

# Determination of higher heating value of petro-diesels using mid-infrared spectroscopy and chemometry

Yahya S. Al-Degs · Mohammed Al-Ghouti ·  
Gavin Walker

Received: 17 January 2011 / Accepted: 7 April 2011 / Published online: 11 May 2011  
© Akadémiai Kiadó, Budapest, Hungary 2011

**Abstract** Higher heating value (HHV) is probably the most important property of the fuels. Bomb calorimeter and derived empirical formulae are often used for accurate determination of HHV of fuels. A useful empirical equation was derived to estimate HHV of petro-diesels from their C and H contents:  $\text{HHV (in MJ/kg)} = 0.3482(\text{C}) + 1.1887(\text{H})$ ,  $r^2 = 0.9956$ . The derived correlation was validated against the most common formulae in the literature, Boie and Channiwala–Parikh correlations. Accordingly, accurate determination of C and H contents is essential for estimation of HHV and avoids using a bomb calorimeter. However, accurate estimation of C and H contents requires using expensive and laborious gas chromatographic techniques. In this work, chemometry offered a simple method for HHV determination of petro-diesels without using bomb calorimeter or even gas chromatography. PLS-1 calibration was used instead of gas chromatography to find C and H contents from the non-selective mid-infrared (MIR) spectra of petro-diesels, HHV was then estimated from the earlier empirical equation. The proposed method predicts HHV of petro-diesels with high accuracy and precision, with modest analysis costs. The present method may be extended to other fuels.

**Keywords** Higher heating value · Petro-diesel · Gas chromatography · Bomb calorimetry · Mid-infrared (MIR) spectroscopy · Chemometry

## Introduction

Diesel fuel is a common term that usually describes any fuel used in diesel engines. The most common diesel fuel is obtained from crude oil, which is often referred to as petro-diesel [1]. Petro-diesel is derived from crude oil by fractional distillation at temperature range 175–300 °C and normal pressure [1]. Chemically, petro-diesel is composed of 75% saturated hydrocarbons (mainly paraffins including normal and branched cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alky benzenes) [1]. The density of petro-diesel is  $\sim 850 \text{ kg m}^{-3}$ , about 15% higher than gasoline ( $720 \text{ kg m}^{-3}$ ) [1]. Petro-diesel is a highly consumed commodity; USA consumption in 2006 was 200 billion liters, which is mainly used in transportation and heating systems [2]. One of the most important properties that should be regularly determined for petro-diesels is the heating value (HV). HV is the amount of energy that released as heat when a unit mass or volume of a fuel is completely combusted with oxygen and usually expressed as either the higher heating value (HHV) or the lower heating value (LHV) [1, 3]. HHV, also known as the gross calorific value, of a fuel is defined as the released heat from a specific quantity (maintained at 25 °C and 1.0 atm) when it is completely combusted and the combustion products have returned to the initial temperature. HHV is identical to the thermodynamic heat of combustion [4]. In fact, HHV includes the heat of condensation of gaseous products (mainly gaseous  $\text{H}_2\text{O}$ ) that produced upon combustion, while, LHV excludes heat of water

Y. S. Al-Degs  
School of Chemistry, The Hashemite University,  
P.O. Box 330127, Zarqa 13115, Jordan

M. Al-Ghouti  
Arts and Sciences Unit, Fahad Bin Sultan University,  
P.O. Box 15700, Tabuk, Kingdom of Saudi Arabia

G. Walker (✉)  
School of Chemistry and Chemical Engineering,  
Queen's University Belfast, Belfast BT9 5AG, UK  
e-mail: g.walker@qub.ac.uk

condensation [4]. Therefore, HHV is significantly higher than LHV if the condensation energy is high. HHV is about 7% higher than LHV for petro-diesel, while, it is 15% higher for H<sub>2</sub> due to the higher hydrogen content compared to petro-diesel. Practically, HHV is determined by bomb calorimeter where fuel is combusted with oxygen in a sealed steel container at 25 °C [4, 5]. After cooling the reaction container to 25 °C, the released energy is calculated which accounts for the heat of combustion and heat due to condensation of gaseous water, i.e., HHV [4]. HHV of petro-diesels are often close to 45 MJ kg<sup>-1</sup>, which is on average, higher than heating value of biomass materials (10–20 MJ kg<sup>-1</sup> or kJ g<sup>-1</sup>) but lower than HHV of methane gas (55 MJ kg<sup>-1</sup>) [6].

The international standard method, ASTM D240, is the most adopted method for accurate estimation of HHV of most fuels including petro-diesel [4–6]. However, this method has some disadvantages, such as regular calibration of the bomb calorimeter, long analytical procedure, difficulties in sample preparation and high analysis costs [4]. Accordingly, many efforts have been made to provide simpler methods for predicting HHV from the elemental composition of fuels [3, 4, 6–8]. For example, HHV of petro-diesels were empirically estimated from the contents of carbon and hydrogen as following [3]: HHV = 0.3032(C) + 0.1423(H), with a prediction error of only 0.4% [3]. For liquid hydrocarbons like gasoline and petro-diesels, the most validated formula was derived by Boie [9]:

$$\text{HHV (MJ kg}^{-1}\text{)} = 0.3517(\text{C}) + 1.1626(\text{H}) + 0.1047(\text{S}) - 0.111(\text{O}).$$

For solid lignocellulosic fuels, HHV were fairly predicted as [7]: HHV (MJ kg<sup>-1</sup>) = 33.5(C) + 142.3(H) – 15.4(O). In addition to the elemental composition, saponification value, iodine value, density, viscosity, and molecular weight were correlated with HHV for many fuels [10, 11]. The HHV of vegetable oils were found to be fairly correlated with density *d*: HHV (MJ kg<sup>-1</sup>) = 79.014 – 43.126 *d* (*r*<sup>2</sup> = 0.938) [12]. Accordingly, chemical and physical analyses have been highly correlated with HHV of many liquid fuels as these offered reasonable alternatives to ASTM D240 for HHV estimation. Prediction of HHV of petro-diesels from density (*d*), sulfur level (*s*), water content (*x*), and ash content (*y*) is also an official method, which is often adopted in advanced fuel laboratories [8]:

$$\text{HHV (MJ kg}^{-1}\text{)} = (51.916 - 8.792d^2 \times 10^{-6}) [1 - (x + y + s)] + 9.420s.$$

Recently, Channiwala and Parikh have derived a unified formula, using elemental composition of large number of fuels, which predicts HHV of gaseous, liquid, and solid fuels [6]: HHV (MJ kg<sup>-1</sup>) = 0.3491(C) + 1.1783(H) + 0.1005(S)

– 0.1034(O) – 0.0151(N) – 0.021(Ash). With only a few exceptions, this formula [6] can predict HHV of wide spectrum of fuels with average absolute error of 1.45%. Even though not directly stated in the work of Channiwala and Parikh [6], the elemental composition of fuels seem to be more significant for predicting HHV compared to the approximate analysis data. Correlations that are derived from the elemental composition of petro-diesels [3, 6, 9] are extremely useful, however, a disadvantage is that they need an elemental analysis as input data, which requires expensive chromatographic analysis [13].

However, Fourier transform infrared (FTIR) spectroscopy, either mid-IR (MIR) or near-IR (NIR), are among the most trusted analytical techniques in monitoring the quality of petro-diesels blends [14]. IR techniques are non-destructive, very reliable, easy to apply, offer rapid analysis, with no sample treatment required [14]. FTIR can be described as a molecular “fingerprinting” method with a high sensitivity toward many fuels. MIR spectroscopy rapidly provides chemical information on a very large number of compounds and the absorption bands are sensitive to the physical and chemical states of individual constituents [15]. Recently, multivariate calibration (also known as chemometry) has found many applications in petrol chemistry, which extend from detecting impurities to multi-component determination [14–17]. The ultimate aim of multivariate calibration is to find useful relationships between data from relatively low cost procedures like FTIR and from expensive, lengthy analyses [18, 19]. In addition to their accuracy, chemometric methods have been used for clustering different fuel samples and detecting outliers [18, 19]. However, few studies have reported using chemometry for estimating HHV and other important fuel parameters from spectroscopic data [20].

In this work, a simple analytical method is developed to estimate HHV of petro-diesels. Three steps are adopted during method development: (a) an empirical formula is developed to correlate HHV with elemental composition of petro-diesels using bomb calorimetry and gas chromatography; (b) partial least squares (PLS-1) calibration is trained for accurate prediction of C and H contents from MIR spectra of petro-diesels; (c) for a new sample, the MIR spectrum is recorded and the optimized PLS-1 method is applied to determine C and H contents, and HHV is estimated from the derived correlation from (a).

## Experimental

### Collection of petro-diesel samples

One hundred samples were collected from ten local petrol stations located in Amman area, Jordan. Fifty milliliters of

each sample was stored in a sealed glass bottle and kept in a dark, cooled environment. The Jordanian Petroleum Refinery Company is the main supplier of petro-diesels (85%) in Amman with the remaining imported from neighboring countries. It is important to note that the composition of the samples will depend not only on the supplier specifications, but also on the residual level in the main station tank. Therefore, each sample represents a unique chemical identity because of the inherent differences in the station tank levels upon filling. The samples were carefully filtered to remove colloids prior to analysis.

#### Determination of HHV using ASTM D240

An oxygen bomb calorimeter (IKA Calorimeter system C2000, Petrotest Instruments GmbH, Germany) was employed to estimate HHV of diesel samples. An accurately weighed sample (0.8–1.0 g) was placed directly in a stainless steel capsule (2.5 cm diameter and 1 cm deep) and burned with oxygen at a pressure of 3.0 MPa according to ASTM D240 [5]. The sealed capsule was then placed inside a 2-L water bath that placed in an adiabatic container. Upon thermal equilibration of the whole system, the sample was combusted. The HHV (in MJ/kg) of the sample at room temperature was calculated from the temperature increase in water bath  $\Delta T$  as following [5]:  $\text{HHV} = (C\Delta T - e_1 - e_2)/m$ , where  $C$ ,  $e_1$ ,  $e_2$ , and  $m$  are the calibration constant of the calorimeter (MJ/K); correction factor for the heat of combustion of the ignition wire (MJ); the heat of formation of the acids (MJ); sample mass (kg), respectively. Before analysis, the calibration constant was estimated from the combustion of pure benzoic acid as described in the instrument manual.

#### Elemental composition determination of petro-diesels by gas chromatography

The contents of carbon, hydrogen, nitrogen, and sulfur in the samples were determined using gas chromatography (EuroVector EA3000 Instrument and Software, Italy). Diesel samples were carefully weighed using a highly sensitive ( $\pm 0.001$  mg) balance (Sartorius, Germany). 1.0  $\mu\text{L}$  sample (which is equivalent to 0.7 mg) was carefully delivered to a small aluminum cup and then placed inside a tube furnace connected with GC. The sample was combusted at 1000 °C in an oxygen atmosphere and the final combustion products were  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{SO}_2$ . The gases were separated at 115 °C using 2.0 m length PTFE-GC column. The flow rate of the mobile phase was maintained at 110 ml/min. The eluted gases were detected using thermal conduction detector (EuroVector EA3000). A five-point calibration graph was prepared for each gas, before fuel analysis, and used for quantitative determination

of gases. The elemental composition (in wt%) of the petro-diesels were estimated from the amounts of liberated gases.

#### Spectral measurements and software

MIR spectra of petro-diesels were recorded in duplicate over 400–4000  $\text{cm}^{-1}$  spectral range using a Shimadzu IR Prestige-21/FTIR-8400S spectrophotometer (Shimadzu, Japan). The liquid samples were carefully placed in a fixed length KBr cell and the spectra were sampled at 5  $\text{cm}^{-1}$  resolution, and digitised absorbance values (720 spectral points/spectrum) were determined. The data treatment and the chemometric calculations were undertaken using Excel<sup>®</sup> and MATLAB<sup>®</sup> software.

#### Multivariate calibration

The extent of correlation between C, H, N, and S content and HHV's of samples were estimated by calculating a correlation matrix [18]. Principal component analysis PCA was applied to elemental composition data and HHV's to find the optimum correlation [19]. Many of the 100 tested samples were of similar HHV (0.01 MJ/Kg difference) and of close chemical analysis, therefore, these were excluded from the study. Thirty samples of petro-diesel were carefully selected from the initial batch; the samples of high variations in energy values and chemical composition were selected for multivariate calibration. As will be discussed later, PCA revealed that HHV showed high correlation with C and H content of fuels. Therefore, the next step is to apply PLS-1 to develop informative calibration relationships between MIR data and C/H content. Twenty samples were used to build the calibration model and the remaining ten samples were kept for validation. Initially, the spectral absorbance of petro-diesels were pre-processed, the instrumental noise in the spectra were removed or minimized by applying 5-points window Savitzky–Golay filter [18], the negative absorbance values were removed, and the data were mean-centred. PLS-1 method, an inverse calibration model, was used to create regression formulae to estimate content of C and H from MIR spectra for new samples. The general regression equation was used [15, 18]:  $c_{\text{un}} = pa$ , where  $c_{\text{un}}$ ,  $p$ , and  $a$  are the atom content, the optimized calibration vector obtained by PLS-1 algorithm [15, 18, 19], and the MIR spectrum of the unknown sample. The minimum prediction error of both C and H atoms in the validation set was observed at four PLS-1 latent variables. Multivariate analysis was applied over the entire MIR range (400–4000  $\text{cm}^{-1}$ ) using 720 points/spectrum and on carefully selected sub-regions as well be discussed later. Detection of outliers in the calibration and validation sets was carried out by estimating Mahalanobis distances for the samples [21]. As a final step, PLS-1 was used to

extract C and H content in new diesel samples that were not involved in the calibration, and the estimated HHVs of these samples were compared with ASTM D240 results. The analyses costs and time taken for these procedures were critically evaluated.

## Results and discussion

It should be noted that multivariate calibration has found many applications in petroleum analysis. For example, the technique was applied to both MIR and NIR spectroscopic data to detect gasoline adulteration without running the tedious liquid or gas chromatographic methods. Using multivariate calibration the highly overlapped and non-selective IR signals were resolved and the identity of the mixtures was identified with high accuracy [15]. Determination of fatty acid in palmitolein was undertaken by treating MIR spectra with PLS-1 [22]. Pimentel et al. [14] have applied multivariable calibration on MIR and NIR spectroscopic data to detect low levels (1–5%) of biodiesel in petro-diesel blends and the authors noted the reasonable cost and the short analysis time of the procedure. Among the employed chemometric methods, PLS-1 is the most popular in analytical chemistry with this attributed to the following [23], (a) it employs full data, which is critical for multicomponent analysis, (b) its calibration models ignore the effect of other co-existed compounds except the target analyte, and (c) a short analysis time with no sample clean up or even physical separation in many cases.

### Correlating HHV of petro-diesels with elemental composition

Higher heating value of petro-diesel which mainly composed of C, H, N, and S (Table 1) cannot be estimated directly from the heats of formation of CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>2</sub>, and SO<sub>2</sub> products because petro-diesel is formed from complex mixtures of compounds (saturated and aromatic hydrocarbons), hence, complex oxidation reactions with radical formation upon burning are all possible which produces variation in energies compare to estimated values.

As an example, the total amount of released energy including condensation of water vapor was estimated for sample 6 (Table 1). The total combusted mass was 0.70185 mg ( $\pm$  0.001 mg) which contained 0.6151 mg C, 0.08675 mg H, 1.2633  $\mu$ g N, and 6.1061  $\mu$ g S. The heat of formation of H<sub>2</sub>O, CO<sub>2</sub>, NO<sub>2</sub>, and SO<sub>2</sub> gases (assuming complete combustion under experimental conditions) are –242, –393.3, 34.0, and –297.0 kJ/mol; respectively, while the heat of condensation of H<sub>2</sub>O is –41.0 kJ/mol [1]. Accordingly, the estimated amount of released energy that is attributed to the earlier masses is 41.14 MJ/kg, which is

**Table 1** Elemental composition and HHV of petrodiesels

Sample	C/wt%	H/wt%	N/wt%	S/wt%	HHV/kJ g <sup>-1</sup>
<i>Calibration set</i>					
1	84.72	15.28	0.14	0.67	47.58
2	87.04	12.96	0.19	0.65	45.75
3	85.74	14.26	0.15	0.95	46.78
4	86.75	13.25	0.13	0.68	45.86
5	84.00	15.88	0.17	0.95	48.06
6	87.64	12.36	0.18	0.87	45.21
7	84.56	15.44	0.19	0.86	47.83
8	87.71	12.20	0.17	0.87	45.20
9	85.69	14.31	0.17	0.75	46.92
10	83.50	16.40	0.16	1.00	48.62
11	86.72	13.28	0.18	0.50	46.00
12	83.40	16.60	0.16	1.03	48.81
13	85.25	14.75	0.15	1.00	47.33
14	84.31	15.66	0.11	0.87	48.02
15	86.25	13.75	0.12	0.92	46.48
16	85.99	14.01	0.16	0.77	46.71
17	84.98	15.02	0.14	0.37	47.44
18	86.14	13.86	0.19	0.53	46.52
19	86.50	13.50	0.17	0.88	46.19
20	85.34	14.66	0.16	0.93	47.19
<i>Validation set</i>					
21	86.73	13.27	0.14	0.55	46.06
22	85.55	14.36	0.16	0.65	46.95
23	84.64	15.36	0.17	0.74	47.82
24	86.07	13.93	0.17	0.85	46.34
25	87.12	12.66	0.13	0.99	45.49
26	84.06	15.94	0.18	0.99	48.33
27	83.51	16.10	0.16	0.99	48.44
28	84.42	15.58	0.18	0.65	47.92
29	85.12	14.96	0.16	1.04	47.55
30	86.37	13.63	0.18	0.70	46.35

Elemental composition/wt% was obtained by GC

Higher heating values HHV were determined by ASTM D240 [5]

Relative standard deviations (RSD,  $n = 3$ ) were 0.53 and 0.82 for GC and ASTM D240 measurements; respectively

about 9% lower than the experimental value (45.15 MJ/kg).

ASTM D240 is an important standard method for HHV determination of liquid hydrocarbon fuels ranging in volatility from light distillates to residual fuels, using bomb calorimetry [3, 4]. Under normal conditions, this method is common for gasoline, kerosene, biodiesel and petro-diesel [5]. The reported HHVs in this study ranged from 41 to 46 MJ/kg which is typical for petro-diesels and reflects the high combustion energies [1]. Even though the level of S seems to be insignificant (0.4–1.0% by mass), accumulation of acidic gases like SO, SO<sub>2</sub>, and SO<sub>3</sub> would be

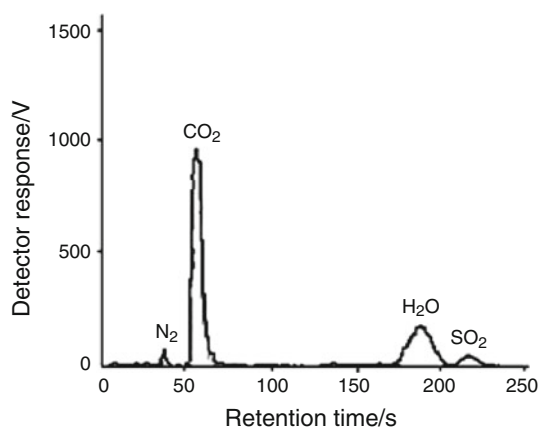


Fig. 1 Gas chromatogram obtained for sample 13

produced from the huge consumption of this fuel. The level of S is above the permitted level which should be less than 0.5% [3] to ensure low emissions of gases. Elemental composition of petro-diesels were determined with high precision (RSD = 0.53%) using standard gas chromatographic method. The results were shown in Table 1. A typical gas chromatogram is presented in Fig. 1.

As shown in Fig 1, the gases were completely separated in a short time with retention times of 31, 49, 170, and 211 s for N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub>, respectively. The high polarity of H<sub>2</sub>O and SO<sub>2</sub> gases increased their affinity toward the polar stationary phase and postponed their elution from the column. The low percentages of N and S in diesel samples are indicated from the low peak-intensity of their corresponding gases, as shown in Fig. 1. As reported earlier, many studies have indicated that HHV of petro-diesels and other common fuels show high correlation with elemental compositions [3, 4, 6–9]. Therefore, it is essential to assess the correlations between HHV and elemental composition. Such correlations can be obtained by estimating a correlation matrix of the data presented in Table 1 [4]. The correlation matrix (5 × 5 dimension) which is symmetric around its diagonal is presented in Table 2.

As can be noted in Table 2, HHV demonstrates high correlation with C and H content, with positive correlation (0.9973) with H% and negative correlation with C% (−0.9949). However, a poor correlation was observed between HHV and other atoms ( $r^2 < 0.5$ ). The high and negative correlation (−0.9976) is expected because C and H atoms make up the vast majority of petro-diesel (>99%), therefore, as C levels increases H levels should decrease and vice versa (See Table 1).

The data presented in Table 1 were subjected to PCA to derive an empirical relationship between elemental composition (4 independent variables) and the dependent HHV variable. The data were mean-centered prior to PCA

Table 2 Correlation matrix calculated using data presented in Table 1

	HHV	C	H	N	S
HHV	1				
C	−0.9949	1			
H	0.9973	−0.9976	1		
N	−0.0301	0.0426	−0.0341	1	
S	0.3115	−0.316	0.3003	−0.1114	1

analysis and the following empirical equation was obtained using samples 1–20 in Table 1:

$$\text{HHV} = 0.3482(\text{C}) + 1.1887(\text{H}) + 0.0019(\text{N}) + 0.0559(\text{S}) \quad (1)$$

$$r^2 = 0.9957$$

A *t*-test was used as a statistical indicator to assess the significance of each coefficient in Eq. 1 provided that more experiments (20 experiments) were performed than number of coefficients (4 coefficients). The significance *t*-test was carried out as following [18]: (a) the square covariance matrix (4 × 4 dimensions) was calculated where the diagonal values of this matrix represents the variance (*v*) for each parameter, (b) *S*<sub>resid</sub>, the error sum of squares, which was determined from the experimental HHV (HHV<sub>exp</sub>) and those obtained by Eq. 1 (HHV<sub>estim</sub>) for all samples was calculated as following:  $\sum_{i=1}^n (\text{HHV}_{i,\text{exp}} - \text{HHV}_{i,\text{estim}})^2$ , where *n* is the number of samples, (c) determination of mean error sum of squares (*s*) by dividing *S*<sub>resid</sub> by number of degrees of freedom. Degrees of freedom = *N* − *P*, where *N* is number of experiment (20 in this case) and *P* is the number of coefficients (4 coefficients), and (d) estimation of *t* value,  $t = \frac{b}{(sv)^{1/2}}$ , the higher this ratio, the more significant is the coefficient at the desired confidence level. The obtained *t* values were: 9.6, 23.6, 0.62, and 2.39 for C, H, N, and S coefficients, respectively. Using two-tailed *t* test table, *t* table (99%, 16) is 2.79. Accordingly, the coefficients of N and S are insignificant for HHV prediction while coefficients of C and H are very significant. Without affecting its HHV (MJ/kg) prediction, Eq. 1 is reduced to:

$$\text{HHV} = 0.3482(\text{C}) + 1.1887(\text{H}) \quad r^2 = 0.9956 \quad (2)$$

The obvious correlation between HHV and C/H is expected because both atoms make up a large fraction of petro-diesels (see Table 1). The positive and high correlation between HHV and H% is also expected because as H content increases the amount of water produced increases and more condensation energy is obtained. This is illustrated in sample 12 where the maximum HHV was observed. The prediction power of Eq. 2 was further tested by finding HHV of new fuel

samples not included in the correlation derivation (samples 21–30 in Table 1) and the relative error of prediction REP% was calculated to assess the performance of Eq. 2:

$$\text{REP}\% = 100 \times \left( \frac{\sum_{h=1}^n (\text{HHV}_{i,\text{exp}} - \text{HHV}_{i,\text{estim}})^2}{\sum_{i=1}^n (\text{HHV}_{i,\text{exp}})^2} \right)^{1/2} \quad (3)$$

The obtained REP% value was only 0.26%, which reflects the high accuracy of the derived empirical equation. This confirms the results of other researchers, in that HHV value can be correlated to the elemental composition of fuels. An accurate and fast estimation of C and H levels in petro-diesels is necessary to determine HHV and avoid using expensive and laborious bomb calorimeters. As will be shown in the following section, a simple chemometric method based on analysis of MIR data with PLS-1 is proposed to estimate C and H contents and finally determine HHV using Eq. 2. Demirbaş [3], Channiwala-Parikh [6], and Boie [9] reported different formulae for HHV prediction for liquid fuels. The formula derived by the first author was primarily for petro-diesel, while, the other authors derived formulae that can work for wide spectrum of fuels including petro-diesel. Due to their high popularity, the aforementioned correlations were used to find HHV of our samples (samples: 21–30 Table 1) from their C and H contents and the overall performance of all formulae were compared. The obtained REP% values were 0.26, 0.28, 0.25, and 1.23% corresponding to Eq. 2, Boie, Channiwala-Parikh, and Demirbaş equations, respectively. Demirbaş's formula showed a large REP% value while the other formulae gave similar prediction powers as Eq. 2.

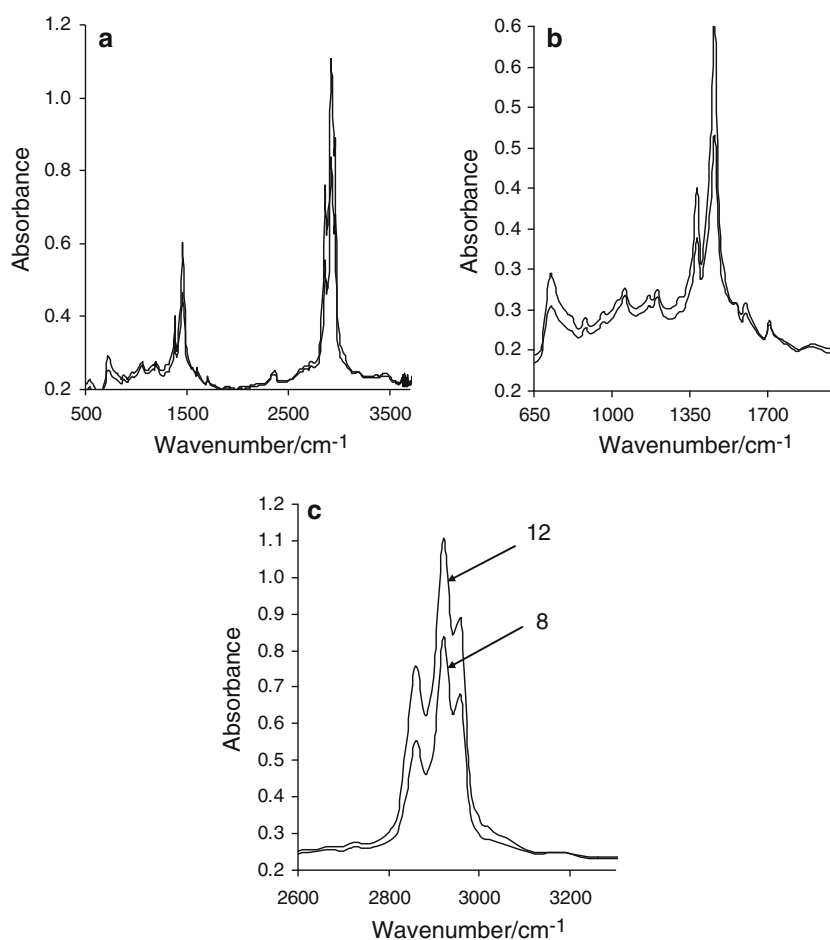
#### Determination of C and H contents using MIR/PLS-1

Representative MIR spectra of petro-diesels (samples 8 and 12) are presented in Fig. 2.

The spectral features depicted in Fig. 2a are typical for petro-diesels and identical spectra were reported in literature [14]. The aim of depicting MIR spectra of samples 8 and 12 is due to the samples having high variations in their elemental compositions and also in HHVs. The large variations in the chemical composition should be reflected in the sample spectra. Figure 2b showed that both samples have identical spectral behavior over 650–1600  $\text{cm}^{-1}$ , while, the maximum variations in the intensity of MIR bands was observed at 2856, 2926, and 2956  $\text{cm}^{-1}$  as indicated in Fig 2c. At 2926  $\text{cm}^{-1}$ , there is 34% increase in the absorbance value in sample 12 compared to sample 8. This was mainly attributed to the large H% content which is 36% higher in sample 12. The difference in C content in samples (about 5% higher in sample 8) is insignificant

(compared to the H difference in both samples) and cannot account for the large spectral variations in the samples. Accordingly, univariate calibration at 2926  $\text{cm}^{-1}$  was carried out and the regression equation, ( $H\% = 0.28A_{2926 \text{ cm}^{-1}} - 3.18$ ,  $r^2 = 0.6578$ ) was used to predict H% in diesel samples. High REP% values were obtained (25–53%); this was expected as using one spectral point in the calibration is not sufficient and more data points are necessary in order to improve the selectivity of the calibration. The non-selectivity problem is common in FTIR analysis and can be eliminated by including informative spectral regions and using inverse calibrations algorithms [19]. For estimation of C and H contents from non-selective MIR overlapped bands, multivariate calibration by PLS-1 was applied. In principle, PLS-1 is a simple and convenient calibration method for resolving mixtures and could be applied for determination C and H contents in petro-diesels from MIR spectra. The multivariate data were gathered in matrix **A** which contains the spectral data of dimension  $20 \times 720$  and two separate vectors of dimension  $1 \times 20$  containing the reference values of C and H, as obtained by GC. Due to the high co-linearity in calibration data, the classical least squares method was invalid for predicting fuel composition from MIR data. Co-linearity (i.e., the linear relationships between absorbance at multiple wavenumbers) is a significant disadvantage that may negatively affect the accuracy and precision of the calibration method. A good estimation of co-linearity in a data matrix is the condition number [15, 19], a matrix of high co-linearity has a high condition number and cannot be involved calibration. The condition number of matrix **A** was 2,407, which reflected the high degree of co-linearity and also the non-selective nature of MIR signals. The high co-linearity in calibration data was eliminated by decomposing matrix (**A**) using the elemental composition of C/H atom. With the aid of PLS-1 algorithm,  $\mathbf{W}_{n \times h}$ ,  $\mathbf{P}_{h \times n}$  matrixes and  $\mathbf{q}_{h \times 1}$  vector were obtained. where  $h$  represents the number of optimum PLS-1 latent variables needed to perform accurate calibration. The calibration parameter **b** was obtained as following [15, 19, 23]:  $\mathbf{b} = \mathbf{W}(\mathbf{P}^t\mathbf{W})\mathbf{q}$ . The PLS-1 calibration was carried out separately for each atom. The presence of outlier(s) was also investigated in all samples by estimating Mahalanobis Distance MD from elemental composition and spectral data [21]. Using data presented in Table 1, the covariance matrix **B** ( $5 \times 5$ ) was initially calculated and used to estimate MD as:  $\sqrt{\mathbf{b}^t(\mathbf{B})^{-1}\mathbf{b}}$ , where **b** is the mean centered vector (elemental composition or absorbances) of the sample [18]. The obtained MD values (calculated from elemental composition data) ranged from 1.30 to 1.42 indicating the absence of outliers, and the standard samples represent one cluster. For spectral data, the score matrix ( $20 \times 6$ ) was used

**Fig. 2** MIR spectra of samples 8 and 12 displayed at different spectral ranges: **a** 500–3500  $\text{cm}^{-1}$ , **b** 650–1550  $\text{cm}^{-1}$ , and **c** 2600–3200  $\text{cm}^{-1}$



as input data to find MD values using the same earlier formula and the values were in the range 12–16, which also confirms the absence of outliers. For higher quality calibration, the initial spectral data (720 absorbances/sample) was further filtered to obtain the informative spectral regions. Various criteria have been developed to allow for the effect of wavelength selection prior to multivariate calibration [24]. In this work, the method proposed by Alba et al., 2002, was adopted to select the optimum wavelength regions prior to multivariate calibration [25]. Simply, the correlation coefficients between the atom content (in the calibration set) and the corresponding absorbance at each wavenumber were estimated. For both atoms, the most informative spectral regions were within 400–670 and 2840–2970  $\text{cm}^{-1}$ , which contain 184 data points/spectrum. The second region (2840–2970  $\text{cm}^{-1}$ ) contains the characteristics vibration bands of C–H bond [15]: 2960, 2950, 2925, 2915, 2870, and 2855  $\text{cm}^{-1}$ . The earlier bands are attributed to  $\text{sp}^3 \text{CH}_3$  (asymmetric),  $\text{sp}^2 \text{CH}_2$  (olefinic),  $\text{sp}^3 \text{CH}_2$  (asymmetric),  $\text{sp}_3 \text{CH}$ ,  $\text{sp}^3 \text{CH}_3$  (symmetric), and  $\text{sp}^3 \text{CH}_2$  (symmetric). The spectral region 3400–3600  $\text{cm}^{-1}$  is totally excluded from analysis due to the negative correlations with C and H content. After selecting the informative spectral regions,

checking for outliers, and latent variables determination, the power of PLS-1 for C and H quantification from MIR data can be tested. Critical values of calibration and validation including recovery, RSD, RMSD (root mean square difference),  $r^2$  (square of correlation), and REP (relative error of prediction) were reported to assess the analytical performance of PLS-1 for quantification of H and C content in petro-diesels [26, 27]. The results are summarized in Table 3.

As indicated in Table 3, all statistical quantities confirm that PLS-1 was accurate and precise for quantitative determination of C and H in petro-diesels. PRESS, RMSD, recoveries, and RSD all reflected the outstanding performance of PLS-1 and  $r^2$  values were high for both atoms, which confirm the high degree of fit between PLS-1 values and those obtained by GC. It is interesting to note that the atoms were predicted using high number of latent variables (6–7) and this was attributed to the large spectral overlap in the characteristics bands of C–H bond in the sample. As indicated in Table 3, the PLS-1 has a high prediction power for both atoms in the validation set with satisfactory REP% values (0.21–1.22%). The following conclusion was deduced from the earlier discussion: PLS-1 was capable for

**Table 3** Assessment of PLS-1 method for determination of C and H contents in petrodiesels from their MID spectra

Parameter	C/wt%	H/wt%
<i>Calibration set</i>		
Informative spectral regions/cm <sup>-1</sup>	2840–2970	400–670, 2840–2970
Analytical range/wt%	83–87	12.0–16.6
LVs <sup>a</sup>	7	6
PRESS	0.85	0.92
RMSD <sup>b</sup>	0.20	0.20
<i>r</i> <sup>2b</sup>	0.9954	0.9976
Recovery <sup>c</sup>	101.2	99.63
RSD	0.42	0.61
<i>Validation set</i>		
Recovery	98.9	99.0
RSD	0.38	0.57
REP% <sup>b</sup>	0.21	1.22
<i>r</i> <sup>2</sup>	0.9922	0.9990

<sup>a</sup> PLS-1 latent were variables calculated using cross-validation method [18, 19]

<sup>b</sup> Calculated as outlined in Refs. [26, 27]

<sup>c</sup> Recovery values were calculated using reference values obtained by GC (Table 1)

resolving the non-selective MIR spectra and find C and H levels in petro-diesels with high accuracy and precision.

Precision, accuracy, and ruggedness of the proposed method

The proposed analytical procedure could be applied in official laboratories for routine analysis of diesel samples, therefore, the inter/intra-day precision and accuracy of the PLS-1 procedure was evaluated. More over, ruggedness of the method was also carefully assisted. Three different samples (5, 15, and 25 in Table 1) were analysed in five

replicates during the same day (intra-day precision) and five consecutive days (inter-day precision). The RSD% values of inter and intra day indicated that the precision was good as shown in Table 4. The accuracy of the analytical method was expressed as percentage of relative error between experimental HHV values and the values obtained using Eq. 2. An acceptable size of relative error was obtained (<0.5% in all trials) as indicated in Table 4. Method's ruggedness was expressed as the RSD% of the same procedure applied by three analysts as well as using three different spectrophotometers. The results of ruggedness are provided in Table 4 and indicated that the proposed method has a reasonable degree of ruggedness (RSD: 1–3%).

Determination of HHV for new petro-diesel samples

The next step is the application of the proposed analytical method for HHV determination for new petro-diesel samples that were not included in the original calibration. Five petro-diesel samples were carefully selected from different five petrol stations, the samples were filtered and stored at cooled place until day of analysis. For each sample, MIR spectrum was recorded and the HHV was determined using ASTM D240 method. PLS-1 method was applied to find C and H contents from MIR spectra as discussed earlier, and HHVs were estimated using Eq. 2. Five determinations were carried out for each sample. Table 5 summarizes the output along with statistical results.

As presented in Table 5, *t* and *F* statistical tests were applied to determine whether the results of both methods were comparable, or not, under the experimental conditions and at 95% confidence level. Before applying *t* test, *F* test was applied to compare the standard deviations of the methods. As can be noted, the standard deviations of both methods are not significantly different at 95% confidence level where *F* calculated values < *F* table value. The *t* test was applied to determine if the results of ASTM D240 and

**Table 4** Assessment of precision, accuracy and ruggedness of the MIR/PLS-1 method

Sample	HHV <sup>a</sup>	Intra-day			Inter-day			Ruggedness	
		PLS-1 prediction <sup>b</sup>	RE%	RSD%	PLS-1 prediction <sup>c</sup>	RE%	RSD%	Inter-analyst RSD%	Inter-instrument <sup>d</sup> RSD%
5	48.06	48.12	0.12	0.88	48.22	0.33	0.92	1.22	2.1
15	46.48	46.41	0.15	0.92	46.38	0.22	0.63	1.03	3.2
25	45.49	45.39	0.22	0.55	45.53	0.10	0.23	0.95	1.9

<sup>a</sup> Calculated using ASTM D240 in kJ g<sup>-1</sup>

<sup>b</sup> Calculated using MIR/PLS-1 and Eq. 2 in kJ g<sup>-1</sup>

<sup>c</sup> Three different analysts were involved

<sup>d</sup> Three different spectrophotometers were used



**Table 5** Determination of HHV of new petrodiesel samples by ASTM D240 and MIR/PLS-1 method

Sample	ASTM D240	MIR/PLS-1	<i>F</i> calculated	<i>t</i> calculated
1	46.11 (0.62)	46.26 (0.81)	1.78	0.19
2	45.28 (0.57)	45.53 (0.71)	2.10	0.34
3	45.63 (0.44)	45.66 (0.79)	5.73	0.05
4	45.94 (0.29)	46.03 (0.56)	373	0.18
5	45.32 (0.60)	45.36 (0.69)	1.32	0.05

Time and cost of HHV determination <sup>a</sup>		
	ASTM D240	MIR/PLS-1
Assay time	1.0 h	10–15 min
Total cost (in JD) <sup>b</sup>	40	5

Results are average of five determinations ( $\pm$ SD), *t* table (0.05, 8) = 2.31, *F* table (0.05, 4, 4) = 9.605

<sup>a</sup> The provided data were for one determination

<sup>b</sup> One JD (Jordanian dinar) is currently equivalent to 1.41 US dollar

MIR/PLS-1 are comparable within the experimental error. At 95% confidence level, the results of *t*-test indicate that there is no significant difference between two methods for determination of HHV in petro-diesels, *t* calculated < *t* table in all cases. The analysis time and cost for HHV determination by both methods were provided in Table 5 for comparison. ASTM D240 requires a long timeframe which is consumed for setting and calibrating the calorimeter, sample preparation, and attainment of thermal equilibration in the system. In addition, this procedure is expensive where pure oxygen is needed for sample burning and large volumes of acetone and chloroform are often required for cleaning sample holders after burning. The MIR/PLS-1 method was less expensive and faster compared to ASTM D240 and the expenses are mainly to cover solid KBr and organic solvents used in cleaning. Moreover, the proposed method is simple, does not need expert analysts and can be easily implemented in most fuel laboratories.

## Conclusions

A simple, cheap and easy-to-implement analytical protocol was developed for accurate estimation of HHV for diesel samples. Both C and H content were accurately quantified using MIR data and PLS-1 calibration. Finally, HHV was predicted from the formula:  $HHV = 0.3482(C) + 1.1887(H)$ . Five petro-diesels obtained from different stations were analyzed by the proposed method to find HHV, the results clearly indicated that MIR/PLS-1 gave comparable results to official ASTM D240 method. The proposed method is simple and can be adopted by most fuel analysis laboratories.

## References

- Song C, Hsu CS, Mochida I. Chemistry of diesel fuel. New York: Taylor & Francis; 2000.
- Energy Information Administration. The official energy statistics from the USA government. Washington: USA Department of Energy; 2006. <http://www.eia.doe.gov/>
- Demirbaş A. Combustion properties and calculation higher heating values of diesel fuels. *Pet Sci Technol*. 1998;16:785–95.
- Friedl A, Padouvas E, Rotter H, Varmuza K. Prediction of heating values of biomass fuel from elemental composition. *Anal Chim Acta*. 2005;544:191–8.
- ASTM D240-02 standard. Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter. Annual book of ASTM standards. Washington: ASTM; 2007.
- Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel*. 2002;81:1051–63.
- Demirbaş A. Fuel properties and calculation of higher heating values of vegetable oils. *Fuel*. 1998;77:1117–20.
- ASTM D4868-00 standard. Standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter. Annual book of ASTM standards. ASTM, Washington; 2005.
- Boie W. Fuel technology calculations. *Energietechnik*. 1953;3: 309–16.
- Sadrameli SM, Seames W, Mann M. Prediction of higher heating values for saturated fatty acids from their physical properties. *Fuel*. 2008;87:1776–80.
- Demirbaş A. Relationships derived from physical properties of vegetable oil and biodiesel fuels. *Fuel*. 2008;87:1743–8.
- Demirbaş A. A direct route to the calculation of heating values of liquid fuels by using their density and viscosity measurements. *Energy Conserv Manag*. 2000;41:1609–14.
- Ahmaruzzaman M. Proximate analyses and predicting HHV of chars obtained from cocracking of petroleum vacuum residue with coal, plastics and biomass. *Biores Technol*. 2008;99:5043–50.
- Pimentel MF, Ribeiro GM, da Cruz RS, Stragevitch L, Pacheco Filho JG, Teixeira LS. Determination of biodiesel content when blended with mineral diesel fuel using infrared spectroscopy and multivariate calibration. *Microchem J*. 2006;82:201–6.
- Al-Degs YS, Al-Ghouti M, Amer M. Determination of motor gasoline adulteration using FTIR spectroscopy and multivariate calibration. *Talanta*. 2008;76:1105–12.
- Oliveira JS, Montalvão R, Daher L, Suarez PAZ, Rubim JC. Determination of methyl ester contents in biodiesel blends by FTIR-ATR and FTNIR spectroscopies. *Talanta*. 2006;69: 1278–84.
- Divya O, Mishra AK. Multivariate methods on the excitation emission matrix fluorescence spectroscopic data of diesel–kerosene mixtures: a comparative study. *Anal Chim Acta*. 2007;592: 82–90.
- Brereton RG. Chemometrics. 1st ed. England: Wiley; 2003.
- Naes T, Isaksson T, Fearn T, Davies T. Multivariate calibration and classification. United Kingdom: NIR Publications; 2004.
- Lestander TA, Multivariate Rhén C, IR N. Spectroscopy models for moisture, ash and calorific content in biofuels using bi-orthogonal partial least squares regression. *Analyst*. 2005;130: 1182–9.
- De Maesschalck R, Jouan-Rimbaud D, Massart DL. The Mahalanobis distance. *Chemom Intell Lab Syst*. 2000;50:1–18.
- Che Man YB, Setiowaty G. Application of Fourier transform infrared spectroscopy to determine free fatty acid contents in palm olein. *Food Chem*. 1999;66:109–14.
- Pagani AP, Cabezon MA, Ibanez GA. Simultaneous kinetic-spectrofluorometric determination of levodopa and carbidopa using partial least-squares regression. *Anal Sci*. 2009;25:633–8.

24. Al-Degs YA, El-Sheikh AH, Al-Ghouti MA, Hemmateenejad B, Walker GM. Solid phase extraction and simultaneous determination of trace amounts of sulphonated and azo sulphonated dyes using microemulsion-modified-zeolite and multivariate calibration. *Talanta*. 2008;75:904–15.
25. López-de-Alba PL, López-Martínez L, De León-Rodríguez LM. Simultaneous determination of synthetic dyes tartrazine, allura red and sunset yellow by differential pulse polarography and partial least squares. A multivariate calibration method. *Electroanal*. 2002;14:197–205.
26. Hemmateenejad B, Abbaspour A, Maghami H, Miri R, Panjehshahin M. Partial least squares-based multivariate spectral calibration method for simultaneous determination of beta-carboline derivatives in *Peganum harmala* seed extracts. *Anal Chim Acta*. 2006;575:290–9.
27. Abbaspour A, Najafi M. Simultaneous determination of Sb(III) and Sb(V) by partial least squares regression. *Talanta*. 2003;60:1079–84.