{\max} - T_0)} = 10.13 \pm 0.13\ \mathrm{kJ/K}(n = 10) \quad (2)$$

2.2.2. Instrumentation

An oxygen bomb calorimeter (IKA Calorimeter system C2000, Petrotest Instruments GmbH, Germany) was used to obtain the GHC of the automotive diesel. The Petrotest is a static and manual calorimeter with temperature resolution of 0.002 °C, capable of oxygen charging pressures up to 40 atm, and can liberate up to a maximum 33,400 J per charge. The fuel samples were placed directly in a stainless steel capsule (2.5 cm of diameter and 1 cm of deep) and burned with oxygen at a pressure of 3.0 MPa according to ASTM D240 [3].

Approximately 1 g of sample is placed inside a sample cup in a pressure vessel (oxygen bomb) which is in contact with an ignition wire conNHCted to two electrodes. The bomb is then sealed, purged, and pressurised up to 40 atm with pure oxygen. The sealed bomb is then placed inside a 2-L water bath which is inside an adiabatic container. Upon thermal equilibration of the system at ambient temperature, the sample is ignited and completely combusted. The GHC (kJ/g) of the sample at room temperature is calculated from the temperature rise of the water bath ΔT ($\Delta T = T_{\max} - T_o$) (K), which is typically a few degrees Kelvin, the calibration factor C (J/°K), and the mass of the sample m (g) according to

$$\mathrm{GHC} = (C\Delta T - e_1 - e_2)/m \quad (3)$$

where e_1 and e_2 are the correction factors for the heat of combustion of the ignition wire and the heat of formation of acids, respectively, in units of kJ.

There are no direct methods for measuring the NHC – which is the GHC minus the latent heat of vaporisation of the water produced during the reaction. The NHC is relevant to flaming combustion where water is in the gaseous state at flame temperatures of ≈1000 K. As a result, the latent heat of water at 298 K is subtracted from the GHC because this amount of heat is required to maintain the combustion product water in the gaseous state.

2.3. Chemical analyses of the diesel samples

2.3.1. CHN analysis

The contents of carbon (C), hydrogen (H), and nitrogen (N) in diesel samples have been measured by standard methods of elemental analysis using a "EuroVector (EA3000, Italy)". The content of oxygen has been calculated as the difference between 100 and the sum of the other constituents. About 1 mg of sample was incinerated at 1000 °C in oxygen atmosphere in a tube furnace and the final reaction products CO_2, H_2O, and N_2 quantitatively determined by gas chromatography using a thermal conduction detector. Typical analysis errors for diesel samples are in the range of ±0.3 wt.%.

2.3.2. Ash content – ASTM D482

About 1 g of sample contained in a suitable vessel was ignited and allowed to burn until only ash and carbon remain. The